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Studies in the Life and Work of Jean Baptiste André Dumas (1800-1884): The Period up to 1850

by

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ABSTRACT

Jean Baptiste Dumas (1800-1884) was an outstanding experimental chemist who gave a sense of direction to the study of organic chemistry in the second quarter of the 19th century. He did this by framing hypotheses boldly and fruitfully, believing in the simplicity of nature's fundamental relationships and a need for classification as a means of emphasising this. Stress has been placed on the important period of Dumas' formation in Geneva, his research in physiology and the transition period in Paris where he was drawn to chemical research by appointments at the Ecole Polytechnique and the Athénée. An interest in industrial chemistry led to his textbook in applied chemistry and to the founding of an industrial journal and school. In the Collège de France he gave an influential course on chemical philosophy. His election to the Academy in 1832 was followed by appointments to the Faculty of Sciences and the Faculty of Medicine, where he gained a reputation as an outstanding professor of chemistry, and a guide for research students, both French and foreign.

His practical contributions to chemistry included procedures for measuring vapour densities, organic nitrogen analysis and accurate determination of atomic weights, to which he was led by Prout's hypothesis. His unique combination of creative intuition, sound judgment, a strong reliance on experimental data and a virtually limitless capacity for work made possible his seminal contributions to the theory of organic chemistry: ethers, amides, substitution, types, a law of fat acids. New compounds were discovered as a result, but more important, he laid the foundations for more general modes of classification, the homologues and types of one of his students, Gerhardt. Dumas was the first to make extensive and successful use of chemical formulae and equations to explain reactions in organic chemistry. His influence on classification of the elements and atomic theory was profound. This thesis provides the necessary documentation to integrate the various aspects of Dumas' life and work up to 1850, after which he became increasingly involved in national politics and administration.

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ABBREVIATIONS

(i) Archives, Libraries and Institutions

ACF	Archives du Collège de France
AEP	Archives de l'Ecole Polytechnique
Arch. Acad. Sci.	Archives de l'Académie des Sciences
Arch. Nat.	Archives Nationales
Athénée	Athénée Royale de Paris
Bibl. de Genève	Bibliothèque de la Ville de Genève
Conservatoire	Conservatoire des Arts et Métiers
S.P.H.N. de Genève	Société de Physique et d'Histoire naturelle de Genève

(ii) Journals

Annalen	Annalen der (Chemie und) Pharmacie
Ann. Chim.	Annales de Chimie
Ann. Chim. Phys.	Annales de Chimie et de Physique
Ann. Ind.	Annales de l'Industrie française et étrangère
Ann. Phil.	Annals of Philosophy
Ann. Phys.	Annalen der Physik
Ann. Sci. Nat.	Annales des Sciences naturelles
Ann. Soc. Sav.	Annuaire de Sociétés Savantes de la France et de l'Etranger
Bibl. Univ.	Bibliothèque Universelle des Sciences, Belles-lettres, et Arts
Bull. Acad. Roy. Belg.	Bulletin de l'Académie Royale des Sciences, des Lettres, et des Beaux Arts de Belgique
Bull. Soc. Chim.	Bulletin de la Société Chimique
Bull. Soc. d'Enc.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale
Bull. Soc. Philom.	Bulletin de la Société Philomatique
Comptes Rendus	Comptes rendus hebdomadaire des séances de l'Académie des Sciences
Froriep, Notizen	Notizen aus dem Gebiete der Natur und Heilkunde
Jahres Bericht	Jahres Bericht über die Fortschritte der physischen Wissenschaften
J. Pharm.	Journal de Pharmacie
J. Phys.	Journal de Physique
J. de Physiol.	Journal de Physiologie expérimentale
Mém. Acad. Roy. Belg.	Mémoires de l'Académie Royale des Sciences, des Lettres, et des Beaux Arts de Belgique
Mém. Acad. Sci.	Mémoires de l'Académie des Sciences
Mém. Soc. d'Arcueil	Mémoires de Physique et Chimie de la Société d'Arcueil
Mém. Soc. d'Hist. Nat.	Mémoires de la Société d'Histoire naturelle de Paris
Mém. S.P.H.N. de Genève	Mémoires de la Société de Physique et d'Histoire naturelle de Genève
Nat. Anzeiger	Naturwissenschaftlichen Anzeiger der allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften

Phil. Mag.	Philosophical Magazine
Phil. Trans.	Philosophical Transactions of the Royal Society
Proc. Verb. Soc. Philom.	Procès verbaux de la Société Philomatique
PVAS	Procès verbaux des séances de l'Académie des Sciences
Rev. Hist. Sci.	Revue d'histoire des sciences et de leurs applications
Rev. Sci.	Revue Scientifique (Quesneville)

(iii) Books, Pamphlets and Memoirs

August Memoir	Mémoire sur la formation de l'éther sulfurique
December Memoir	Mémoire sur les éthers composés
DSB	Dictionary of Scientific Biography
Eloges	Discours et Eloges Académiques
G	Gautier: Inauguration de la Statue de J.B.A. Dumas à Alais
January Memoir	Mémoire sur les combinaisons du phosphore, et particulièrement sur celles de ce corps avec l'hydrogène
Leçons	Leçons de la Philosophie Chimique
October Memoir	Mémoire sur quelques points de la théorie atomistique
Props. Physiol.	Propositions de Physiologie et de Chimie médicale
Statique Chimique	Essai de Statique Chimique des Etres organisés
Traité	Traité de Chimie appliquée aux Arts

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CHAPTER 1

THE FORMATIVE YEARS

"During the first part of my life ... literature was my only interest. My life was so enjoyable because of it that I did not even suspect the existence of the advanced sciences that I am pursuing these days with unlimited enthusiasm." (1)

By 1840 Jean Baptiste Dumas was at the height of his career. An outstanding practical and theoretical organic chemist, he was recognised by his contemporaries and students as an excellent professor of chemistry, whether general, analytical, organic or industrial. He had maintained a working knowledge, of the sciences related to pharmacy as well as a familiarity with most of the others. Accepted as a talented speaker, he was esteemed as a director of research. But at the age of 17, when he left his birthplace to study pharmacy, all that was in the future. Though his education in Alais had not been completely devoid of science, he could hardly have dreamed of the vast panorama that would be revealed to him in Geneva as he read, attended courses and associated with internationally known scientists. The foundation of his career, laid during a period of nearly six years in the busy Swiss city, is the central theme of my opening study. Nevertheless, some attention must be given to his life in Alais, where several events occurred that appeared to be of no great significance when viewed individually, but were sufficiently important when considered collectively to account for his crucial decision to exchange a happy life at home (2) for an uncertain existence in a strange city 500 kilometres away.

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1. Extracts from five letters written by Dumas in Geneva to his father in Alais were quoted by Emile Justin Armand Gautier (1837-1920) during a discourse given in Alais on 21 October 1889. In the printed version (<u>Inauguration de la Statue de J.B.A. Dumas à Alais</u>, Paris, 1889) much longer extracts from the same letters were contained in some of the extensive footnotes that were added. The letters were dated 1817, 8 November 1818, 3 November 1819, 1820 and 16 November 1821. In references they will be designated by <u>G</u>, the year they were written and the page on which the quotation may be found in Gautier. I have been unable to locate the originals. The extract quoted to introduce this chapter was written by Dumas in 1818. <u>G</u>, Letter of 1818, p.41.

2. In 1818 Dumas referred to his former life in Alais as "the time of happiness which I spent with you". <u>Ibid</u>. Two years later, after describing his life in the Le Royer home in Geneva, he wrote: "I only know of one haven in the world where I could imagine a happier existence, father, and you know where I would look." <u>G</u>, Letter of 1820, p.41.

The industrial city of Alès in France's Département du Gard is in the Cévennes mountains, just 75 kilometres north of Montpellier. Known as Alais during the nineteenth century, it was the scene of bitter religious struggles from time to time. One of these occurred in the aftermath of the Napoleonic era. Whatever may have been their attitude towards it, the Dumas family must have been involved, at least indirectly. Dumas' father, Jean Baptiste, (b. 1763) Secretary of the Municipal Hospice, was a staunch Catholic, a descendant in the Catholic branch of a divided family tree (3). On 25 June 1798 he married Marie Madeleine Bastide (1780-1843) (4), and "in one of the poorest and most obscure lanes" (5) of Alais, Jean Bàptiste André was born on 16 July 1800 (6).

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3. Theirs was not a wealthy family. Dumas' grandfather André was a manufacturer of stockings. His wife, Jeanne Chapon, gave birth to Dumas' father on 29 August 1763. Général Jean Baptiste Dumas, La Vie de Jean Baptiste Dumas (1800-1884), Mimeograph, Paris, 1924, Genealogy. Dumas' father tried to finance a career in art by becoming the private secretary of the Marquis de Calvières but dissatisfied, he soon returned to Alais. His painting of the Virgin Mary was carried in local processions accompanied by the young Jean Baptiste. Ibid., p.8. The religious convictions imprinted upon him by his parents were developed and practised throughout his lifetime, as many sources have attested.

4. She was born in Alais on 23 December 1780. "Some time after the death of her husband she came to Paris to spend the rest of her days living with her son, Jean Baptiste." Ibid. She died 20 July 1843. This was the second marriage for Dumas' father; his first wife, Jeanne Deveze, was 42 when she died in Alais on 21 November 1795, apparently childless. Ibid., Genealogy.

5. René Vallery-Radot, La Vie de Pasteur, Paris (Flammarion) 1900, p.149.

6. The date most frequently quoted, 14 July, is incorrect. Later authors seem to have accepted the date given in the biography by Hofmann, August Wilhelm, "Scientific Worthies XIV - Jean Baptiste André Dumas", Nature, 21 (Extra Number, 6 February 1880), pp. i-xl. (Though listed as XIV, it should have been XV). Dumas' birth certificate was dated "27 messidor an 8". Y. Chatelain, Dictionnaire de Biographie Francaise, Paris, 1933-, Vol. 12, 1968-70, Col. 129. He was the second of five children. Three died when they were young. Gén. Dumas, op.cit.(1-3), p.8. The fate of his older brother, who became director of a dye works in Puteaux, near Paris, will be discussed in Chapter 3.

It would be surprising if the instruction given to him by intelligent and artistic parents during his early years did not encompass a study of the local history, geography, agriculture and industry as has been suggested (7). What was even more important however was the environment they provided, in which he could develop his natural curiosity, creative ability and intuition.

His formal studies began in the college of Alais, where from 1808 he was given an excellent classical education (8). An outstanding student, he could have looked forward to a very promising career in one of the professions if an unfortunate incident had not occurred in the early part of 1816 that caused him to sever his connection with the college quite abruptly before he received the Baccalauréat ès Lettres. It would appear at first sight that this deficiency was inconsequential. Its repercussions were felt for 15 years! (9). For this reason, the following account of the incident merits narration in full:

> "Profiting from the momentary absence of their teacher one day, the students created an uproar in class. Dumas, pensive and absorbed, was tracing with his hand on a wall map of France the march of the Roman armies in Caesar's Commentaries, when the Principal of the college arrived, attracted by the noise. Dismayed, he seized the first student that he encountered, the only one standing, and

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7. Hofmann, op.cit.(1-6), pp. i-ii.

8. The first signs of his ability as a writer and orator were recognised there. In 1815 he wrote a "Discours au Roi à l'Occasion de sa Rentrée en France" which was long posted in the college's hall of honour. He worked quickly. Among several others who matriculated from the college and who later achieved fame were: Jean Baptiste Seraph Joseph Comte de Villèle (1773-1854) and Gaspard Monge (1746-1818), both mentioned by Gautier, whose father had begun his student life there not long after Dumas had entered.

9. The effects of this lacuna will become apparent in the course of my thesis. Dumas never did obtain the certificate.

> struck him violently on the head with a ring of keys. It was Dumas. Bleeding and innocent, he immediately left the college, refusing to return despite the excuses and entreaties made by the director both to father and son." (10)

Though he would not return to school, his interest in study in no way decreased. He furthered his education by extensive reading in the municipal library in Alais, where he helped his father to catalogue a large collection of books that the city had just received (11). Many years later Dumas acknowledged the importance of the time spent there:

> "The opportunity that I was given in my youth to make profitable use of the library in Alais and to pass my leisure hours there decided my future. Thanks to the help of this regular association with our great authors I was able to complete my literary education, begin my scientific studies, enlarge my circle of ideas, and understand that work is the law of life. I have never forgotten the service rendered to me by the library in Alais." (12)

This vicarious awareness that "work is the law of life" was soon supplemented by a more direct experience. His father, concerned about

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10. Gautier, op.cit.(1-1), pp. 38-39. The scar that he carried throughout life on his upper right forehead may well have been a permanent souvenir of the blow. A vivid impression of the incident remained with him for years. Even had he been so inclined, attending another college would have been financially prohibitive. Other reasons, probably including pride and sensitivity, would have prevented him from undertaking the examinations involved at a later date.

11. Gén. Dumas, op.cit.(1-3), p.11. They had come from the estate of a priest who had collected an extensive library while he was attached to the imperial court and had brought it with him when he became a Curé in Alais.

12. Ibid. This quotation is inscribed beneath the bust of Dumas which is located in the library. At that time he was its sole habitué. It was "abandoned by everyone, even its guardian". Gautier, op.cit.(1-1), p.7.

how Jean Baptiste would earn a living (13), consulted a relative, Etienne Bérard (1764-1839) (14), owner of a chemical factory at La Paille (15) and treasurer of the Ecole de Pharmacie in Montpellier (16). Not surprisingly, Bérard suggested a career in pharmacy: "It is an honest occupation, sometimes even lucrative. It awakens and maintains scientific instincts. Indeed, some distinguished chemists have begun

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13. When wartime service was a distinct possibility Dumas had been persuaded by a cousin Auguste Bérard (1796-1852) that life as a naval officer was not undesirable. Ibid. Although Jean Baptiste was attending the college in Alais at the time, he had not followed the special curriculum offered to prepare students for the naval examinations. With the help of a tutor, a young man who had just graduated from the Ecole Polytechnique in Paris and had settled in Alais, he was in the process of making up the deficiencies, especially in mathematics, when the events of 1814-15 brought an end to his interest. Thus a naval career was out of the question.

14. Gautier's term, "sein parent", op.cit.(1-1), p.7, no longer in use, was an expression describing a relationship between two people of different families who were nursed by the same woman when they were babies. Bérard, son of Jacques Bérard and Marguerite Daniel, was born in Alais on 28 March 1764. Dulieu, Louis, "Le Chimiste Etienne Bérard", Revue d'Histoire de la Pharmacie, 10 (1950-52), 40-44 (40). Gautier's reference to Bérard's son August as Dumas' cousin (see note 13) must be taken in this light.

15. Bérard had been a préparateur for a chemistry course given by Jean Antoine Claude Chaptal (1756-1832) who invited him to become an associate in the founding of his first chemical products factory in 1787 at La Paille, a suburb of Montpellier. The next year they were joined by a business man, Martin. When Chaptal opened a factory near Paris he gave up the one at La Paille, which from 31 December 1798 became Bérard, Martin & Cie. Ten years later to the day, Martin retired, dividing a profit of 307,226 francs! Bérard assumed sole ownership, and subsequently passed it on to his sons. Ibid., pp. 40-41.

16. Ibid., pp. 41-42. This was one of the first two schools of pharmacy established in France. The other was in Paris. Six were provided for by the law of 21 Germinal an 11 (11 April 1803). Prevet, François, Histoire de l'Organisation Sociale en Pharmacie, Paris (Recueil Sirey) 1940, p.99. Bérard's father-in-law Jean Etienne Salette who died in 1813 had been treasurer at the school in Montpellier from its inception. When Bérard took on the additional burden of successor to Salette, he insisted that his other son Jacques Etienne (1789-1869) return from Paris to help in the direction of the chemical factory at La Paille.

their careers in dispensaries." (17) As a consequence of this advice, Dumas was soon apprenticed to the pharmacist Bourgogne in the rue Peyrolerie in Alais.

Although schools of pharmacy were founded in 1803 (18), attendance was not compulsory for those who wished to become pharmacists. Candidates had only to "practice the art in a legally established pharmacy" for eight years (19); succeed in examinations at the end of that period (20); pay the expenses involved (21); and promise before the Prefect of the Département "to practice their art with moral integrity and fidelity" (22). However, the second class diploma thus

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17. Gautier, op.cit.(1-1), p.8, does not use quotation marks. He may have had access to a letter which he paraphrased.

18. By decree of 25 April 1777 the apothecaries of France were allowed, indeed encouraged to unite in independent organisations called colleges of pharmacy. The college of Paris developed courses in pharmacy and in the physical and natural sciences for apprentices, but government schools were not formed until 1803. Prevet, op.cit. (1-16), p.95.

19. Although this seemed to continue the apprenticeship system, an advantage was given to those who attended a school of pharmacy for they were able to begin their career after only six years; three in the school and three in a pharmacist's shop as a sort of apprentice. Law of 21 Germinal, No. 8. Ibid., p.799. Candidates were required to enregister annually, either at the school in cities where one existed, or in a register kept for the purpose at the Commissariat of Police or the Mairie.

20. The examinations, two in theory (principles of the art of pharmacy; botany and the natural history of simple drugs) and one in practice (performance of at least nine chemical and pharmaceutical exercises) were the same whether the candidate attended a school or not, and could not be administered to him until he had reached the age of 25. Where no school existed, students were examined both in theory and practice by a board of examiners composed of the doctors assigned to examine those who wished to become health officers and four pharmacists (named for a period of five years). A candidate succeeded by satisfying at least two-thirds of the members of the board. Ibid., pp. 802-04.

21. They were only 200 francs compared with 800 francs demanded of those who attended a school. Both had to pay the additional cost of materials used during the practical examination. Ibid., p.804.

22 Ibid., p.806.

obtained would only allow them to practise in the Département. A first class diploma, on the other hand, earned by attending one of the schools for three years as part of their programme, would allow them to open a shop anywhere in France (23). To further encourage candidates to enter a school rather than take up a simple 'apprenticeship', the government avoided imposing any formal education as a mandatory prerequisite (24).

For those who, like Dumas, were studious by nature, the value of the programme offered by the government was obvious. Hampered financially, he was unable to follow it. But he soon became dissatisfied with the kind of training he was receiving, apparently limited to mechanical, often menial tasks (25). He decided that there was no point in continuing unless he could attend a school, and that was impossible in Alais. Apparently Paris was out of the question, although Jacques Etienne Bérard may have suggested that possibility (26). There was a school of pharmacy in nearby Montpellier, which also boasted a newly created Faculty of Sciences where he could have attended additional lectures without registering. He might have been able to live with the Bérards and been

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23. Ibid., p.805.

24. The baccalauréat was not required as a step towards the first class diploma until 1840. Not until 1854 were those pursuing the second class diploma obliged to do so at a school of pharmacy. The second class diploma was finally abolished in 1898. Ibid., pp. 102-03.

25. Gautier, op.cit.(1-1), p.8, mentioned some of these tasks, indicating that he had obtained the information from Dumas himself, Jacques Etienne Bérard (for whom Gautier had been préparateur in Montpellier), Paul Bérard (grandson of Etienne and préparateur for Dumas), Ferdinand Roux of Alais and Charles Adolph Wurtz (1817-1884).

26. This proposition would have been firmly rejected by Dumas' father because of his own experience in that city (see note 3). Certainly Bérard had powerful friends in Paris, who, on his recommendation, would have assisted Dumas in any way possible, though the fact that he did not have a baccalauréat might have been an obstacle.

financed by them temporarily. There was, however, another direction in which he could go. Over the years, particularly during the French occupation, students from various regions in France had obtained apprenticeships in Geneva. While it was true that no school of pharmacy existed in that city, there were courses available in the requisite sciences, offered by professors who enjoyed a certain renown (27). One of them, Augustin Pyramus De Candolle (1778-1841), was a close friend of Bérard. They had both been members of the Society of Arcueil and De Candolle had held the Chair of Botany at the <u>Ecole de Médecine</u> in Montpellier from 1808 until 1816 before accepting a similar position in his native city (28). Though he had not begun teaching there until late in 1816 (29), he was well-known by the Genevan savants, among whom he could count many friends. Very probably Bérard wrote to De Candolle early in 1817 seeking an apprenticeship in pharmacy for his young 'cousin'. De Candolle soon discovered that Jacques Antoine Le Royer (1765-1826), who had succeeded his father Augustin (1729-1815) as

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27. Among French speaking centres of science education and research, only Paris ranked ahead of Geneva.

28. Crosland, M. P., <u>The Society of Arcueil</u>, London (Heinemann), 1967. It seems likely that Bérard had gone to Paris at Chaptal's suggestion, and that the latter had introduced him into the group at Arcueil. Bérard was in Paris in 1807. <u>Ibid</u>., p.316. It was through Chaptal's interest that De Candolle obtained the Chair of Botany in 1808 (<u>ibid</u>., p.118), a move which strengthened his ties with the Bérards. When Jacques Etienne returned to Montpellier in 1813 to assist his father, his friendship with the botanist deepened.

29. On 6 January 1816 De Candolle accepted the position created for him in Geneva, but he was unable to begin teaching until November of that year for a number of reasons expressed in a letter to Pierre Prévost (1751-1821) who had recommended his appointment. The letter, Bibl. de Genève, <u>Manuscrits adressés à Prévost</u>, <u>I</u>, fol. 281-82, was written from London on 19 February 1816. In a letter, <u>ibid</u>., fol. 283-84, written from Montpellier 3 June 1816, he noted that he would not be able to leave that city definitively before the beginning of August.

proprietor of the pharmacy Le Royer and Tingry (30), was willing to accept an apprentice. While De Candolle's intercession was essential so far as Dumas was concerned, there was another factor that influenced Le Royer's decision. His son Auguste (1793-1863) had become a master pharmacist on 28 February 1817, so that Dumas could be apprenticed to Auguste (31). If Dumas' parents raised objections, particularly the problems associated with living in a Protestant environment (32), they soon became aware that there was no better way for their son to pursue the career they had chosen

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30. Augustin, member of a family that had practised pharmacy in Geneva continuously since 1616, became a master pharmacist in 1753. His nomination to the Council of 200 in 1775 led to involvement in governmental affairs, and in 1777 he accepted Pierre François Tingry (1743-1821) as an associate. Tingry was born in France but had become a Genevan citizen in 1773 and an agrégé pharmacist in 1774. Augustin renounced all governmental duties in 1794 and accepted his son Jacques Antoine as an associate in 1796. Galiffe, J. B. G., Notices Généalogiques sur les Familles Genevoises depuis les premiers temps jusqu'à nos jours, 7 vols., Geneva, vol. 6, 1892, p.366-82.

31. Jacques Antoine's many letters written to Tingry during his training period at Strasbourg (1782-84) under Spielmann, Bibl. de Genève, Ms. fr. 2150, fol. 47 ff., indicated that he was adopting Tingry's scientific attitudes, especially towards the importance of experimentation. In 1784-85 he attended lectures by Antoine François de Fourcroy (1755-1809). He was critical of Fourcroy's teaching methods, particularly the speed of presentation and lack of experimentation. Ibid., fol. 67. It may be that he was influenced by both these men, the one in a positive manner, the other negatively, to adhere to the phlogiston theory, or at least to the old methods. By 1817 he would have been out of step, and quite happy to have his son train the new apprentice. Further, it was good experience for Auguste to learn how to train an apprentice while he could turn to his father for assistance, and Dumas would benefit from Auguste's more recent education in Strasbourg.

32. Dumas would be living with the Le Royers who were Protestants (Archives d'Etat de Genève, Recensement F.3, Douane, 1822) in a city that was strongly Calvinist. Nevertheless Jean Baptiste would have been able to point out that there was a Catholic Church there and that he would be able to practise his religion freely. Furthermore, the tension that plagued Alais did not exist in Geneva, so that he would be able to work in a more relaxed atmosphere.

for him. Their consent removed the last obstacle. Dumas' departure was described in the following manner:

> "Dumas left his birthplace and his beloved family full of youthful hopes, with a little money and a knapsack on his back. He began the journey to Geneva with some letters of recommendation for Théodore de Saussure, Gaspard de la Rive and P. De Candolle. These words that he carried with him, written in his father's hand, served as his resource for the journey: My second son is leaving for Geneva on 26 April 1817. I recommend him to God, the sovereign protector of travellers." (33)

The sadness that Dumas experienced during the long journey (34) was soon dispelled when he arrived at the Le Royer home in Geneva (35). In this bustling Swiss city radiating peace and freedom after so many years, welcoming at one and the same time those who had been enemies so recently, Dumas began his scientific career. Only a year after his arrival, he wrote to his father:

> "What pangs I suffered when I sensed my complete nothingness, when I saw the narrow and limited structure of my college education collapse in an instant. This initial impression of discouragement and sadness was

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33. Gautier, op.cit.(1-1), p.8-9. The letters of recommendation, for Nicolas Théodore de Saussure (1767-1845), Charles Gaspard de la Rive (1770-1834) and De Candolle, were given by Bérard and Baron Louis Augustin D'Hombres Firmas (1785-1857), a naturalist interested in scientific farming who had been an honorary member of the Société de Physique et d'Histoire Naturelle de Genève since 1812 and Mayor of Alais for at least that long. Some time after Dumas' arrival, De Candolle wrote to D'Hombres Firmas: "Your young protégé gives us the greatest hopes." Ibid., p.40.

34. The misery that Dumas encountered along the route, brought on by many years of war, followed by a season of heavy rain that had destroyed the crops that year was retraced by Hofmann, op.cit.(1-6), p. ii, who recalled that Dumas never forgot the journey and often talked about it later in life.

35. Gén. Dumas, op.cit.(1-3), p.13, wrote: "The day of his arrival in Geneva was marked by a happy event in the Le Royer family, the birth of a grandson, later the professor Marignac, who became well-known in science." Evidently there are dating problems. Dumas left Alais on 26 April according to his father's note. The many sources I have consulted, including his biographer Ador, E., Jean Charles Galissard de Marignac, Geneva, 1894, all agree that Marignac was born on 24 April. He died in 1894.

> soon replaced by a fiercely competitive spirit which has never left me. It supported me when I forced myself to stay up late at night, and when I undertook difficult studies." (36)

He had come to study pharmacy. Before he left Geneva less than six years later, he had published research in no less than five sciences related to that profession - botany, chemistry, physics, pharmacology and physiology - and in a sense had already begun teaching! Attributing this success solely to motivation would demean other factors that enabled him to achieve his goal. These must be sought in his milieu - a new home and family; the pharmacy where he worked; the students with whom he associated; his teachers, including those who wrote the books he read; the laboratories in which he worked, either alone or with others.

The centre of Geneva rests on a small hill. At the base on the north side, the old rue Basse runs parallel to the Rhone River at the point where it enters Lake Leman. Lined with the shops of merchants, fronted by the huge domes that characterised many of the city's streets in Dumas' time, the rue Basse had acquired new names. At the western end it had become known as the rue des Allemands (37). The pharmacy of Le Royer and Tingry was at number 49 on the north side of the street (38). On the second floor of the same building, Jacques Antoine Le Royer

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36. G., Letter of 1818, p.10. This competitive spirit remained with him throughout his life.

37. The north side of the rue Basse had become (from west to east): rue des Allemands dessous, rue du Marché and rue de la Croix d'Or. The south side had become: rue des Allemands dessus, rue du Terraillet and rue des Orfèvres.

38. The rue des Allemands dessous had been called the rue du Lyon d'Or. When the numbering system was changed to avoid duplication of numbers on both sides of the street, it simply was known as the rue des Allemands and No. 49 became No. 11. Early in the 20th century the building was replaced and this street was given the name rue de la Confédération.

lived with his wife, the former Marguerite Soret (1765-1848), their son Auguste, Dumas and a servant (39). The floor above was occupied by Jacob Galissard de Marignac (1773-1864) (40), his wife, Suzanne Le Royer (1790-1870), sister of Auguste, their two children, Marie, born in 1816 and Jean Charles, the future chemist, born at the time of Dumas' arrival, Suzanne Marignac (b. 1752), mother of Jacob, and two servants (41). In his new home, Dumas found an atmosphere of affection and security, that freed him from the ordinary cares of living (42) and a haven of peace and tranquility that made reading and reflection possible. It was thus an important passive influence that allowed Dumas to direct his energies completely towards his goal. Later his room also served as a place where he could do microscopic research.

Dumas' work at the pharmacy contributed to his development in several ways. During his first few months in Geneva before the beginning of lectures, he extended the basic knowledge and skills acquired in Alais,

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39. In the Recensement of 1822 (see note 32), Victorin Monier of French origin (Vaucluse), a student in pharmacy, Catholic, and the same age as Dumas, was also listed as living with Le Royer. It is difficult to say when he arrived.

40. Jacob, a Conseiller d'Etat, was grandson of Pierre Galissard de Marignac (1712-1780) who had emigrated from Alais and become a citizen of Geneva in 1733. Attinger, Victor and others, Eds., Dictionnaire Historique et Biographique de la Suisse, (Société Générale de l'Histoire), Neuchâtel, Vol. 3, 1928, p.308.

41. Recensement of 1822. The first and fourth floors were occupied by other families. Dumas read to Suzanne Marignac, who was nearly blind, nearly every night. By choosing works of merit he was able to continue his own literary development. Gén. Dumas, op.cit.(1-3), p.14.

42. It appears that Dumas was well mothered. While Gén. Dumas, ibid., suggested that Susanne Marignac was a second mother, and Ador, E., op.cit.(1-35), p.4, assigned this role to Suzanne Le Royer, it would seem more likely that Marguerite Le Royer performed it.

so that his presence would be an ever greater asset to Le Royer. He referred to this activity as the <u>work</u> of the pharmacy. It was his means of support as an apprentice, and he could expect that it would be when he had become a pharmacist. In the laboratory behind the pharmacy where he learned some of the techniques necessary for his work, he was also initiated into the practical methods of research by the Le Royers, especially Auguste, and Tingry. Here too he applied methods described in the textbooks that he had purchased or to which he had been given access. The pharmacy itself was a casual meeting place for many doctors and scientists (43). The opportunity to meet them, to be part of informal discussions on the latest research, was an invaluable learning experience. Though his hours were probably set during term to make possible attendance at lectures and a study routine, he was given much greater flexibility in his working hours at other times, and after he had terminated formal studies at the end of the summer term in 1819, because there were at least four people working in the shop. In 1820 he wrote to his father:

> "Happily the bonds of friendship between my noble master, M. Le Royer, and I, allow me to use profitably all the free moments that the work of the pharmacy leaves me, and to make use of the laboratory instruments with neither restraint nor constraint. We share our work, our pleasures and our difficulties with the most perfect equality. ... If it suits me to be away, he takes my place in all of the details of my life." (44)

It was in this environment that Dumas began what became his first published research, with Le Royer. Some time in the summer of 1819 he was approached by Dr. Jean François Coindet (1774-1834) who wished to

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43. Ibid. and Gautier, Léon, La Médecine à Genève jusqu'à la fin du 18e Siècle, Geneva, 1906, p.366.

44. G., Letter of 1820, pp. 40-41.

know whether a sample of sponge ash contained iodine. Since goitre had always been a serious problem in Switzerland, Coindet was aware of the healing value of the ashes of certain sponges (45). While reading a work by Louis Claude Cadet de Gassicourt (1731-1799) he found a reference to yet another sea-sponge whose ashes were recommended and he began to suspect that the curative agent was being absorbed from the sea-water (46). Aware that iodine had been found in seaweed (47), he reasoned that the recently discovered element might also be present in sponges and might well be the sought-after agent. Within a few days Dumas had analysed the sample and had proved certainly that the sample contained iodine.

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45. This treatment had been used since the time of Arnald of Villanova (about 1240-1311).

46. Ludwig Wilhelm Gilbert (1769-1824) in his Annalen der Physik, 66 (November 1820) 227-40, gave a resumé of a memoir "Entdeckung eines zuverlässigen Heilmittels gegen den Kropf in der Jodine" that Coindet had read at a meeting of the Société de Physique et d'Histoire Naturelle de Genève on 25 July 1820. The memoir is not mentioned in the minutes for that meeting. Gilbert began: "M. Coindet said that about a year ago, when he was looking for a recipe in a work of M. Cadet de Gassicourt, he found that Russel recommends the ashes of fucus vesiculosus under the name Aethiops vegetabilis against goitre." Ibid., 229. Aware of priority problems, Gilbert pointed out: "M. Fyfe [Andrew Fyfe (1792-1861)] in Edinburgh proved that sponges really contained iodine towards the end of the year 1819; but, as Dr. Coindet said, he had already discovered the extraordinary action of iodine on goitre six months earlier." Ibid., 230. Le Royer and Dumas indicated, moreover, that they had experimented with iodine for 15 months from the time that "Dr. Coindet began to prescribe this remedy." Naturwissenschaftlichen Anzeiger des allgemeinen Schweizerischen Gesellschaft für die gesammten Naturwissenschaften, 4 (Insert - 1 September 1820), 1-4 (4). Issues of this obscure journal (hereafter Nat. Anzeiger) were published monthly by Karl Friedrich August Meisner (1765-1825) in Zurich from 1 July 1817 until December 1821. Four issues in 1822 and a final 2 in 1823 completed the set of 60 issues (5 years). Articles were written either in German or in French.

47. Iodine had been intensively studied by Joseph Louis Gay-Lussac (1778-1850), Humphry Davy (1778-1829) and others during the preceding decade. For example, see Ann. Chim., 91 (1814), 5-160.

Preliminary laboratory tests showed that the element did attack goitres. Then began a period of searching for the best form in which to administer it. Dumas wrote later:

> "Full of confidence in him, we sought every means of procuring for him in a state of perfect purity, the various preparations that he wished to submit to examination, and we have tested all procedures for making the desired substances so that we could appreciate the degree of accuracy and precision (48) that one could expect from each of them." (49)

These investigations, carried out over a 15 month period, satisfied Dumas and Le Royer that the best medicaments were the pure iodides of the alkali metals potassium and sodium. They stated clearly: "We believe that our preference for iodides or iodised iodides (50) is in greater conformity with chemical ideas and the exacting demands of medicine." (51) The principal purpose of the article, undoubtedly written by Dumas, was to describe their work as simply as possible, to encourage pharmacists to adopt the procedures they had devised. After reducing to three the various objections that had been offered to the use of iodides rather than pure iodine, they disposed of them (52), then described carefully methods

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48. "exactitude et régularité"

49. Nat. Anzeiger, 4 (Insert - 1 September 1820), 1.

50. Iodine dissolves readily in potassium iodide solution forming a complex (modern formula KI_3)

51. Ibid., 1-4. Coindet had continued to prescribe a solution of iodine in alcohol despite its disagreeable properties, and the authors allowed that this might be necessary in very severe cases. But, as they pointed out, Jean Jacques Colin (1784-1865) and Henri François Gaultier de Claubry (1792-1878) had already observed that substances rich in hydrogen convert iodine to hydriodic acid. Le Royer and Dumas had found that alcohol did this.

52. i) The iodides are not as active as iodine; response: only when they were not properly prepared. ii) The preparation of iodides is too difficult for most pharmacists; response: a method to follow that was not. iii) Certain patients must be treated with pure iodine; response: exceedingly few would not respond to iodised iodides.

that were sure for making the two iodides (53). They assured pharmacists of their willingness to give assistance in any practical aspect of these preparations and to continue to search for even simpler procedures, so that "the use of iodine would not be discredited in any way, either because of an application arising from a misunderstanding, or a defective preparation." (54) In reading the article, one sees a secondary purpose manifesting itself. They had done a great deal of work with iodine:"We have handled many pounds of iodine, which has given us numerous opportunities to observe the action of various reagents on that substance." (55) They expected to use their studies as a source for several articles, of practical as well as theoretical value:

> "We propose to survey completely [the study of iodine] so that a situation such as this, as fortunate as it is rare, may benefit science. For this purpose we will publish as soon as possible a complete study of iodides whose properties have illustrated the use of several laws of statics which merit the attention of chemists." (56)

Over and above these considerations, they were interested in the controversy, still unsettled, concerning the elemental character of chlorine and iodine. While Dumas counted himself among those who shared

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53. Ibid., 3. By reaction with hydrogen sulphide gas, iodine in water solution (no excess solid) was converted to hydriodic acid which in turn was exactly neutralised by pure potash to avoid impurities of excess potash or free acid, and prevent formation of iodates. The procedure and difficulties involved were discussed in detail. Sodium iodide could be easily prepared by Gay-Lussac's method, reaction of the sub-carbonate of soda (Na_2CO_3 in modern notation) with zinc iodide prepared by reacting zinc with iodine in the presence of water. He referred the reader to the original memoir (see note 47) for details. Potassium iodide could not be prepared in this way.

54. Ibid., 4. Dumas' italics.

55. Ibid.

56. Ibid.

Gay-Lussac's views rather than those of Berzelius, he was not yet willing to offer his own thoughts:

> "We will await the results of some experiments which we are doing, and from which we hope to draw consequences of great interest, before taking an active part in this discussion." (57)

It is interesting to see lifelong attitudes already appearing in Dumas' writing: "proofs drawn from analogy", "a generalising mind", counting himself among "persons who wish to hold themselves to positive knowledge", "theories ... based on well-known facts".

Dumas was influenced too by the students with whom he associated. He had not been in Geneva long before he began to meet the young men who were apprenticed to the other pharmacists in the city. During the summer months he joined them in field trips devoted to botany, possibly to assist De Candolle, who was occupied that summer with the creation of a botanical garden for the city (58). When the coming of winter brought an end to such activities, they decided to continue their association by holding meetings every Tuesday in quarters rented inexpensively for the purpose. Daniel Colladon (1802-1893), son of a pharmacist who was actively interested in research, may have been part of the group. During the first meeting, a discussion of how they should occupy themselves revolved around social activities until Dumas suggested that they should use the time to further their knowledge of science. Late in 1817 he wrote to his father:

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57. Ibid., 1.

58. This project was budgeted 28 December 1816. The garden was publicly inaugurated 19 November 1817. Borgeaud, Charles, Histoire de l'Université de Genève: 3. L'Académie et l'Université au XIX Siècle (2 vols.), Geneva (Georg & Co.), Vol. 1, 1934, p.31.

> "In my turn I spoke of work. The others rebelled. I presented the advantages. Soon I had a majority and whether they did so out of shame or conviction, everyone consented to devote the entire evening to work. So here I am, a member of the Société française de pharmacie ..." (59)

In his persuasive arguments, Dumas would have pointed out that their meetings were initiated by the desire to be with others who were attracted to the sciences. Why not use the opportunity to share their interest in a constructive manner? At the same time they would learn how to do research, organise it, present it in an open forum and defend their conclusions. Everyone would benefit from the ensuing discussion. Moreover, these efforts would be an excellent preparation for participating in similar activities carried out during meetings of the learned societies to which they aspired to belong one day. In the letter to his father he continued:

> "We build a good fire and each reads in turn a memoir of his own composition. It then becomes the object of our discussions, which are always peaceful because we are aware that each of us has his own inadequacies." (60)

There are apparently no memoirs in existence that are known to have been read at any of these meetings. However a memoir by Dumas does exist on which he wrote the following information: "No. 1, Lu à la Société 18 9bre 1818. à Naturwissenschaftlichen Anzeiger 3 août 1818." (61) Though it may have been read at a meeting of the Société de Physique et d'Histoire Naturelle de Genève (referred to hereafter as the

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59. G., Letter of 1817, p.9. Probably Dumas used this name in the letter for want of an official designation.

60. Ibid.

61. Institut de France (Paris), Archives de l'Académie des Sciences (Hereafter Arch. Acad. Sci.), Fonds Dumas, Carton 3.

S.P.H.N. de Genève) (62), it could well have been the fruit of research done in preparation for a paper first read to the 'Société Francaise de Pharmacie'. On the other hand it may have been read only to his fellow students and not the S.P.H.N. de Genève (63), despite the fact that he believed it to be publishable.

There is no information available on how long the student group remained in existence. On 3 March 1822 a similar group was founded by six young men, among them Colladon, with the name Société de Philosophie (64). Since Colladon wrote later that this Society was founded in 1818 (65), it is possible that the 'Société Française de Pharmacie' continued in existence and was simply formalised, although it is more probable that there was an interim period when meetings were suspended. It has been said that Dumas gave a course in chemistry to the members of the Society (66). He would hardly have been competent enough to do so before the

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62. There is no indication in the minutes of the Society that it was read. Nor was it published in Nat. Anzeiger, in which memoirs or summaries of work by members of the Society frequently appeared. There may have been an attempt to save the struggling journal by linking it more closely to the Society (a digest of its meetings was included for a time), but when Meisner became too ill to continue he had no successor.

63. There are other undated manuscripts from the period, in biology for the most part, which may have been memoirs of one kind or another but may be lecture notes.

64. Regulations, patterned on those of the S.P.H.N. de Genève, were drawn up in the first few meetings. Bibl. de Genève, Procès Verbaux de la Société de Philosophie, Ms. fr. 1679. Only the first record book (3 March 1822 - 1 May 1824) is extant.

65. "With the help of some friends I founded a scientific society that we called the Société de Philosophie, into which one could only be received by reading an original memoir. ... This society, founded in 1818, remained in existence until 1826 or 1827; at that time our society was liquidated because many of us had begun a career or had left Geneva, and our collection benefited the national museum." Colladon, Jean Daniel, Souvenirs et mémoires 1802-1893, Geneva, 1893, p.67.

winter of 1818 or even 1819. A course of the scale hinted at by Colladon would probably have been given even later, perhaps more than once. In any case, Dumas continued his interest in the student society even after he had become a member of the S.P.H.N. de Genève, as Colladon recalled later:

> "We invited several professors or scholars, among others MM. P. De Candolle, Th. de Saussure, J. B. Dumas, L. Necker, Macaire, Aug. De la Rive, Marcet, Choisy. M. Dumas attended most frequently, and he sought to put us on our mettle by speaking to us about the great advances in chemistry. Thus he discussed dyeing with indigo, madder, etc. [The others] simply communicated summaries of their principal memoirs." (67)

While he probably attended other meetings, Dumas read only one notice to the students in 1822, on the chemical composition of what he later called alkaloids (68). It was work that he completed with Joseph Pelletier (1788-1842) in 1823 and will be discussed in later chapters. Evidently Dumas' relationship with his fellow students in pharmacy began as both a learning and teaching situation, but he had quickly surpassed them by intensive study and was regarded by them as both a savant and a teacher.

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66. Hofmann, op.cit.(1-6), p. iii, called it "a course of experimental chemistry" and indicated that Dumas improvised the necessary apparatus. Colladon, in a letter to Pothier published in Pothier, C. A. Francis, Histoire de l'Ecole Centrale des Arts et Manufactures, Paris, 1887, p.478 refers to "the lectures that he [Dumas] gave us in Geneva at the Société dite de Philosophie that I had founded with some friends", and says that these lectures formed the basis for Dumas' course given later at the Athénée in Paris.

67. Colladon, op.cit.(1-65), p.67. Of those he listed, the names of the following appear here for the first time: Louis Albert Necker (1786-1861), Jean François (called Isaac François) Macaire (1796-1869), Auguste Arthur De la Rive (1801-1873), François Marcet (1803-1883), Jacques Denis Choisy (1799-1859).

68. "Notice on a part of chemistry still little known, the analysis of plants, particularly directed towards the purpose of seeking and identifying exactly the active principle in plants which are used as remedies." The meeting was on 28 November, Colladon presiding, and the number and stature of visitors to this meeting was sufficient to warrant their listing by the secretary, the first time that this had been done.

His personality traits, his interests and a certain native talent led him in that direction. Without the experience he obtained in Geneva, it would be difficult to explain the early success he achieved in this aspect of his life in Paris.

Dumas loved to read and this was an important factor in his development as a scientist. He had arrived in Geneva rather late for beginning courses in the Academy, so he was probably advised by both Le Royer and De Candolle to wait until the next semester. During the time that he was free from duties at the pharmacy he studied basic textbooks to make up for the deficiencies in his scientific background. Works by Lavoisier in chemistry, De Candolle in botany and Biot in physics became his scientific 'primers' (69). Such journals as the Annales de Chimie et de Physique and the Journal de Physique taught him both what topics were currently being investigated and ways in which research was presented (70). Sometime late in 1817 or early in 1818 he began an intensive study of the

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69. Lavoisier, A., Traité Elémentaire de Chimie, Paris, 1789; De Candolle, A. P., Théorie Elémentaire de la Botanique, Paris, 1813; Biot, J. B., Traité de Physique Expérimentale et Mathématique 4 vols., Paris, 1816 (esp. vol. 1). Among many others that he read were Bezout's mathematics (Gautier, op.cit.(1-1), p.10) and several that Dumas refers to in his early articles: Mémoires de la Société d'Arcueil, Paris, 1807-1817; Thomson, Thomas, Système de Chimie, Paris (Dumas probably read the second French edition which appeared in 1818); Berzelius, J. J., Essai sur la Théorie des Proportions Chimiques, Paris, 1819 (transl. by the author).

70. Hofmann, op.cit.(1-6), p. iii, indicated that Dumas had read the former. References to articles published in it appear in several articles written by Dumas while he was in Geneva. Dumas contributed at least two articles to the Journal de Physique during that time also. In several of the 31 cartons of Dumas' papers (Arch. Acad. Sci., Fonds Dumas) there are folders with small cards in them, each card bearing the title and location of articles in the latter journal. While it is tempting to think that he made a file of these in Geneva, it is more likely that this was done in Paris while he was preparing his textbook.

Essai de Statique Chimique written by Claude Louis Berthollet (1748-1822) (71). In a lecture given at the Collège de France in 1836, Dumas described for his students the difficulty that he had experienced with that abstruse work:

> "It has no more sincere admirer than I; it was on my mind almost constantly for three or four years; between the ages of seventeen and twenty-one I read, reread and meditated on it. Often I blamed myself for not being able to understand it; as I see it now the fault was as much the author's as my own. I read it with pen in hand, extracting, reflecting, commenting on it. Both the Essai and my efforts to understand it have been extremely useful. Through that work, Berthollet trained me for the study of chemistry, and I can say, in a way, that if I have the right to speak to you today, if your attention is given in a spirit of good will, I owe it to my study of Berthollet's statics." (72)

Another essential factor in Dumas' growth in scientific knowledge was the guidance and inspiration given by outstanding teachers; a brief outline of the educational system will help to provide a framework within which their influence may be assessed. When Napoleon decreed the existence of the University of France in 1808, Faculties were created in Geneva as well, since it was at the time a part of the French Empire. However, the courses changed little. Statutes sent from Paris were simply modified to suit the existing situation. Thus, for example, officials in Geneva asked for, and were accorded three professors in place of one for physics and astronomy: Pierre Prévost, general physics;

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71. Berthollet, C. L., Essai de Statique Chimique, 2 vols., Paris, 1803. Early evidence of Berthollet's influence through this work will be found in the passage from Dumas' memoir on iodine quoted on p.17, reference 56.

72. Dumas, J. B. A., Leçons sur la Philosophie Chimique Professées au Collège de France en 1836, collected by Amand Bineau, Paris, 1837, pp. 379-80. Since this work will be referred to frequently in my thesis, it will be cited simply as Leçons. Other French editions (Brussels, 1839 reprinted 1972, Paris, 1878, 1937) are pageinated differently. It is unlikely that anyone at the time studied Berthollet's work so carefully, especially after Proust's law of definite proportions was generally accepted.

Marc Auguste Pictet (1752-1825), experimental physics; and Jean Frédéric Théodore Maurice (1775-1851), applied mathematics. Not one, but two professors of chemistry were named: Tingry, general chemistry and Henri Boissier (1762-1845), chemistry applied to the arts (73). Louis Jurine (1751-1819) was given a Chair of Zoology; Jacques Necker de Saussure (1757-1825), botany; Théodore de Saussure, mineralogy; and Simon Antoine Jean L'Huillier (1750-1840), pure mathematics. Adjoints were named but did not function for the most part. Prévost became Doyen and André Marie Ampère (1775-1836) was appointed in May 1810 as the first inspector. The new Faculty did not have time to establish itself in suitable public quarters before French rule in Geneva came to an end in 1814 (74). A deep division in the new government delayed a decision between a return to the educational system of 1789 and the creation of an independent University modelled on the French system. Pending the solution of this dilemma, Boissier, who had been made rector, obtained permission from both factions to reopen the Résidence de France as a Musée Académique. On 26 August 1818 De Candolle wrote to Dr. Louis André Gosse (1791-1873):

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73. Bourgeaud, op.cit.(1-58), p.171. By his own wish, Gaspard De la Rive received no remuneration as honorary professor of pharmaceutical chemistry. In 1818 when he became titular of the Chair of General Chemistry "which Tingry had occupied until then without fulfilling its principal duties", he did so under the same condition. Ibid., p.123. De la Rive's version of Tingry's course will be discussed later in this chapter.

74. In 1794 the French representative in Geneva vacated the Résidence de France on the Grand Rue. The same year the government bought the collections of Pictet and Tingry and installed them in the residence which had been designated as a museum. These two professors were then hired by the government to extend public instruction to scientific topics. When the French annexed Geneva in 1798, the building became a prefecture and the equipment was returned to private quarters.

> "We are establishing a Museum in the old Residence; the laboratory of chemistry is organised and M. De la Rive will give his course there this winter; the rooms destined for natural history are being organised and will be ready in the autumn, I hope, to receive the donations which our countrymen would wish to make; finally, the upper floor of the same building is given over to a Reading Society which already has 170 members, a library of 2000 volumes, and receives almost all the scientific and literary journals published in various languages. That, sir, is what we have accomplished in one year." (75)

Until then courses had been divided between the College of Geneva and private laboratories.

As an extern, Dumas was not obliged to follow any prescribed programme. He was free to attend those classes which would assist him to achieve his goal, a knowledge of those sciences upon which he would be examined for his diploma in pharmacy. During the first year (1817-18), he attended De Candolle's new course in natural history (76), and those of Jean Jacques Schaub (1773-1825), algebra (77); and Pierre Prévost,

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75. Bibl. de Genève, Papiers Gosse, Correspondance de Louis André Gosse Ms. 2662, fol. 130-31. De Candolle also advised Dr. Gosse, who was travelling in Austria and Italy sending back books and specimens, that he had given a summer course in the botanical garden, "which has more than 2500 species after only a year of existence."

76. De Candolle taught both botany and zoology in his elementary course in natural history, with emphasis on taxonomy and physiology. Later it became a two year course, alternating each year. Thirty regular students and several externs attended his lectures initially, and the number grew over the ensuing years.

77. Schaub had been an adjoint in applied mathematics from 1809. "He was the teacher of Sturm, Colladon, J. B. Dumas, Auguste De la Rive, the beloved guide of a whole new generation who became famous." Borgeaud, op.cit.(1-58), p.161. Among the professors described by Colladon, op.cit.(1-65), p.74, Schaub was listed as the professor of algebra. Colladon seems to have attended lectures one year later than Dumas. Jacques Charles François Sturm (1803-1855) and the other three mentioned all became members or Correspondents of the Academy of Sciences in Paris, and remained lifelong friends.

general physics (78). It is unlikely that Tingry was teaching at this time, which suggests that no course in chemistry was offered that year (79), and it may explain Dumas' absorption with Berthollet's work. In his second year, Dumas certainly attended De la Rive's lectures. As will be seen, during the year 1818-19 Alexander Jean Gaspard Marcet (1770-1822) frequently collaborated with De la Rive in these lectures (80). Dumas also attended Pictet's lectures in experimental physics, which drew the largest audience of both students and externs (81). It is quite possible that he

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78. Colladon described it as a kind of statics or elementary mechanics course. Prévost also taught a course in philosophy "comprising a history and study of sensations". Ibid. Though I have no evidence that Dumas followed either course, the former would have been a useful preparation for Pictet's lectures which he did attend.

79. Neither Boissier nor Tingry had taught chemistry for some time. Illness prevented Gaspard De la Rive from teaching during 1817-18. "Named Premier Syndic for 1817, he performed his duties competently, but the impairment of health which resulted forced him to seek a rest for several months. During this time he travelled in France and England. On his return, 19 June 1818, he resigned his position as Conseiller d'Etat to resume his duties as honorary professor in the Academy, which he continued until 1829." Montet, Albert de, Dictionnaire Biographique des Genevois et des Vaudois qui se sont distingués dans leur pays ou à l'étranger, 2 vols., Lausanne, 1877-78, vol. 2, pp. 378-79.

80. "The two friends sometimes taught in the same chair, and, so to speak, side by side." Bourgeaud, op.cit.(1-22), p.123. Marcet and De la Rive had been friends from their youth in Geneva. Exiled for five years in 1794, they had gone to Edinburgh together for medical studies, in which both had excelled. De la Rive had returned to Geneva in 1799, but Marcet had settled in London, where he had taught chemistry at Guy's Hospital. After the restoration of peace in Geneva, he divided his time between the two cities until he was given the Chair of Medicine in the Academy, made available by the death of Jurine in 1819.

81. A copy of Pictet's course in 1811-12 was made by one of his students, Carl Ritter. It was published in 1864 by G. Kramer who was interested in Ritter, and translated into French by Frédéric Roget in Etrennes genevoises, III, Genève, 1879. Pictet was editor of the Swiss journal Bibliothèque Universelle (begun as Bibliothèque Britannique). "Nephew of de Saussure, he had a superb stock of physics equipment for the time and a great talent for teaching." Colladon, op.cit.(1-65), p.74. The reference was to Horace Benedict de Saussure (1740-1799), father of Nicolas Théodore. Hofmann and most other biographers have said that Dumas was taught by Pictet.

continued with De Candolle's course and was present for others as well, such as Necker's course in geology. From among these professors three must be singled out because of the special influence that each exerted on Dumas' research in Geneva and his future as a chemist: De la Rive, de Saussure and De Candolle.

In the beginning of Dumas' eulogy of Auguste De la Rive there are several vignettes from the life of his father, Gaspard, given by his student in gratitude to the man who had had such a strong influence on his own life (82). Dumas recalled certain aspects of De la Rive's personality, methods and aims as a teacher. Striking similarities with those of Dumas suggest that the Genevan strongly influenced his student. Dumas refers to his "disinterested teaching", "affable, kind, paternal, good-humoured" nature, "satisfaction at seeing that he was understood" and "joy experienced in experiments well done". He "taught with clarity and simplicity". Frequent experimental demonstrations captured the audience whatever might have been the level of their ability or interest. As Dumas indicated:

> "Because of many well-chosen experiments, his teaching was useful for young men who wanted to probe deeply into theories as well as for men of industry looking for ways to apply the art. In addition, he set himself the task of introducing the serious study of chemistry into the education of the cultured, whom he attracted by the brilliance of the phenomena presented, and held by directing their spirit from these lowly reactions of the artisan to the loftiest or subtlest concepts of natural philosophy." (83)

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82. On 28 December 1874, Dumas as Permanent Secretary of the Academy of Sciences read a eulogy of one of its Correspondents, his friend, Auguste De la Rive. "Eloge historique d'Arthur Auguste De la Rive", Revue Scientifique, 14-15 (July 1874-January 1875) 648-58. This gave him the opportunity to say a few words about Gaspard who had not been a member.

83. Ibid., 649.

Since Dumas had attached great importance to the use of large-scale apparatus in the determination of atomic weights after 1840, it is not surprising that he made the following remark:

> "De la Rive kept the taste for large pieces of apparatus that he had acquired while he had studied in England (84); his wealth allowed him to buy them; his laboratory was English and his Voltaic piles were unrivalled on the continent for their importance." (85)

But he made it clear that his mentor had belonged to the French school of thought, not the English:

> "His fellow countryman and friend, Dr. Marcet, a distinguished chemist who lived in London, had come to Switzerland to spend the winter. He found this preference for the opinion of the Paris school nearly insupportable. He claimed the right to lead the elite audience that Gaspard De la Rive gathered around his chair, to the ideas of the London school, to those of Davy whose renown was then immense. Thus the students in the chemistry course had the singular good fortune of attending lectures given by two professors, exposing in turn the views to which they gave their preference on the same topics. They advanced little by little from conventional and classical areas of instruction to the very boundaries of knowledge (86). In such lectures, which were like meetings of the Academy, they pointed out the problems to be resolved; they awakened curiosity; the listeners were impassioned, divided on the opinions given and in the end they applauded the two friends." (87)

It is unlikely that Dumas ever used this technique in teaching, but certainly it taught him to weigh carefully any proposition having implications for chemical theory before making a carefully hedged decision about its validity (88).

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84. He had obtained his medical diploma in Scotland, but had just returned from a visit of several months in England and Dumas may have thought in those terms. Indeed De la Rive may have referred to England frequently in his lectures.

85. Ibid.

86. "à ces hauteurs où la pensée flottante commence à hésiter."

87. Ibid.

Dumas drew upon De la Rive's course for organisation and content as well. He was particularly attracted to the blend of theoretical and applied chemistry that characterised De la Rive's approach (89). It became a part of the course he gave to his fellow pharmacy students in Geneva. He developed it considerably, added his own organisational features at the Athénée and Ecole Centrale and published a textbook based on it (90). Certainly atomic theory, the backbone of the Traité and a focal point of Dumas' activity for many years, was a major theme in De la Rive's course. Indeed it is quite probable that Dumas first began a serious study of the theory in that course. As he said of his professor: "He considered Dalton's atomic doctrine as a fortunate hypothesis; no one contributed more towards its popularisation on the continent." (91)

De la Rive also exerted a more direct and immediate influence on Dumas' research. It would not have been surprising if Dumas first learned of the law of constant proportions from him, for it was certainly to him that the student turned when he had completed a study of hydrates

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88. This was contrary to the opinion of Justus von Liebig (1803-1873), who on several occasions accused Dumas of precipitant theorising.

89. De la Rive was a member of both the S.P.H.N. de Genève (pure science) and the Société des Arts de Genève (applied science). Among the founders of the latter Society were its first president, H. B. de Saussure, Pictet, who followed him in that position and Tingry, whose Cours de chimie à l'usage des Artistes was sponsored by the Society. In 1825 Pictet was succeeded by De Candolle who retained the presidency until his death also. De Candolle was one of the founders of the Société d'Encouragement pour l'Industrie Française in 1801, which may have taken as its pattern the Société des Arts de Genève as well as the Society of Arts in England.

90. Dumas, J. B., Traité de Chimie Appliquée aux Arts, 8 vols., Paris, 1828-46. Since this work will be referred to frequently in my thesis, it will be cited simply as the Traité. All other treatises will be given their full title.

91. Loc. cit.(1-83).

undertaken to test the law. His work was commended but he was advised that much the same research had been carried out not long before by Berzelius. This may well have been his first encounter with the work of the Swedish chemist for he began to study it seriously about this time. It was not long before he had found another topic related to the course that invited experimental study, the atomic volumes of substances in the solid state. This time there was no question about the originality of the topic but De la Rive expressed the opinion that there was little value in pursuing it, even though his student had indicated that only tentative conclusions could be reached without the use of a good vacuum pump (92). For a time he and Le Royer were busy with important pharmaceutical research. When Dumas resumed his study of atomic volumes he was joined by Le Royer. In May 1821 the pharmacy student read a memoir on the topic. In October he sent the following letter to the editor of the Journal de Physique:

> "A month ago I had the honour of sending you a copy of my memoir on the Volume of Atoms and a short note on the Analysis of Frog Urine. I neglected to mention the latter to you. But on 12 September I received the Annales de Chimie and I saw in it an article by M. John Davy on the urine of two types of frogs in which he announces the presence of urea ..." (93)

Though this memoir, "Essay on the Atomic Volume of Substances" was still not in print in October, it was finally published in what became the June issue, marred by "serious typographical errors" as the editor of the

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92. The need for a vacuum pump was expressed in Dumas' original memoir, Arch. Acad. Sci., Fonds Dumas, Carton 4.

93. A rough copy of the first part of this unpublished letter (Ibid., Carton 8), which has been reproduced, was dated 23 October 1821. The rest disappeared when the bottom half of the page was torn away. John Davy (1790-1868) was Humphry's brother.

Bibliothèque Universelle wrote in a brief note added to the article on frog urine that had been submitted by Dumas and Prevost (94). Further discussion of the memoir will be left to Chapter 4.

Augustin Pyramus De Candolle left his birthplace, Geneva, at the age of 18 to study medicine in Paris. Very quickly he became interested in botany, and within four years he was knowledgeable enough to undertake the preparation of a new edition of a fundamental botanical work, Flore Française, at the request of its author, Jean Baptiste Pierre Antoine de Monet de Lamarck (1744-1829) (95). In it De Candolle revealed his own approach (96) to the indispensable tool of the botanist - classification. As the number of plants known had increased enormously because of voyages involving scientific as well as geographic exploration, the need for a more objective taxonomic method became more urgent. In the Flore Française De Candolle turned to the only system that could be applied rigorously, a natural one "tending to place each being among those with which it has the

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94. "Analyse de l'urine de Grenouilles", Bibl. Univ., 19 (February 1822), 115-17. "We are taking this opportunity to protest on the part of one of the authors of this memoir (M. Dumas), against the manner in which the one he wrote in collaboration with M. Le Royer, pharmacist, on the atomic volume of substances has been printed in the Journal de Physique of June 1821; grave typographical errors have slipped into it. Here are some of the main ones ..." Bibl. Univ., 19 (1822), 117. Eight were listed on the following page (e.g. p.6, line 11: 321 in place of 231) which even now cause difficulties in understanding the memoir.

95. De Candolle, A. P., Flore Française, Paris, Vol. 1-5 (1805), Vol. 6 (1815).

96. In 1813 he elaborated and refined it in his textbook (one of those listed earlier in this chapter (note 69).

greatest number of important similarities" (97). Despite the problems inherent in its use, he saw it as the only truly scientific approach to classification (98). It was in De Candolle's classes and in reading his textbook that Dumas absorbed a similar attitude.

Dumas' earliest efforts in this regard were directed towards the application of the natural method to elements and compounds. He had become convinced that the atomic volumes of solids could be used as a basic means of classification in the same way that such necessary organs of plants as stems or roots served to assist in classifying plants. Although his initial efforts were far from satisfying, a statement in his memoir on atomic theory read to the Academy of Sciences in Paris in 1826 makes it abundantly clear that he fully intended to continue in this direction:

> "Beyond the essential purpose of this series of investigations ... I propose another, no less important in my eyes, the natural classification of the elements.
> By natural classification I understand a disposition of these substances in groups, based on characteristics important enough to be considered capable of determining all their secondary properties.
> These characteristics are the various ways in which these substances combine, their heat capacity and the volume of their atom taken in the solid state." (99)

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97. De Candolle, op.cit.(1-95), p. iii. Bernard de Jussieu (1699-1777) was the first to attempt such a system. It was developed by his nephew, Antoine Laurent de Jussieu (1748-1836), but De Candolle made the very important modification that morphology must be the sole basis for taxonomy, to the exclusion of physiology. He described the artificial system as a useful empirical art "which has no other purpose than the recognition of each plant and its isolation within the kingdom". Ibid.

98. In the Flore Française, De Candolle used Lamarck's artificial system (i.e. forcing a choice between two characteristics) as the key to the natural method. "I have divided this work into two parts: the one artificial, destined to make known the names of the plants of France; the other natural, destined to make known, in so far as is in my power, the structure, history and relationships of these same plants." Ibid., p. v.

99. Dumas, J. B., "Mémoire sur quelques Points de la Théorie atomistique", Ann. Chim. Phys., 33 (1826), 340.

The similarity to De Candolle's approach is so evident that it led Stanislao Cannizzaro (1826-1910) to say of Dumas:

> "He knew how to organise the history of elements and compounds in such a way that their comparison was spontaneously evident and analogies were recognised.
> In this way he perfected and introduced into the teaching of elementary chemistry the method of comparison used by Gay-Lussac in a more arid and less attractive form in his courses at the Botanical Garden.
> Dumas kept this method of classification which was not only a characteristic of his own mental outlook, but also the fruit of his studies with De Candolle." (100)

The search for a natural method of classification was at the heart of Dumas' approach to organic chemistry as well (101). Not surprisingly, his interest in organic chemistry arose directly from his pharmacy studies. Most substances having pharmaceutical activity were obtained from plants or animals and were mixtures of compounds, one or more of which brought about the desired effect. The first step in understanding the process entailed ~~chemical statics~~, the isolation and analysis of the active chemical compound. Equally important, however, was the question of what was happening in the organism that resulted in its return to health. This led Dumas into physiological studies, from a chemical viewpoint. Furthermore, if healing involved chemical interactions, as he was led to believe on the basis of his work for Dr. Coindet, then a study of reactions, i.e. chemical dynamics, was necessary. He soon realised that too little was known about the statics of organic chemistry to permit any serious investigation of its dynamics. Even when enough qualitative and

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100. Cannizzaro, S., "Discours prononcé à la mémoire de J. B. Dumas dans la séance du 4 mai 1884 de l'Académie R. des Lyncéens", (transl. from the Italian by Félix Le Blanc), Bull. Soc. Chim., 1884, 130-41 (134).

101. For an extended article on this topic, see Kapoor, S. C., "Dumas and Organic Classification", Ambix, 16 (1969), 1-65.

quantitative information was available about known pure organic compounds to be able to write formulas for them as Jöns Jakob Berzelius (1779-1848) had done, there was no obvious basis for their classification. Without it organic chemistry could not be regarded as a science. Dumas wrote in 1834:

> "If one were to suppose that all organic substances had been analysed, that their atomic weights were rigorously established, would a science exist if all of these facts remained isolated and without inter-relationship? No, without any doubt a true organic chemistry would still not have been created, because, though sciences are based on facts, they only acquire their scientific character when all of the facts find a place within the system, grouped by a reliable concept that leaves unfilled spaces to discover and reveals general ideas and predictions arising from this methodical arrangement." (102)

Knowledge of physical properties alone was not enough. But determination of chemical properties required some understanding of dynamics. Dumas saw that the best place to break into this circle would be to compare compounds that were similar in some way. He began a study of ethers while he was still in Geneva. Once the circle was broken, finding other such groups would eventually lead to a unified natural method of classification. Involved in this, of course, was a definition of the limits of organic chemistry. As he said:

> "I limit organic chemistry to the study of definite compounds existing in the organic kingdom or produced by reactions on substances which are part of it.
>
> But you see, that means falling once again into a definition based uniquely on the origin of substances and entirely independent of their own nature. I have searched in vain for another definition, and it is precisely because I have been powerless to discover it that I have gradually come to believe that organic chemistry and mineral chemistry are one." (103)

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102. Dumas, J. B., "Considérations générales sur la composition théorique des matières organiques", J. Pharm., 20 (1834), 261-94 (262).

103. Ibid., 267 (my italics).

Although he had broken the circle six years earlier, the number of known organic compounds was still relatively small. Just as a rigorous application of the natural method to botany demanded information on a host of specimens, so a need arose for many hands, using basic techniques, to isolate the 'specimens' of organic chemistry, pure organic compounds.

De Candolle also exerted a direct and immediate influence. Because of his admiration for the botanist, Dumas may have considered a career in botany even before he had made an important discovery concerning plant hybrids while on an outing with a fellow student, Jean Baptiste Antoine Guillemin (1796-1842) (104). In 1819 he wrote, in a letter to his father:

> "I have gone at it [a work in botany] so briskly that it will be ready for publication some time during the coming summer. Since this work is concerned with plants that only grow in northern or alpine regions, I was planning a trip to Berlin which would provide the means of comparing the vegetation of our glaciers with that of a country much nearer the pole." (105)

Although he indicated to his father that this was a means to an end (106), it is not at all clear that he had given up botany as a career option.

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104. Dumas, J. B., and J. B. Guillemin, "Observations sur l'hybridité des plantes en générale et particulièrement sur celle de quelques gentianes alpines", Mem. Soc. d'Hist. Nat. de Paris, 1 (1823), 79-92 (82). References to this work are confusing because in the inital volume of the journal a selection of memoirs were published that had been read to the society at an earlier date. This memoir on hybridisation was read in 1821. It was not published until 1823. Soon after, Alphonse De Candolle (1806-1893), son of Augustin and member of the Société de Philosophie, read an extract of it, discussed it and added some thoughts of his own. Bibl. de Genève, Procès Verbaux de la Société de Philosophie, Ms. fr. 1679, p.84 (meeting of 30 October 1823). The gentians mentioned in the work provided an excellent opportunity for a study on hybridisation because of their isolation, number and restriction of varieties. As a pharmacy student Dumas was probably interested in the plant because its roots were the source of a drug used as a bitter tonic.

105. G., Letter of 1819, p.42.

106. This will be discussed further in Chapter 2.

However, he never did make the trip. Other activities absorbed his time and Guillemin departed for Paris where he read the memoir and finally saw it published in 1823.

Dumas' interest in organic chemistry came through his pharmacy studies, but it was encouraged and directed by Nicolas Théodore de Saussure (107). If their relationship is taken into account, the similarity in their research activities is less surprising (108). Son of the eminent geologist Horace Benedict de Saussure, Théodore began his scientific career with atmospheric studies. His first publication was on the density of air (109). His method, viewed in the light of that used by Dumas for determining vapour densities, is not without interest:

> "To utilise the principle (110), Théodore de Saussure used a glass bulb, in the form of a flattened ellipsoid, and tightly closed. Its large diameter was 345 millimetres, the small 334. De Saussure took as unity the weight of the bulb in air at a temperature of 14.4°, barometric pressure of 758 millimetres and humidity of 75 degrees of a hair hygrometer. For this type of experiment very sensitive balances are necessary, his was accurate to 25 milligrams." (111)

Although he used it primarily to verify with great precision "Mariotte's law ... that the density of air is proportional to the pressure it

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107. Although De Saussure was listed as honorary professor of mineralogy and geology in the Academy from 1802-1835 he never gave a course. Most authors suggest that it was due to his shyness and timidity but Pilet, P. E., D.S.B., Vol. 12, 1975, p.123, says that de Saussure, who left Geneva to live in England during the Revolution, was invited to return to occupy a chair in plant physiology at the Academy. When he was named to the other position he requested a leave of absence and never did teach.

108. I am not aware of any source in which this has been mentioned.

109. J. Phys., 36 (1790), 78-.

110. The author referred to the principle that a body weighed in air loses weight equal to the weight of air displaced.

111. Biographie Universelle, Paris, Vol. 81, 1847, p.177.

supports" (112), it was quite suitable as a method for comparing densities of any gases. This investigation led him to examine the role of the atmospheric gases, particularly oxygen and carbon dioxide, in the germination of seeds and the growth of plants as well as other questions in plant physiology (113). Through his many discussions with de Saussure, Dumas developed an interest that facilitated his decision to do research in animal physiology with Prevost and led eventually to a more complete understanding of the material link between animals, plants and the atmosphere (114).

De Saussure's research led him to develop a method of analysis for organic compounds, in which oxygen was the oxidant. He continued to use it (115) despite the introduction by Gay-Lussac and Thenard of procedures in which oxygen compounds were chosen as oxidants. Certainly he would have instructed Dumas in the techniques and procedures involved, discussing compounds found in plants or derived from them that he had analysed: starch; the sugars formed from it; fermentation products, especially alcohol; ether and its relationship to alcohol (116); essential oils. Dumas' attention was drawn to all of these in the course of his research. By 1833 he had

112. Ibid. The law, often attributed to Robert Boyle (1627-1691) was announced independently, though later, by Edmé Mariotte (1620-1684).

113. His memoirs began in 1797 and were compiled in a separate publication. De Saussure, T., Recherches chimiques sur la végétation, Paris, 1804.

114. This will be discussed in Chapter 10.

115. His method was published, J. Phys., 64 (1807), 316-354, and numerous analyses of organic compounds, Ann. Chim. Phys., 13 (1820), 259-84; 337-62.

116. Ann. Chim., 89 (1814), 273-305. His analyses for these two compounds were very good. From them he concluded that they were compounds of water and olefiant gas and that there was half as much water in ether as in alcohol.

already made a significant beginning in his effort to bring order into a part of chemistry that had resisted even the inroads of analysis. De Saussure wrote:

> "I am extremely flattered that you have sent me the latest volume of your important work on chemistry applied to the arts. You have dealt with the most evidently useful aspect of that science and presented the goals achieved by all our research. You have done so with the order, scholarship and talent that was needed for such an undertaking.
> It is surprising that in addition to this you have been able to complete the many analyses with which you have been involved. It gives me great pleasure to see that you have not forgotten the promise you made to me in this matter." (117)

In 1827-28 Dumas published seminal studies of ethers that were begun in Geneva, as a consequence of reading the textbook by Jean Baptiste Biot (1774-1862) on experimental physics. Biot had used information obtained by Jean André Deluc (1727-1817) on the expansion of fixed and volatile oils to derive a general formula for the expansion of liquids (118). The substances Deluc had used were mixtures for the most part (119) and unrelated. Dumas decided to analyse several liquid compounds that were analogous, in an attempt to simplify the relationship, or perhaps even correct it. Whether de Saussure suggested that ethers would be ideal for such a study, or Dumas arrived at this conclusion himself, he

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117. Unpublished letter from Théodore de Saussure to Dumas from Chambéisy, written 3 August 1833. Bibl. de Genève, Ms. Saussure, 189, pp. 147-48.

118. Biot, op.cit.(1-69), Vol. 1, p.210. The 'formula' was: $\delta_t = at + bt^2 + ct^3$, where t represented temperature on a mercury thermometer in Réaumur degrees; δ_t was its real expansion; a, b and c were coefficients which were constant for a particular liquid but dependent upon its nature. Biot modified the formula suitably to take into account such factors as the expansion of the glass.

119. Biot gave Deluc's data, Ibid., 197, which were taken from "Recherches sur les Modifications de l'Atmosphère".

would have been guided by his mentor in the preparation of these ethers. He may even have done his experiments in de Saussure's private laboratory. Hofmann states that Dumas worked on ethers "for the better part of 1819 and 1820" (120), simply trying to prepare pure ethers that could be used in the experiments. His inability to do so led him to concentrate upon the ethers and the expansion experiments were abandoned. According to Hofmann, Dumas communicated his experimental results to the S.P.H.N. de Genève, "insisting more especially on the probability of these bodies being compounds of ether and not of alcohol with anhydrous acids" (121), but there is no record in the minutes of the Society that he did so.

It was through de Saussure that Dumas entered yet another sphere of influence that was important to his future, the S.P.H.N. de Genève, founded in 1790 by several young men who wished to share their interest in science and who were joined by several Genevans whose reputations were already established as scientists. In a notice on the history of the Society written in 1821, one of the founders, Jean Pierre Etienne Vaucher (1763-1841) described their meetings which were characterised by a particular friendliness (122):

> "The meetings took place every month at the home of the different members in succession. Properly speaking they

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120. Hofmann, op.cit.(1-6), p. vii. Dumas did a density determination of éther nitrique bien pur on 2 March 1821, indicating that he was still working on ethers at that time. Arch. Acad. Sci., Fonds Dumas, Carton 7. It is significant that de Saussure published many analyses of organic compounds in 1820 (see note 115).

121. Hofmann, loc.cit.(1-120).

122. Vaucher remarked: "During an interval of 30 years, I do not recall that I witnessed any stormy discussion, or heard any of those bitter or cutting remarks that often make such meetings disagreeable." Mem. S.P.H.N. de Genève, 1 (Second part) (1821) xiii-xxxiii (xvii).

> were meetings of friends, who, after conversing informally on various topics, met to hear a memoir read by the person in whose home they had been received, who was always the temporary president. Afterwards, those present commented on the memoir. Finally, different members communicated observations on other topics, and we went our way with the desire to see one another again and the feeling that we had acquired new insights into interesting matters." (123)

He also wrote that members made a point of repeating at these meetings experiments of particular interest to them, described in journals or in letters received. The meetings were often attended by foreign scientists who were visiting Geneva or passing through. While Dumas was in Geneva, these included Ampère, Berzelius, Biot and Dominique François Jean Arago (1786-1853) (124). Some of the visitors became honorary members (125). The list includes the names of several scientists of some importance in this thesis, whom Dumas probably met for the first time in Geneva: Baron Friedrich Heinrich Alexander von Humboldt (1769-1859) (1805), Ampère (1814), Pelletier (1820) and Jean Victor Audouin (1797-1841) (1821) (126).

It was almost six months after his arrival that Dumas was first

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123. *Ibid.*, xiv-xv. The Society had no permanent president, but did have a secretary and treasurer.

124. Vaucher also named several internationally known scientists, including Berthollet, who attended meetings before Dumas arrived in 1817. Berzelius visited Geneva in the summer of 1819. It would have been the only opportunity that Dumas had of meeting the Swedish chemist who became his adversary on many issues.

125. Names for honorary membership were offered by members. Normally some contribution (such as a memoir) was expected prior to such nomination, but as an exception to the rule Pelletier's name was advanced and he was elected without such a contribution. The complete list of members and honorary members from the beginning to 1821, with the date that each became a member is given *ibid.*, 1 (First Part) (1821) viii-x.

126. The year in which they became honorary members is indicated. Two others, D'HombresFirmas, Mayor of Alais, and André Marie Constant Duméril (1774-1860) with whom Dumas later worked at the *Faculté de Médecine* of Paris, became honorary members in 1812.

escorted to a meeting of the Society by de Saussure on 23 October 1817 (127). The eminent plant physiologist introduced Dumas to his nephew L. A. Necker who, as host, was presiding that day and read a paper on his geological trip in Scotland (128). After admitting in a letter to his father that he had been a little overwhelmed at first, Dumas picked out for identifying comments several of those present whom he recognised:

> "The members of the society who are living are no less famous than those who have died: the physicist Pictet, editor of the journal Britannique; M. Maunoir, who invented an artificial pupil to restore the sight of the well-known Beaumarchais; M. De la Rive, always dreaming, introspective, seeking proofs for the deluge and explanations for the formation of mountains (129); M. De Candolle, friendly in society, very knowledgeable in his work, reasonable in everything; he spoke on botanical geography. M. de Saussure offered the results of his work on Petroleum. ... M. Tingry, cheerful as always, his reflections interspersed with good-humoured pleasantries. I also saw M. Jurine, the respected doctor, whose reputation and learning I knew; ... The group consisted of all these renowned or distinguished men, many others unknown to me, and some foreigners, mostly Englishmen." (130)

In the course of the next two years, Dumas met every member of the society

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127. The date has been established by concordance between the passage (reference 130) from a letter written by Dumas in 1817, and the minutes of the meeting of 23 October 1817 contained in the Registre des Séances of the S.P.H.N. de Genève, Bibl. de Genève, SP 27 (February 1817-February 1818), pp. 58-71.

128. Non-members attended only when invited by a member, who was obliged to present him to the president of the day. "For several years M. de Saussure brought young Dumas over to the president of the day without fail, a few minutes before the beginning of each meeting, to present him officially." Gén. Dumas, op.cit.(1-3), p.18.

129. This must be a description of Gaspard De la Rive, who was the first of that name to become involved with science, as Dumas himself noted later. Loc.cit.(1-82), 648. He must have made an error in identification at the time, since this does not seem to have anything to do with De la Rive's interests, nor could he be described as a dreamer or introspective.

130. Letter of 1817, quoted by Gén. Dumas, op.cit.(1-3), p.18.

officially and gradually came to know them and be known by them. Through his work in connection with the student society and with Le Royer in the pharmacy, he gained the respect of his fellow pharmacy students and acceptance among the older generation of scientists as well.

In May 1821 he and Le Royer applied for membership in the S.P.H.N. de Genève. They had fulfilled the first requirement when their research on iodides had been published in September 1820. The second requirement was the reading of an unpublished memoir. Le Royer had agreed to collaborate with Dumas in continuing his earlier investigation of atomic volumes, and they completed it in April or May 1821. De la Rive agreed to sponsor them for membership (131). The minutes for the meeting of 17 May contain the following information: "M. Deluc presiding. MM. Le Royer and Dumas read a memoir on the atomic volume of substances." (132) A summary was made by the secretary, who noted the questions that were raised by P. Prévost, De la Rive and de Saussure, and the answers, all given by Dumas. At the end of the meeting De la Rive proposed Le Royer and Dumas for resident membership. They were elected on 14 June 1821 (133).

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131. Sponsorship by a member who was expected to examine the work was required and De la Rive knew more about the work than any other member.

132. Bibl. de Genève, Registres des Séances de la S.P.H.N. de Genève, SP 29, Séance de 17 mai 1821. The president was Jean André Deluc (1763-1847), son of J. A. Deluc whose work on the expansion of liquids was mentioned earlier.

133. They paid their fees on 3 September. The registration fee was 12 sols, 9 deniers. The annual fees were double that figure (25/6) until 1 January 1822, when they became 32/6. Since they were accepted after 1 June, they were required to pay fees for a half-year (25/6 in all). After decimalising from 1798-1813 due to the French occupation, Geneva returned to the old monetary system from 1813-1839.

Dumas quickly became an active member of the Society and his name appeared frequently in the minutes of meetings. On 28 June he read an "Essai sur les Animalcules Spermatiques de divers Animaux" describing research that he had undertaken with Dr. Jean Louis Prevost (1790-1850) (134). On the strength of this memoir and an article published earlier on blood, Jean Louis was proposed for membership by Pierre Prévost and later elected (135). In the same meeting Dumas and Le Royer were proposed for membership in the Société Helvétique des Sciences Naturelles. Dumas probably attended the meeting in Bâle from 23-25 July in which the proposal was approved (136). He and Prevost continued their investigation of blood, reading memoirs on that topic on 23 August and 15 November. On 2 May 1822 they read their "Mémoire sur les Organes Mâles de la Génération chez quelques Animaux à Sang Froid" and at the following meeting on 16 May, Dumas presiding, Prevost read their "Essai sur la Faculté Contractile des Muscles" (137). From time to time memoirs detailing research that Dumas

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134. This memoir was among the first to be approved for insertion in a new publication of the Society. Bibl. de Genève, Minutes de la Commission chargée de l'Impression des Mémoires de la S.P.H.N. de Genève, SP 30 (1820-37), Séance de 19 juillet 1821. It appeared in Mém. S.P.H.N. de Genève, 1 (First Part) (1821) pp. 180-208.

135. Dumas and Prevost had just had the first of their memoirs on blood accepted for publication. Bibl. Univ., 17 (1821), 215-29. Jean Louis, whose name is often accented though it should not be, was not a close relative of Pierre.

136. Approval came in the session on 25 July. Ibid., 333. Ampère became an honorary member of this society in the same meeting. De Saussure was one of those who founded the society in 1815.

137. Both of these memoirs were further developed before publication in Paris in 1824 and 1823 respectively. In both cases Prevost replied to the questions, which were primarily biological rather than chemical.

had done with others were read: Studies on hybrids with Guillemin, 7 March 1822; sulphur chloride analyses with the pharmacist Jacques Peschier (1769-1832), 21 March; analyses of the acetates of silver and mercury with Le Royer, 4 April; analysis of indigo, also with Le Royer, 18 April. At other meetings he commented on memoirs, announced recent scientific discoveries or read correspondence of general scientific interest (138). He presided over the meetings of 16 and 30 May 1822. On the occasions when members raised questions following the reading of his memoirs, he replied adroitly and to the satisfaction of those present. His active participation in the meetings of the society added a dimension that informal contact with the men of science could not give. It provided him with the background necessary to become involved in the meetings of the Academy of Sciences as soon as he arrived in Paris to stay. Challenged by the critical minds of the men who were advancing the frontiers of science in Geneva, he found little difficulty facing their counterparts in Paris.

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138. For example, he read a letter from D'Hombres Firmas, his patron, concerning a meteor that had fallen in the Ardèche region of France.

CHAPTER 2

DUMAS' PHYSIOLOGICAL RESEARCH

"Studied in this manner, physiology will undoubtedly have a rational foundation and it will turn out that the part of animal life relating to material phenomena will be reduced to chemical, physical or mechanical conditions. We have already demonstrated that muscular irritability is easily represented in its minutest details by means of a well-known electrical activity; now we are going to point out the material conditions and, so to speak, the mechanics of generation; soon we will have the honour of communicating to the Academy our recent experiments touching on the important phenomenon of secretion. In following our various results, it will be seen, astonishingly, that laws become simpler in the measure that the facts on which they rest are studied more thoroughly." (1)

Although Dumas began research with Jean Louis Prevost as a student of pharmacy, generally interested in the related sciences and particularly attracted to chemistry, he soon became an accomplished theoretical and experimental physiologist. His fundamental microscopic studies with Prevost restored microscopy to its proper place as a physiological tool (2). Their examination of blood demonstrated that chemical and physical methods could be used to make important advances in physiology. By applying simple measurements and close observation over a long period of time, they made basic discoveries that dispelled some of the mystery surrounding the reproductive process and in so doing they mounted a strong attack against the a priori theories of vitalism. Dumas could have spent the rest of his life in physiological research, but he was able to fulfil a long-standing desire to live in Paris while he was still in the midst of his work with Prevost, and eventually he gave himself completely to chemical research and the teaching of chemistry. Because he did so, the emphasis in this study will be placed on the chemical aspects of his physiological research and the setting in which it was done.

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1. Ann. Sci. Nat., 1 (1824), 12. This passage is quoted from the first of a series of articles on a new theory of generation by Prevost and Dumas. The "manner" of studying to which they referred may be summarised briefly: From careful observations made during various stages of the reproductive process in several animals, they derived particular 'laws' (generalisations) governing those stages, then drew these together into a unified theory of reproduction.

2. In 1858 Henri Milne Edwards (1800-1885) was able to say: "I must point out here that the re-establishment of microscopic observations, brought about 30 years ago by MM. Prevost and Dumas whose work on blood corpuscles excited a lively interest, was a real service to science." Milne Edwards, H., Leçons sur la Physiologie et l'Anatomie comparée de l'Homme et des Animaux, Paris, Vols. 1-14, Vol. 1, 1858, p.45. Milne Edwards also acknowledged the contribution made by Giovanni Battista Amici (1786-1863), the Italian physicist who did so much to improve the microscope at about the same time. Prevost and Dumas had been using an Amici microscope long before one was available in Paris.

In the Le Royer pharmacy Dumas encountered the practical aspects of the profession, especially the use of pharmaceutical compounds in medicine. Aware that the restoration of health must be brought about by some kind of chemical interaction when such substances were used (3), he saw the need to determine the nature of these interactions. But this required a new approach to physiology, one that emphasised its physico-chemical side. About this time a young Genevan who had studied medicine abroad returned to his native city with the same ideas. Jean Louis Prevost had read the works of the French anatomist Etienne Geoffroy Saint Hilaire (1772-1844) some time during his studies in Protestant theology in Geneva (4). On the point of being ordained he made the decision to pursue a career in physiology instead. He attended lectures in Paris, including those given in comparative anatomy by Geoffroy Saint Hilaire and physiology by François Magendie (1783-1855). To further his plans and at the same time broaden his education, he elected to continue his studies in Edinburgh. On 1 August 1818 he was awarded the degree doctor of medicine (5). After practising in Dublin and London for several months, he travelled in France and Germany for a time before returning to Geneva finally in the summer

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3. He had seen the effects of iodine and iodides on goitres.

4. Born in 1790 of wealthy parents, Prevost attended the college in Geneva, from which he was awarded the baccalaureate in 1811. The same year he entered the Faculty of Protestant Theology. Several years later he wrote to the French anatomist: "It was while reading your works that I became interested in comparative physiology; I would have dedicated my life to it had circumstances not prevented me from doing so." Extract from an undated letter, Bulletin No. 47, Librairie de l'Abbaye, Paris.

5. The title of his thesis was: "On the Use of Baths and Affusions". Gosse, L. A. and T. Herpin, "Notice biographique sur le Dr. Jean Louis Prevost", Bibl. Univ., 4e Sér., 15 (1850), 265-300 (267).

of 1819 (6). Part of this time was spent in Paris observing the effects of kidney excision on the health of animals (7). Not long after his return to Geneva, he visited his relations, the Le Royer family, and was introduced to Dumas. At the time Le Royer and Dumas were immersed in the research undertaken at Coindet's request. Prevost soon realised that the interests of the apprentice, his work habits and his approach to problems were quite similar to his own (8). Within a short time he invited Dumas to join him in pharmaco-physiological research, the isolation of the active agent of a drug, digitalis, used in medicine as a heart stimulant, which would then be studied to determine its mode of action at the physiological level (9). Though they were unsuccessful (10), it was the

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6. Dumas described Prevost as "a young and learned doctor who travelled in France and Germany after doing brilliantly in examinations in Edinburgh, Dublin and London". G., Letter of 1819, p.43. Despite this he was unable to practice in Geneva until he had been examined by the Medical Faculty of the Academy on 28 August 1820. Prevost mentioned the date of this event in a note to Tingry on 23 August. Bibl. de Genève, Collection de B. Reber, Ms 2146.

7. The notes containing his observations on nephrotomised animals are marked Paris and dated from 16 April to 29 May 1819. Arch. Acad. Sci., Fonds Dumas, Carton 3, Doss. "Résection des reins".

8. Dumas wrote to his father that year: "Since I have begun my studies, I have encountered only one person practising [medicine] whose ideas have been directed in the same channels." G., Letter of 1819, p.43.

9. Dumas noted: "One of the principal reasons I can give for having prolonged my stay in Geneva is the pleasure and advantage of working with him on physiological experiments that he has pursued for several years." Ibid. The drug digitalis was obtained by drying the leaves of the foxglove plant, digitalis purpurea. Apparently Prevost had attempted to isolate it some time earlier. Hofmann, op.cit.(1-6), p. iv.

10. Although the physiological effects of digitalis were observable, the chemical properties of the drug were unknown and isolation required a bioassay, a long and tedious process even today. The problem was far more complex than they could have imagined, since there were several agents present, each acting a little differently, some of which underwent enzymatic degradation when the leaves were dried. The chief constituents of the dried leaves are the glycosides digitoxin and gitoxin. Trease, G. E., A Textbook of Pharmacognosy, London, (Baillière, Tindall and Cox), 1961, p. 506-12.

beginning of several years of close collaboration, marked by a growing respect for one another's abilities and a deepening friendship. Observers who knew them were able to remark later:

> "Both of them possessed a creative imagination linked to an indefatigable perseverance; both of them were deft and skilful in the use of delicate instruments in their anatomical and chemical research, and the microscope acquired a new value in their hands." (11)

Undoubtedly Prevost had read the outstanding textbook written by Anthelme Richerand (1779-1840) (12), and had advised Dumas to do so. Thus while they continued their efforts to purify digitalis, they were also studying what little was known about the composition of blood, aware that the effects followed from the chemical interaction of the two. Reading Richerand raised so many other questions in their minds of vital importance to the advance of physiology that they hardly knew where to begin. Taking their cue from this well organised textbook, they decided to investigate the most important systems first, the nervous and circulatory systems (13). They began their first memoir on blood with the

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11. Loc.cit.(2-5), 268.

12. Richerand, A., Nouveaux Eléments de Physiologie, 6e Ed., 2 Vols., Paris, 1814. Modelled on the Primae Lineae Physiologicae of Albrecht Haller (1708-1777), it first appeared in 1801, and for many years it was regarded as the best textbook of general physiology available. Richerand's many revisions kept it current. He was able to take Amaldi of Milan to task for a "voluminous" criticism of the second edition in 1813 (after the fifth edition had already corrected all of the faults he had criticised. Richerand, op.cit., Vol. 1, Avertissement). Prevost may have read this edition while he was convalescing from typhoid fever in Paris in 1814-15.

13. "All the impressions received by the sense organs are reported to the brain; from it decisions go forth, giving birth to the voice and voluntary movements. The circulatory system carries the molecules which are necessary for nutrition, and those which must be rejected from the body. The nervous and circulatory systems are also the only ones, which, provided with a central organ (the brain and heart), extend to all parts of the body through 'emanations' that begin or end in those organs (the nerves, the arteries and veins)". Ibid., p. 134. Richerand continues the analogy showing the relationship of the other organs and systems to these, drawing the whole into a single classification scheme before examining each part in detail.

following statement:

> "When one reflects on the evolution and persistence of animal life, one sees that the unknown action which the blood exercises on the nervous system is the indispensible, perhaps sole necessary condition for maintaining vitality." (14)

But examination of this interaction presumed a knowledge of the individual systems, which in turn demanded a knowledge of their composition and properties, and the function of the parts as well as the whole. In pursuing their objective, the authors envisioned in each of the systems, a principle or active agent whose similarity in various animals would render a comparative study fruitful. Though they regarded the nervous system as more important, they began their investigation on the circulatory system, because the blood and the "functions which prepare it or fashion it for the needs of life" (15) were more amenable to study. By making detailed physical and chemical observations with emphasis on the quantitative aspects, they hoped to amass "a great variety of exact and well-determined data so that they could clear a pathway into the study of the nervous system" (16), in which they were particularly interested. The enormity of this task did not escape them. They were attempting to re-lay the very foundations of physiology. They considered the work on the purification of digitalis, a substance which could become an excellent tool, to be of great importance and Le Royer was invited to continue this

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14. "Examination of blood and its action in the various phenomena of life.", Bibl. Univ., 17 (1821), 215. The introduction to this article, which laid the groundwork for the extensive studies that they intended to undertake, was not included in the article when it appeared in Ann. Chim. Phys., 18 (1821), 280-296.

15. Ibid.

16. Ibid., 216.

research (17) while Dumas and Prevost focused their efforts on the study of blood.

They began their work together in 1819. By 1821 they had gathered enough data on several topics to begin publishing a series of articles, not only on blood, but also on other body fluids. The initial article was the first in the three part study of blood (18). In the first part the authors described the shapes and measured the sizes of the globules (corpuscles) of blood, using the standard method of microscopic measurement (19). The globules were found to be in the form of circular plates in some animals (e.g., man, dog, rabbit) and elliptical plates in others (e.g., duck, snake, frog). In each globule they observed a colourless spherical or ovoid body, always about the same size no matter what the size or shape of the globule, or what animal, sometimes causing a large

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17. Partington, J. R., A History of Chemistry, 4 vols., London (MacMillan), Vol. 4, 1964, p. 244-45, indicated that Le Royer was the first to extract the active principle. His work appeared in a memoir, "Du principe actif contenu dans la digitale pourprée", Bibl. Univ., 26 (1824), 102-06. All references to the work by Partington will be to Vol. 4 unless otherwise indicated.

18. Bibl. Univ., 17 (1821), 215-29 and 294-317; 18 (1821), 208-20; Ann. Chim. Phys., 18 (1821), 280-96; 23 (1823), 50-69 and 90-104. The reasons for the long delay in the publication of the second and third parts in the latter journal will be examined later in this chapter.

19. "It consists in making the object viewed in the microscope with the right eye coincide with a measuring rule placed alongside and looked at with the left eye." Ibid., 18 (1821), 285. The magnification of the microscope used was 300x and the measuring rule a glass plate divided in millimetres and demimillimetres. Ten observations were made for each measurement given. They were involved in this work in the autumn of 1820. On 17 November Dumas wrote to Tingry: "One of this year's issues of the Annales de Chimie et de Physique contains some observations on the diameter of the globules of blood made by Sir Everard Home (1756-1832). Since Dr. Prevost and I are involved in similar studies, we would be very grateful if you would please send us that issue." Bibl de Genève, Collection de B. Reber, Correspondance de P. F. Tingry, Ms 2145.

protuberance. These observations combined with those made during transfusion experiments led them to conclusions regarding this medical procedure "which is too highly regarded, and has seen nothing but abuse in an ignorant and barbarous century" (20): If the blood of donor and receiver consists of differently shaped globules, transfusion will result in rapid death; if the globules are of the same shape but differ in size, as is found to be true in different species, a partial recovery occurs before death, which takes place within six days; if, however, the size and shape of the globules are the same, as is the case when the species is the same, recovery is fairly rapid and complete (21). The seminal character of this important research by Prevost and Dumas was emphasised by Hofmann (22).

The second part of the memoir was a chemical study of the components of blood: serum albumen; the red gelatinous material of which the globules were formed; and the colourless body inside of the globule. They found the serum albumen to be quite similar to egg albumen, and the products of their coagulation, fibrin and egg white respectively, were also found to be similar (23). To avoid changes due to chemical action, the authors

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20. Ann. Chim. Phys., 18 (1821), 294.

21. Though others investigated this problem afterwards at somewhat frequent intervals, there was no real advance beyond the work of Prevost and Dumas until the classification of blood into types was introduced in 1909 by Karl Landsteiner (1868-1943) who discovered in 1900 that the blood serum of one person sometimes agglutinated the red blood cells of another. Speiser, P., Dictionary of Scientific Biography (Hereafter D.S.B.) (Ed. C. Gillispie), 1970- , Vol. 7, pp. 622-25. Prevost and Dumas urged that transfusions should no longer be attempted until the nature of blood was better understood, except perhaps in hopeless cases.

22. Hofmann, op.cit.(1-6), p. iv, mentioned nine prominent physiologists, among them Claude Bernard (1813-1878) and Johannes Müller (1801-1858), who used these experiments as a starting point for their own work, and he indicated that he could have listed several others.

23. The methods used for coagulation were: heat, alkali, acid, electricity and alcohol. They found that fibrin and egg white of the highest purity were obtained when alcohol was used.

separated the globules from the serum by simple settling (24). Thus they were able to measure the proportions of the three major constituents of the blood: albumen, globules (including the colourless body) and water. This they did for twenty animals. Their study showed for the first time that:

> "1°. Arterial blood contains more globules than venous blood;
> 2°. Birds have a greater proportion of globules than any other animal;
> 3°. Mammals have less, and it appears that carnivores have more than herbivores;
> 4°. Cold-blooded animals have the least." (25)

In addition, they were able to give definite proof for venous absorption and to use this information to explain anomalies in the proportion of globules.

In a second paper, read the same day, the authors gave an analysis of frog urine (26) which showed the presence of two parts per thousand of urea. In this way they prepared the way for the third part of their memoir read several months' later, in which their study of the function of the kidneys in secretion was described. It had been known that various secretory organs contributed substances to the blood, while others served to remove unwanted material. Since urea was the principle organic component of urine, Prevost and Dumas wondered whether it was formed in the

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24. Berzelius, William Thomas Brande (1788-1866) and ~~Louis~~ Nicolas Louis Vauquelin (1763-1829) had all used chemical action, treating blood as a solution rather than a suspension and the results that they had obtained were misleading.

25. Ann. Chim. Phys., 23 (1823), 68.

26. This paper, read on 23 August, began: "Since a large number of frogs had been put at our disposal, and frog urine had never been examined, we thought it should be analysed." Bibl. Univ., 19 (1822), 115-18 (115). An accompanying physiological study of the battrachian urinary system showed its similarity to that in warm-blooded animals.

kidney, or transported there intact from the site of its formation. If so, where was it formed? Already familiar with the effects of kidney excision from their reading (27) and from Prevost's experiments in Paris, they saw that this operation could provide at least a partial answer to their question. Since the circulatory system was the only pathway by which material could be transferred between the kidney and the rest of the body, the presence of urea in the blood after excision in greater quantity than normal would be a clear indication that urea was formed elsewhere. Operations on a dog showed that removal of one kidney had no effect on the urea content of the blood, but total nephrotomisation caused a large increase in the urea content of the dog before it finally expired. Further verification of this observation led them to draw several conclusions, which, they emphasised, should be carefully dissociated from the observed facts:

1. The sole purpose of the kidney seems to be excretion;
2. All urea formed in the body passes into the kidney and is eliminated;
3. The blood retains all urea formed, when the kidneys are removed;
4. Since people suffering from hepatitis have no urea in their urine, the liver must be involved in its formation;
5. Studies parallel to theirs should be made to determine where other substances excreted in the urine were formed;
6. Urinalysis could become an important means for discovering the

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27. "The removal of only one kidney did not prevent continued secretion; in all cases the removal of two kidneys at once caused the death of the animal at the end of a few days, and opening the corpse always revealed a large amount of bile in the biliary vesicle, in the small intestine and in the stomach, as though the urea had tried to go out that way united with the biliary liquid. These experiments were performed at St. Louis Hospital during 1803." Richerand, op.cit.(2-12), Vol. 1, p.262.

condition of the blood of an individual, and thus aid in the identification of the nature of an illness.

Several distinguished chemists (28) repeated and confirmed the experiments in this part, and the conclusions were generally adopted by physiologists (29).

While care is always necessary in assigning to each of the collaborators in work done in common a particular part, it seems reasonable in this case to assume that work of a strictly chemical or pharmaceutical nature can be attributed to Dumas while the strictly medical aspects were the contribution of Prevost. Dumas began to develop a skill with the microscope while working with De Candolle and De Saussure, and continued to do so during this investigation. Success in the third part depended upon the ability to detect the amount of urea in the blood. But it was necessary first to isolate it. Dumas devised an ingenious method for separating the urea from other organic matter, particularly sodium lactate. The dried serum and clot were boiled with water until there was no further reaction. The clear liquid was dried and the residue treated with alcohol. The solution, containing what Marcet had characterised and called the mucoso-extractive substance (30), was evaporated and this residue was dissolved in water by addition of nitric acid. The solid remaining after evaporation, almost completely a mixture of sodium lactate and urea

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28. Leopold Gmelin (1788-1853), Friedrich Tiedemann (1781-1861) and Eilhardt Mitscherlich (1794-1863) among others.

29. Hofmann, op.cit.(1-6), p. v.

30. This substance was later shown by Berzelius to consist of sodium lactate and a very small quantity of unidentified organic matter. Berzelius did not observe the presence of urea because he was using the blood of a healthy animal in which the concentration is so low that it was undetectable by the means available at the time.

nitrate, was left on unsized paper till the deliquescent sodium lactate had dissolved in the water it absorbed. The urea nitrate was removed, redissolved and converted to urea.

Because the presence of urea in the blood in these circumstances was so important physiologically, Dumas saw that careful chemical analysis was necessary to leave no doubt about the identity of this urea. Since this circumstance affords the first evidence of his aptitude for organic analysis (31) at a time when procedures were undergoing their initial development, a detailed examination of his results will not be without value. Following the procedure introduced by Gay Lussac (32) and extended by Bérard (33), the gaseous products of the copper oxide oxidation of the

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31. In the memoir containing research done at Coindet's request, he had given the results of analysis of iodides.

32. Ann. Chim., 95 (June 1815), 136-231 (154). Gay-Lussac mentioned it in this article almost in passing, although he recognised that it was "so simple that one could repeat it easily in a course". Ibid., 155. An article on ammonium urate submitted to the Annales de Chimie presented him with the opportunity to indicate in the September issue, Ibid., 96 (1815), 53-54, that he had been using the procedure for at least two years. In both articles his analyses were limited to the determination of carbon to nitrogen ratios. His statement that "the complete analysis of uric acid would have required more time than I could devote to it", ibid., 54, suggests that at the time he did not expect the process to be suitable for determination of the hydrogen and oxygen content.

33. In his thesis "Essai sur l'Analyse des Substances animales", defended publicly before the Faculty of Medicine of Montpellier on 9 July 1817 (extract: Ann. Chim. Phys., 5 (1817), 290-98), Bérard described the process, then gave his method for calculating the amount of hydrogen and oxygen: "The oxygen provided by the copper oxide is known from the loss in weight of the latter during the process; and the water is easily evaluated by calculation, or by the difference in weight of the animal matter and the copper oxide before the process, from that of the nitrogen, carbonic acid and oxide after the same process, assuming that in measuring them attention is given to account for the hygrometric water of the gases." Ibid., 291-92. It is not clear whether this was an editorial summary or a quotation. Bérard used the method to determine the composition of several organic substances including urea and uric acid.

urea were collected and measured in a glass tube as a mixture of equal volumes of carbon dioxide and nitrogen. Dumas noted: "The residue ... submitted to examination in a special apparatus which one of us will soon make known (34), has given us results suitable for obtaining the weights of oxygen and hydrogen." (35) He then gave a sample set of data that he had obtained. 0.069 grams of urea gave 46 cm^3 of gas at 0^oC and 0.76 m. pressure, i.e., 23 cm^3 of nitrogen (0.02914 grams) and 23 cm^3 of carbonic acid (36) (representing 0.01258 grams of carbon). Using the apparatus he had devised, he must have found that the residue weighed 0.06765 grams less than the copper oxide (37). This weight represented part of the oxygen involved in the oxidation of the carbon and hydrogen in the urea, the rest coming from the urea itself. From all of this information he was able to calculate that the sample of urea contained 0.00682 grams of hydrogen and 0.02046 grams of oxygen. He then converted the four values to percentages and compared them with those obtained by Bérard (38).

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34. This he did in his work on plant alkalis which will be discussed at length later in this chapter.

35. Ibid., 23 (1823), 98.

36. His own studies served to verify Bérard's observation (as interpreted in the extract) that equal volumes of nitrogen and carbonic acid (carbon dioxide) were formed. Most non-metallic oxides were regarded as acids at this time, and their acid name will be preferred in my thesis. Carbon monoxide, an obvious exception, will be given the name used then, carbonic oxide.

37. As he did not give the value for the weight loss, I have calculated it for the sake of clarification.

38. In his thesis Bérard gave the composition of the compounds he had analysed in percent by weight as indicated. The editor who gave the extract did not do so, preferring to express volume values, "since one could not easily judge, without calculation, their degree of accuracy, [that is] their agreement with the law of definite proportions". Ibid., 292 and 294. Dumas may have recalculated Bérard's values, but it seems more likely that he obtained them directly from his cousin.

These values and those calculated from the formula using current atomic weights are given in Table 2 - 1.

TABLE 2 - 1. The Percent Composition of Urea, N^2CH^4O

	Bérard (1817)	Dumas (1821)	Modern Values
Nitrogen	43.4	42.23	46.65
Carbon	19.4	18.23	20.00
Hydrogen	10.8	9.89	6.71
Oxygen	26.4	29.65	26.64

The difference between his results and those obtained by Bérard, who had used urea from urine, was certainly small enough in view of the difficulties associated with such analyses at the time to justify Dumas' conclusion on chemical grounds that he had indeed been analysing urea obtained from the blood, especially in view of the qualitative observations that supported it. Nevertheless, a brief discussion of the seemingly large variation between their values and those accepted in modern times would not be out of order. Part of the problem might involve the purity of the urea, but this factor was relatively negligible. Incomplete combustion would need to be considered. Despite the use of heated copper filings formation of oxides of nitrogen was evidently a major source of error. Dumas should have obtained 25.73 cm^3 of each gas under ideal conditions; his error, on the low side, was just under ten percent. Clearly the procedure needed perfection. On the other hand, despite the introduction of what he deemed an improvement, he obtained a weight loss in the residue much larger than he should have (39), so that he was forced

39. 0.06765 grams rather than 0.0552 grams, an error of over 20%. It would be attractive to attribute this to formation of NO_2 but that would be an oversimplification.

to assume a value for the hydrogen nearly 50% higher than it should have been! (40) Exact determination of the quantity of water formed and the amount of oxygen used were problems that had yet to be worked out. De Saussure was still sufficiently dissatisfied with the copper oxide method in 1820 that he continued to use combustion with pure oxygen in analysis of organic compounds (41).

It may seem surprising at first sight that Dumas and Prevost did not continue their studies on blood, except in relation to other studies. Several reasons may be given. Organic chemistry, so important for successful investigation of the components of blood was in its infancy; without it further studies of the blood were difficult if not impossible. Then too, in parallel with their studies on blood they had begun research on the process of generation. It is probable that Richerand's textbook was used again to clarify the problems involved, though they would have been aware that knowledge of the process was entirely speculative particularly from the time that the seminal fluid meets "a liquid, or really a small egg which flows into the uterus along the same pathway taken by the semen" (42) to the moment when a living foetus can be detected. Their initial

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40. Of course he was not aware that his error was so great. It should be recalled that Dumas' values approached those of Bérard, which had been sanctioned as it were by the editor who had made the extract of his thesis, not only because the volume equivalents could be reduced to small whole number ratios, but also because these numbers were such that urea could be regarded as a simple addition compound of ammonia (NH^3) and carbonic oxide (CO). Ibid., 295.

41. Ibid., 13 (1820), 259-84 and 337-62.

42. Richerand, op.cit.(2-12), Vol. 2, p. 405. In his long discussion of generation (p. 380-481), the author outlined the principle theories touching on the events of that time span (p. 405-16), prefacing his remarks with the statement: "Everything else we are about to say concerning the mechanism of generation should be considered likely rather than factual."

findings, read to the S.P.H.N. de Genève in 1821, arose from an investigation of the seminal fluid. They concluded that the animalcules spermatiques long known to exist in the fluid were not related to animalcules infusoires (infusoria), that they were formed nowhere except in the testicles, and then only after the age of puberty, and most important, contrary to the opinion held from the time that Lazzaro Spallanzani (1729-1799) had performed his experiments forty years earlier, they were absolutely essential in the act of generation (43). Thus the animalcules were to be regarded as the active principle of semen as the globules were the active principle of blood. Imbued already with the importance of experimentation as a basis for progress in the sciences, Dumas was able to remark "In this work our intention ... is simply to replace the findings of our predecessors, who have left modern physiologists in a painful state of uncertainty, with positive facts, free of all hypothesis." (44)

A third reason for abandoning the studies on blood has other implications as well. By royal ordinance of 22 July 1818 funds donated by Jean Baptiste Antoine Auget Baron de Montyon (1733-1820) for the purpose of establishing an annual prize in experimental physiology were officially accepted. It was announced in several journals:

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43. Dumas and Prevost demonstrated by improved filtration techniques that when the animalcules were certainly removed from the fluid, the fluid could no longer render eggs fruitful. Nevertheless, they praised the Abbé Spallanzani who had approached the topic "in a more positive manner and with the strict logic to be admired in all the works of this capable physicien". Mém. S.P.H.N. de Genève, 1 (1821, Part 1), 183.

44. Ibid., 205. Comparative microscopic examinations of the animalcules of various animals were made both in their normal environment and in surroundings modified electrically or chemically.

> "The Royal Academy of Sciences announces that it will give a medal of the value of 440 francs for the printed work or manuscript addressed between now and 1 December 1819, which seems to have contributed the most to the progress of experimental physiology. Its judgment will be made known at the public meeting in the spring of 1820." (45)

The timing suggests that the offering of this prize may have been the initial motivation leading Dumas to join Prevost in physiological studies and may explain to some extent their absorption with Richerand's textbook, a possible source for a research topic. While the monetary value of the award may have had some attraction for Dumas, it is more likely that he was interested in the prestige associated with such a prize, and the opportunity that it would give him to remain in Geneva, or, better still, to go to Paris after he had completed his formal studies in pharmacy. Once they had made the decision to examine blood, they began working immediately, but it soon became evident that entering the first competition was out of the question. Indeed it was the late spring of 1821 before they had accumulated enough data to begin publication. By November they had read the third part of their memoir on blood, as well as the memoir on animalcules and the two were submitted independently in December for the prize to be given in 1822 (46). On 14 January 1822 a Commission was

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45. Ann. Chim. Phys., 9 (1818), 443. Montyon's donation was anonymous, but his name was attached to the prize after his death.

46. "The Academy received the following works ... 'Essai sur les Animalcules spermatiques de divers Animaux', by MM. Prevost and Dumas; 'Examen du Sang et de son action dans les Veines dans les divers Phénomènes de la Vie', by the same. At the request of the authors, the two works have been sent to the Commission concerned with the prize. Procès Verbaux des Séances de l'Académie des Sciences (hereafter PVAS), Vol. 7, p. 260, Meeting of 24 December 1821. The deadline for the submission of memoirs that year was 1 January 1822.

elected to examine the six memoirs submitted (47). The decision, announced on 8 April 1822, must have been something of a disappointment for Prevost and Dumas (48), even though they could claim the satisfaction of knowing that their work had been read by men who were the outstanding physiologists and anatomists of the time. On the other hand, more opportunities would arise. One could enter the competition as often as one wished. Partly because continued useful research on blood, of the sort that interested them, required a level of chemical knowledge that did not exist at the time, partly because of their declared interest in the interaction of the circulatory and nervous systems, they decided to investigate the origins of these systems. This had already led them to studies of the mechanism of generation, which they now chose to continue, and to extend into the period of foetal development.

This work on generation occupied the better part of two years, during which time they examined with the greatest care the reproductive organs of various animals, birds and fish and their secretions, with special attention to the units of generation, the egg and what they had proved to be for the male, the animalcules spermatiques. They also traced the pathway taken by both and the mechanism by which they united. The memoirs reveal a scrupulous attention to detail in their observations.

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47. Their memoir was sent to Geoffroy St. Hilaire on 22 January, read and sent to Magendie on 4 February, to Duméril on 11 February, to Baron Pierre François Percy (1754-1825) who had replaced Jean Noel Hallé (1754-11 February 1822) on 18 February, and finally to Baron Jean Léopold Nicolas Frédéric (called Georges) Cuvier (1769-1832) the president of the Commission.

48. The winners, Jules Germain Cloquet (1790-1883) on kidney stones and Antoine Des Moulins (1796-1828) on the nervous system, had submitted long memoirs on their research, with many illustrations.

They terminated each part with a series of conclusions which may be summarised briefly (49) as follows:

Part 1. The authors drew together their previous observations and conclusion on the function of the male in generation. In addition to extensive verification of their earlier claims concerning the animalcules, they included the observation that these essential units were completely formed in the testicle, and remained unchanged by any of the fluids in which they moved on the way to their rendezvous with the egg. The particular observation was made that most birds produce these animalcules only during the mating season.

Part 2. Noting that in this part they had only studied amphibia (50) Prevost and Dumas discussed at some length conditions involving the viability of both eggs and animalcules. They noted that eggs released for fertilisation absorbed liquids and extremely small solids in suspension (51), swelling in the process. If the eggs were placed in a liquid free of animalcules, absorption took place but decomposition began almost immediately, and was accompanied by a diminution in fertilisability

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49. A careful assessment of their work is beyond the scope of this thesis. The summary will be followed by comments on major contributions only. It should be noted that Dumas drew the many diagrams involved in the work submitted and its publication. They are all designated as his. Throughout his papers there are many small portraits which he sketched in the process of 'doodling'.

50. "We have given preference to batrachians not because examining them made the study of the facts we had to explore any easier; we are in a position to state the contrary; but it is easy to see that without a considerable amount of material, analogous to that which Harvey owed to the munificence of his royal protector, it is absolutely impossible to undertake such research." Ann. Sci. Nat., 2 (1824), 100. ~~It is difficult to avoid inferring that they believed their work to be of equal significance to that of William Harvey (1578-1657), discoverer of blood circulation.~~ In his De Generatione, William Harvey (1578-1657) described experiments on animals given by Charles I. DSB, VI, p. 159.

51. For example they observed the entry of the coloured matter of blood and ink.

proportional to the time immersed. In the presence of seminal fluid, however, even highly diluted, fertilisation occurred in the normal manner (52). Though they were undoubtedly convinced that the mechanism for this process was the entrance of the animalcule into the egg, they refrained from stating that this is what occurred since they had never seen one entering (53). The authors examined a large number of fertilised eggs, using a lens that magnified ten times (54), observing the changes that occurred for over four days, day and night. In this way they were able to describe for the first time in a highly detailed manner the phenomenon of segmentation which is sure evidence of a successful fertilisation.

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52. Controlled observation of the process showed that the number of eggs fertilised was always less than the number of animalcules available. A certain dilution was optimal. A high concentration of mucus impeded them; high dilution with water favoured decomposition of the egg before their arrival.

53. Such a statement would have been pure conjecture, even though they had observed eggs surrounded by animalcules. Ibid., 133-34.

54. Despite the great improvement made in the microscope by Amici, it was still not suitable for this study. Dumas hoped that the new Selligue microscope would be more useful for examining opaque objects. Ibid., 120. Augustin Jean Fresnel (1788-1827), Charles François Brisseau de Mirbel (1776-1854) and Humboldt were appointed by the Academy of Sciences to examine the latter. Fresnel said in his report (Ibid., 3 (1824), 345-54): "We have compared M. Selligue's microscope to other ordinary microscopes that we have been able to obtain; it must be said that we have found it to be very superior for the study of opaque substances." Ibid., 353. Since they did not have access to an Amici microscope, they noted: "On the relative merits of these two instruments we can quote with confidence the opinion of M. Dumas, who for a long time has used the Amici microscope belonging to the Société du Musée académique de Genève [sic], and who finds that M. Selligue's distinguishes the small details of opaque substances at least as well." Ibid., 352. In "Observations of the Editors on the use of Microscopes", Ibid., 354-65, which was certainly written by Dumas, several additions were made to the thoughts expressed in the report, including the indication that Selligue's microscope merited higher commendation because of a much improved light source which Dumas described in detail.

Part 3. Reporting their work on mammals (dogs and rabbits), the authors emphasised that fertilisation could not occur in the ovary, since numerous observations showed that the animalcules were unable to travel beyond the Fallopian tube, where encounter with the ovule normally occurred several days after copulation (55). The delay was due to the rapid final development of the egg in the ovary, during which time its diameter increased fourfold before it began to move towards the Fallopian tube. The authors searched vainly for these large (7 mm) eggs in the tube, finally discovering that it was the ovule (2 mm at most) that was fertilised. They then examined a mature egg and found that it contained a spherical body, not unlike the ovule except that it was much less transparent. To avoid confusion, they suggested that the egg should be called a vesicule until it had been studied more carefully to discern its relationship with the ovule. They described briefly the initial development of the fertilised egg and expressed their belief that the first system that appeared was the nervous system, which developed around the spinal cord, the first part of the animal to be formed.

Among the numerous original observations that should be attributed to Prevost and Dumas, four of capital importance must be singled out: the absolute necessity of the animalcule (sperm cell) for sexual reproduction; the existence of the ovule inside of what the authors called the

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55. Thus fertilisation immediately after copulation, a theory widely accepted, was out of the question.

vesicule of the ovary (Graafian vesicule) (56); the necessity for contact between the two; and the phenomenon of segmentation as a necessary consequence of fertilisation and a sure sign of its accomplishment (57).

At this point Prevost and Dumas felt that they had accumulated enough original material to submit for judgment in the Montyon competition of 1824. They had read all but the third part of the memoir to the Academy of Sciences in Paris (58). They had read a related memoir "On the Development of the Heart in the Foetus" to the Société Philomatique also in Paris (59). They sent the whole (listed as four memoirs) to the Academy, along with a memoir "On the Phenomena Accompanying the Contraction of Muscle Fibre" (60) which was submitted separately, on 31 December 1823.

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56. The existence of an independent opaque ovule was observed in 1827 by Karl Ernst von Baer (1792-1876), whose outstanding work on mammalian reproduction has been recognised. Nevertheless it was Prevost and Dumas who first discovered this body in the vesicule, and had refused to claim that it was the ovule without the evidence found by Baer, though the suggestion is obvious in their memoir. Ibid., 3 (1824) 135. Baer apparently did not acknowledge the work of Prevost and Dumas. He may not have been aware of it. The only journal in which it appeared apart from the Annales des Sciences Naturelles, was that of Froriep, Notizen, in which it was apparently abridged.

57. Gautier, op.cit.(1-1), p. 43-45 says that Jean Jacques Marie Cyprien Victor Coste (1807-1873), Etienne Reynaud Augustin Serres (1786-1868), Emil DuBois-Reymond (1818-1896) and especially Edouard Gérard Balbiani (1823-1899) support one or more of these statements. J. Théodoridès, Histoire de la Biologie, Paris (Presses Universitaires de France), 1971, p.83 appears to accept these claims and indicates that J. Rostand supports at least the first, Esquisse d'une Histoire de la Biologie, Paris (Gallimard), 1962.

58. The first part was read 6 and 13 October 1823, the second part 10 and 17 November.

59. Bull. Soc. Philom., 1823, 158-66. They later extended this to include the formation of blood, Ann. Sci. Nat., 3 (1824), 96-107.

60. Magendie, J. de Physiologie, 4 (1823), 301-44. It was read 18 and 26 August 1823.

On 14 January 1824 the Commission was selected to judge the memoirs sent in by the six competitors (61). On 7 June 1824 the following announcement was made:

> "Among the works entered in competition for this prize, three memoirs have particularly drawn the attention of the Academy ... The second memoir, registered No. 3, is a lengthy work accompanied by 24 illustrations containing new observations on generation. ... The Academy has decided that each of these three memoirs deserves a gold medal. ... MM. Prevost and Dumas, who have already distinguished themselves in preceding competitions, are the authors of the new observations on generation." (62)

Though he never lost interest in physiology, by this time Dumas had turned his attention almost completely to the study and teaching of chemistry in Paris.

Initially Dumas had approached his work with Prevost primarily from a chemical point of view, but it was not long before he had mastered the techniques of physiology, especially the use of a microscope and was able to think in physiological terms. On the other hand, he had come to Geneva to become a pharmacist. In a sense this aspect of his life remained unchanged. To appreciate how this could be, one must understand his notion of pharmacy, which he expressed in a letter written to his father in 1819:

> "One cannot be a pharmacist without being a chemist, without having a comprehensive knowledge of the natural sciences and without having studied the general progress of medicine. - And I ask you, will I obtain this knowledge by rolling pills?" (63)

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61. The members of the Commission were the same as in 1822. Their names were given in note ~~163~~/47.

62. PVAS, Vol. 8, pp. 97-98. The medal was valued at 895 francs. The authors of the other award-winning memoirs were Marie Jean Pierre Flourens (1794-1867) who had shared the prize the previous year and Hercule Straus. Since Prevost and Dumas had been in only one earlier competition and not won a medal or an honourable mention, it would be interesting to know what the Commission meant when it said "distinguished themselves in preceding competitions".

63. G., Letter of 1819, p.42.

This notion of pharmacy was one that he could only have suspected when he left Alais where he had been limited for the most part to performing mechanical tasks. In Geneva he no longer regarded it as a routine means of earning a living, but as a creative enterprise. By the time he had written the above remarks he had completed his formal studies, and it would appear that his father was pressing him to complete his apprenticeship closer to home so that he could establish himself in that region as a pharmacist. On the other hand Dumas was far from being ready to settle into obscurity. His early studies may have enabled him to succeed in the pharmacy examinations, but this could never have been sufficient as a goal for a young man who was able to say at the age of 18: "What delights, what pleasures accompany the full exercise of our intellectual faculties! Without doubt knowledge is power: it is the banquet of the gods." (64) He was convinced moreover that Paris was the only place where he could continue his intellectual growth in the realm of the sciences, a point which he did not hesitate to make in writing to his father in 1819:

> "Looking at it from another viewpoint, I asked myself whether my studies could provide me with the funds necessary to continue following mathematics, physics, chemistry and botany. ... I must try to find a position in Paris, in a hospital where my work, confined to a brief period of time, would permit me to reserve a part of the day for attendance at public lectures." (65)

Hofmann suggested that Dumas had made up his mind late in 1822 to go to Paris (66). It is evident that he had resolved to do so long before then. Dumas continued: "This is my intention, and to fulfil it more surely, I

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64. G., Letter of 1818, p.41.

65. G., Letter of 1819, pp. 41-42.

66. Hofmann, op.cit.(1-6), p. vii.

am looking for some useful work to undertake [for publication] that will serve as a recommendation." (67) He referred to specific botanical research, already begun, that "would seem to be quite suitable for accomplishing this goal" (68), but to assure his father that he was not wasting his time, he made it clear that he was studying the medical aspects of pharmacy with Prevost. To forestall objections that would surely arise when his father discovered the theoretical nature of the investigations involved during this period of study, Dumas wrote: "It is a point on which I insist in a very special way. I am asking with insistance that you give me complete freedom in the studies that I propose to pursue, and that no pretext be used to prevent me from going in the direction that I am taking." (69) This request was granted, perhaps reluctantly. Having no evidence after a year to indicate that his son was accomplishing anything especially noteworthy, Dumas' father again advised him to return. And again Jean Baptiste presented what he saw as convincing reasons for continuing his studies:

> "I am in an extremely flattering position in Geneva considering my age and education. If I could continue my studies a little longer, it would be easy for me to become acquainted with all the savants of this city and to follow the important work they are doing. In that event, I swear that before another year has come to an end my reputation will be established." (70)

Nor did he fail to indicate that he still intended to become a pharmacist, as his father wished, hinting that the best place in which to do this was

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67. G., Letter of 1819, p.42.

68. Ibid. This was his research on hybrids, undertaken with Guillemin.

69. Ibid., p.43.

70. G., Letter of 1820, pp. 42-43.

Paris:

"It is very easy to see that to attain a certain superiority in our art (pharmacy), it is necessary to devote oneself to the study of chemistry and natural history. That has been perfectly verified by experience; all pharmacists who have become wealthy by honest means have acquired reputations in science that they have deserved. Vauquelin, Pelletier, Planche, Boullay, Bouillon-Lagrange in our own day; Cadet [de Gassicourt], Baumé, Rouelle, Darcet in the past have all excelled in Paris. This superiority was earned solely through [their research in] chemistry." (71)

Yet he wrote with a sense of resignation that if these reasons were unacceptable, and his father still demanded that he return, then he was prepared to do so, even though this went against his own judgment (72). On the strength of his son's promise, Dumas' father gave him another year of grace. Finally, in 1821, Dumas launched his career with the several articles already discussed. His father no longer needed convincing.

Though Dumas remained in Geneva because of his research with Prevost, he never lost sight of his intention to go to Paris, then the capital of the scientific world. In reply to a letter from his cousin J. E. Bérard, Dumas wrote a note from Geneva on 26 February 1822 containing information about his approaching trip to that city:

"I owe you a few details about the purpose of my trip to Paris and I hope that you can be of great assistance to me because of your scientific connections. I am going to spend a month there just to make a few purchases

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71. Ibid., p.42. Those not mentioned earlier in my thesis are: Louis Antoine Planche (1776-1840), Pierre François Guillaume Boullay (1777-1858), Edmé Jean Baptiste Bouillon-Lagrange (1764-1840), Antoine Baumé (1728-1804), Guillaume François Rouelle (1703-1770) and Jean Darcet (1725-1801).

72. "Nature has endowed me with an active mind which will not permit me to limit myself to the 'manipulations' of pharmacy. Is this good or bad? ... However it may be, you can count on my blind obedience to your will, even though I am inclined to disapprove of the arrangements which you have found to be suitable." Ibid., p.13-14. (My italics).

> and to get a good idea of certain things that can only be appreciated after seeing them. I must come back to Geneva at the end of that time to assist at the marriage of my very good friend Le Royer. I will probably remain here until the end of the summer, and not leave until then to spend a longer time in Paris.
>
> But in any case, I have no delusions that I will obtain a favourable position, and my sole ambition is to pursue studies in that city that will enable me afterwards to set up a shop (73). I would be assisted [in this project] if at your suggestion M. Berthollet or M. Gay-Lussac were to accept me in their laboratory on familiar terms (74) not at all as a paid préparateur, but as a serious student whose monetary position will permit him to remain in Paris for two years at his own expense, but who, by himself, cannot possibly acquire the instruments or knowledge found in such establishments.
>
> Would I be presuming too much on the friendship which you have always shown for our family to think that it would not be disagreeable for you to recommend me to those two gentlemen? The friendly manner in which MM. De Candolle and De Saussure have always treated me is my assurance that your interest is effective." (75)

Dumas offered several reasons for his trip. The least important of these may have been the purchases to which he referred (76). Of prime concern were the preparations necessary to facilitate his plans for the future. He had already decided on the end of the summer as the date for taking up residence in Paris, where he would complete his pharmacy studies (77).

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73. "avantageuses à l'établissement que je pourrai former par la suite".

74. "familièrement".

75. This unpublished letter, Bibl. de Genève, Unclassified Manuscript, contains data of value to my thesis and hence has been quoted at length. It was addressed to "M. Bérard, professeur de Chymie, Montpellier" and introduced with the phrase "Monsieur et cher Parent". The letter from Bérard was not available.

76. They may have been personal, though it is possible that he was buying equipment to be used in work with De Saussure or Prevost, or for them. De Saussure's records show that he bought most of his chemicals and equipment in Paris, a practice that was not uncommon among Genevan scientists.

77. He may have intended to follow his father's wishes and set up a shop in Montpellier, but it is more likely that he had Paris in mind for its location.

Finances did not appear to be a problem (78). On the other hand, he wanted to have a "good idea" of the physical aspects of life in Paris. There was also the problem of finding a pharmacy in which to conclude his apprenticeship. Above all, he was anxious to continue the chemical research begun in Geneva, and for this he needed a place to work, preferably in the laboratory of one of the Paris savants (79). He intended to contact his friend Guillemin, who had established his residence in Paris in 1819, had become acquainted with many of the natural scientists there and had been given the care of a private botanical collection (80). Among these scientists, was one whom Dumas wanted to meet, Geoffroy Saint Hilaire, with whom Prevost may have worked (81).

Dumas left unmentioned what may have been the most important reason for his journey. The memoir on blood had been entered into the Montyon competition. Though the prize would be awarded during the public meeting

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78. Since goitre was a very common disease in Switzerland, Le Royer had profited from Dumas' iodide preparations. He was more than generous in return, and Dumas was able to save enough over the ensuing three years to be able to live for two years in Paris.

79. Dumas specified Berthollet and Gay-Lussac. The former, whose work Dumas had studied intensively for four years, had been like a father to Bérard in Paris and continued to consider him affectionately. Crosland, op.cit.(1-28), p.317. Gay-Lussac, editor of the Annales de Chimie et de Physique, had devised the method of organic analysis preferred by Dumas. This method had been the core of Bérard's thesis submitted for the degree Doctor of Medicine in Montpellier in 1817. Ibid., 5 (1817), 290-98. It had received very favourable comments from his friend, Gay-Lussac.

80. It belonged to Jules Paul Benjamin Delessert (1773-1847).

81. Geoffroy Saint Hilaire was also involved in research on generation because of his interest in monstrosities. In 1820 he studied the change in weight experienced by eggs during incubation. In a later article on the same topic, Dumas noted: "Ours had already been completed when the work by M. de Saint Hilaire appeared". Ann. Sci. Nat., 4 (1825), 47-56 (47).

of the Academy of Sciences on 8 April, the names of the winners would be announced in the meeting on 11 March. Dumas was especially anxious to be in Paris at that time because part of their memoir had been criticised in the November issue of the Annales de Chimie et de Physique which had just appeared (82). Early in 1820 they had sent an article to that journal describing their initial research on blood. Apparently it had been returned unpublished (83). After expanding their work considerably, the authors submitted it to the Bibliothèque Universelle, in which it was published in three parts. Except for the introduction (84), the first part was reprinted verbatim in the Annales, with many critical footnotes by the editors. The authors were accused of failure to give sufficient proof for some of their findings, which opposed those of well-known English scientists (85) and especially chided for lack of clarity in some

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82. The Academy of Sciences acknowledged reception of the September 1821 issue in the meeting of October 22, PVAS, Vol. 7, p.236; the December 1821 and January 1822 issues on 18 March 1822, ibid., p.292. Reception of only one of the intervening issues was acknowledged on 7 January 1822 and the date of issue was not mentioned. The November issue appeared either then, or more probably in February, the date I have preferred because Prevost answered the criticisms in Geneva on 21 March. Bibl. de Genève, Registres des Séances de la S.P.H.N. de Genève, Reg. 29, meeting of 21 March 1821.

83. The existence of the original article was established by the editors, who used a footnote to bring out a point of some interest that had been included in that article but had disappeared from the new one: "Over and over we have found proof of this important result in the manuscript which MM. Prevost and Dumas have had the goodness to send us a long time ago." Ibid., 18 (1821), 294 (my italics).

84. It contained their general aims, discussed earlier in this chapter.

85. The editorial support of the observations of the Englishmen particularly those of Thomas Young (1773-1829) suggests that it was Arago rather than Gay-Lussac who wrote the footnotes. The comments were softened by a note of encouragement: "I hope that MM. Prevost and Dumas will view in these remarks nothing more than a desire to see them complete a work which they have begun in such fortunate circumstances." Ibid., 293.

of their statements. No doubt Dumas wanted to defend the claims they had made, not only in this part but in the other two as well.

Dumas set out for Paris on 4 March 1822, perhaps earlier than he had intended (86). There he learned of the fate suffered by the third part. Aware of the great physiological importance of the presence of urea in the blood of a doubly nephrotomised animal, Dr. Pierre Salomon Segalas d'Etchepare (1792-1875) had asked Vauquelin to assist him in the verification of the results reported by Prevost and Dumas (87). Segalas and Vauquelin carefully followed the directions given in the memoir but were unable to substantiate the authors' claims. Fortunately Dumas easily recognised the source of their difficulty. Segalas noted later:

> "When M. Dumas, then visiting in Paris, discovered the difference between the results obtained in these preliminary trials and those found in the many investigations that he had made, he believed, with reason, that the cause lay in the different procedures used for analysis." (88)

But once again the fault lay with the memoir, this time the omission of an important experimental detail, as Segalas was forced to point out:

> "They had made no mention in the memoir of the essential precaution that the [final] washings must be evaporated at room temperature and in a vacuum maintained by the presence of sulphuric acid. Once this modification had been made, the presence of a large quantity of urea was detected in the blood drawn from a dog 60 hours after the removal of its kidneys." (89)

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86. Archives d'Etat de Genève, Etrangers, Ea 1, p.96, No. 479 reads: "p[artit] p[our] Lyon le 4 mars 1822". Lyon was an overnight stop on the road to Paris. In a postcript to his letter to Bérard (see pp. 70-71) Dumas wrote: "I will probably be in Paris the middle of next month".

87. Segalas gave private lectures in physiology and pathology. Shortly after this incident he began a life study of urinary disorders. Vauquelin had done fundamental chemical studies of urea.

88. Bull. Soc. Philom., 1822, 94-95.

89. Ibid.

Dumas had already returned to Geneva when Segalas and Vauquelin completed their verification and confidently announced it at the 15 June meeting of the Société Philomatique, concluding with the statement:

> "M. Segalas is communicating this information today because M. Vauquelin and he had announced that recent experiments had failed to verify the results given, and this could raise in certain minds doubts that would be injurious to two young physiologists to whom the science is already indebted and will probably owe a great deal more in the future." (90)

Because these faults may have been a principal cause for their failure in the Montyon competition, Dumas learned a hard but very valuable lesson in the art of communicating research. Eventually the second and third parts found their way into the Annales de Chimie et de Physique (91).

During his stay Dumas met Pelletier, perhaps at a meeting of the Société d'Histoire Naturelle de Paris (92). A pharmacist as well as professor at the Ecole de Pharmacie, Pelletier had become renowned by isolating the active ingredient (quinine) of quinquina and studying its physiological effects. His research on other compounds in that group of pharmaceutically active substances that became known as plant alkalis led to further recognition. At the same time he was known for his interest in students. He had been an honorary member of the S.P.H.N. de Genève

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90. Ibid. Dumas was able to announce the verification in a meeting of the S.P.H.N. de Genève on 15 August 1822.

91. Publication did not take place until the summer of 1823 when Dumas was living in Paris. Having indicated at the beginning of the second part: "We have repeated our observations many times over during the past two years.", Ann. Chim. Phys., 23 (1823), 51, the authors advised the reader of Vauquelin's verification, adding "We are pleased to note that the strong desire to have our memoir published in this journal has been fulfilled."

92. Pelletier was one of the early members of this society. Other interesting possibilities exist: Gay Lussac may have seen this liaison as the best answer to Dumas' needs. Vauquelin, who had been director of the Ecole de Pharmacie may have been instrumental in bringing the two together.

since 3 November 1820 (93). Most probably Pelletier was very encouraging when Dumas raised the question of continuing his studies and apprenticeship in Paris. His vindication by Vauquelin and Segalas had shown Pelletier that the young physiologist was also quite capable as an organic analyst. The suggestion that they work together on the analysis of the plant alkalis may have come from Pelletier, but it was greeted with warm approval (94).

Dumas would also have made contact with Guillemin, a founding member of the Société d'Histoire Naturelle and probably attended meetings of that society with the botanist. He may have been present on 12 April when Adolphe Théodore Brongniart (1801-1876), who had been secretary of the society since its foundation the year before, read brief summaries of the papers submitted by members during the year, including that of Dumas and Guillemin on hybrids (95). It may have been at this time that Dumas

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93. The unusual character of his election was recorded: "M. Pelletier was elected by ballot as an honorary member of the Society; but it should be noted, since he has addressed nothing to the Society, that it is only because of his interesting discoveries in chemistry that the regulations have been set aside, and the Secretary is to advise him of this when he sends the diploma." Bibl. de Genève, Registre des Règlements de la S.P.H.N. de Genève, p.5, 3 November 1820.

94. The memoir, "Recherches sur la Composition élémentaire et sur quelques propriétés caractéristiques des bases organiques", read 5 May 1823, began as follows: "We were working, the one in Geneva, the other in Paris, at some research on the composition of plant alkalis ...", Ann. Chim. Phys., 24 (1823), 163-91 (163). In his memoir with Le Royer "Analyse de l'Indigo", Dumas noted: "This result is confirmed by those obtained from quinine and some other plant alkalis given us through the kindness of the distinguished chemists who discovered them". Bull. Soc. Pharm. de Paris, No. 8 (August 1822), 377-87 (387).

95. Mem. Soc. Hist. Nat., 1 (1823), 15. While this would have been a particularly attractive meeting for Dumas to attend for other reasons as well, one wonders why Brongniart attributed the memoir to Guillemin alone if Dumas was present.

became a corresponding member of the society (96). While he was in Paris Dumas also attended the meetings of the Academy of Sciences relating to the Montyon prize, and possibly some of those held by the Société Philomatique as well.

While he was in Paris, Dumas' obligation to read memoirs during the March meetings of the S.P.H.N. de Genève was assumed by Le Royer and Peschier (97). He was replaced as president by De La Rive on 4 April and Nicolas Charles Seringe (1776-1858) on 18 April. Dumas then presided in place of Le Royer on 16 and 30 May (98). After that time his participation in the meetings of the society became more passive again. During the hours when he was free from his duties at the pharmacy, he devoted his time to the research on generation and the improvement of techniques needed for a more accurate analysis of organic compounds, especially the plant alkalis which contained nitrogen. His experience in Paris reminded him of the importance of one's reputation to his career. Conscious of

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96. He was one of 45 listed ibid., front (non-paginated). It is probably coincidental that Duméril, Humboldt and Geoffroy Saint Hilaire all became honorary members of the society on 11 April. Full membership was limited to those under 40 years of age who lived in Paris.

97. On 7 February 1822 a schedule of presidents and members assigned to read memoirs at the monthly meetings was drawn up, evidently without reference to the plans of either Dumas or Le Royer. The portion of interest in this thesis has been extracted:

	March	April	May
President	Seringe	Dumas	Le Royer
Reader	Dumas	Le Royer	Dr. Prevost

The memoirs read during this period have already been mentioned in my Thesis, Chapt. 1, pp. 43-44.

98. In view of his forthcoming wedding to Jeanne Marguerite Béranger on 14 May, Le Royer asked to be replaced throughout May. Since Dumas presided during the other meetings that month, it seems likely that he would have done so on 2 May as well, had he been in Geneva. Seringe again offered his services.

his excellent situation in Geneva, he apparently revised his schedule, content to wait a little longer before leaving, to complete his work with Prevost, finish his apprenticeship, take his examinations and become a certified pharmacist. Late in September these plans underwent a further revision when he received an unexpected visitor in his room above the Le Royer pharmacy.

The eminent natural scientist Baron von Humboldt, who was on his way from Paris to the congress of Verona, had decided to rest in Geneva for a few days while visiting friends (99). He had read the memoir by Prevost and Dumas on blood, and because he was interested in furthering the careers of young men who had a penchant for science, he invited Dumas to squire him around the city during his stay (100). Apparently this incident led Dumas to reconsider his plans. He made up his mind to leave for Paris

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99. The Congress of Verona was the last of a series of international conferences arranged in accordance with Article 6 of the Treaty of Paris (20 November 1815). It began on 20 October 1822. On 21 August Humboldt wrote to Jean Baptiste Joseph Dieudonné Boussingault (1802-1887): "It is possible that you will soon read in the Gazette that I am accompanying the King of Prussia to the Congress of Verona. ... If I leave for the Congress, it will not be until 20 September." Mémoires de J. B. Boussingault, 5 Vols., Paris, Vol. 1 (1892), p 280. Humboldt did not join the entourage until after he had left Geneva.

100. Hofmann, op.cit.(1-6), p. vii-viii gave Dumas' impressions of this visit in a long 'quotation' which may be found in Tilden, William A., Famous Chemists, London (Routledge), 1921, p. 207-08, and more recently in Crosland, op.cit.(1-28), p. 442-43. Though the incident undoubtedly occurred, Hofmann's somewhat romanticised description was built on the premise that Dumas had never been to Paris. If that is true, an earlier date must be assigned to Humboldt's visit, but if he was in Geneva at the time indicated, which seems more likely, then Hofmann has attributed to Dumas both a naiveté that is unwarranted in view of his association with the Genevan scientists, and an ignorance of scientific life in Paris that is unacceptable because of his somewhat lengthy stay in the French capital. It would appear more likely that Humboldt, in his rambling conversations, clarified many of Dumas' questions about Parisian life, gave practical suggestions to assist him in achieving the goals he had established for himself and the confidence that he could and would succeed in this endeavour as well as the assurance of his own support, and that of his friends.

as soon as his situation in Geneva would allow him to do so. The only serious impediment to immediate departure was his desire to complete the research on generation, now in its advanced stages. Realising that separation would make further collaboration difficult, he and Prevost worked diligently to give firm evidence for their claims, so that a memoir could be submitted for the Montyon competition before 31 December. In order that they might complete it, Dumas decided to forego till then the lectures that he was eager to attend in Paris and to set aside the interesting analytical investigations already begun on plant alkalis. When it became evident that they would not be able to submit their research without risking failure in that competition for a second time and perhaps invoking further critical comments, they decided to delay entry for a year. Prevost agreed to spend some time in Paris rather than delay his friend any longer. Dumas had already advised the Le Royers that he would be leaving near the end of the year. On 1 January 1823 he departed for Paris (101).

Lectures at many of the schools in Paris were available, at no cost, to anyone wishing to attend them (102). Soon after settling into a room

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101. "M. Dumas left the pharmacy in Geneva on 1 January 1823 to take up residence in Paris." Letter from Marguerite Le Royer (Wife of Auguste) written to Louis André Gosse shortly after the death of her husband. Bibl. de Genève, Papiers Gosse, Ms 2663, Correspondance de Louis André Gosse (H-R), fol. 74-75. A wide spectrum of dates has been given for this departure. Nouvelle Biographie Générale, Paris, Vol. 15 (1856), Col. 171, the first to refer to it, suggested 1821, an error that was continued by several authors. Hofmann was no more precise than 1823. A recent biographer, Y. Chatelain, op.cit.(1-6), Col. 129, noted that Dumas arrived in Paris in January 1823 but offered no evidence for his statement.

102. Fees were charged for sitting examinations and sometimes for registration.

in the Hôtel du Secrétariat de l'Ecole de Médecine (103) Dumas investigated courses given in various educational institutions in Paris and arranged a schedule for himself which included Geoffroy Saint Hilaire's lectures at the Muséum (104), the advanced course in chemistry given by Louis Jacques Thenard (1777-1857) at the Collège de France (105) and perhaps a course at the Ecole de Pharmacie suggested by Pelletier, with whom he would have come in contact soon after his arrival. He also began to attend meetings of the Société d'Histoire Naturelle where he made or renewed acquaintance with Guillemin, Audouin, Adolphe Brongniart and Milne Edwards. He and Prevost began working in the laboratory of Geoffroy Saint Hilaire at the Muséum and by May they had prepared a memoir on "The Use of the Pile in the Treatment of Kidney Stones", which Prevost read to

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103. Letters from Dr. Prevost written from Geneva 28 May and 27 August 1824 were addressed "Rue de Hautefeuille No. 30, Hôtel du Secrétariat de l'Ecole de Médecine, Quartier de l'Ecole de Médecine, Paris." The latter was postmarked Paris 12 September. Arch. Acad. Sci., Fonds Dumas, Carton 3, Dossier "Mém. sur la Génération", Séance du 10 Novembre 1823. His address was listed as "rue Hautefeuille, no. 30" in a list of members of the "Commission de Rédaction du Bulletin pour 1825", Bull. Soc. Philom., 1825. This list was published at the end of the year. Thus it is probable that Dumas went there on or shortly after his arrival, as a result of his preparations during March-April 1822, and remained there till the day of his marriage.

104. Isidore Geoffroy Saint-Hilaire (1805-1861), Vie, Travaux et Doctrine d'Etienne Geoffroy Saint Hilaire, Paris, 1847, p.192, note 1, remarked that Dumas had attended Etienne's lectures. In addition, Isidore quoted the following statement by Dumas: "Until then anatomic philosophy, such as he conceived it, had not existed; it was with us, it was for us, I would even say that it was through us that he founded this course [enseignement], trying each year to overcome new difficulties, fortifying his convictions with new proofs, confirmed in his teachings [doctrines] by their very success with the students." Acad. des Sci., Funerailles de M. Geoffroy Saint Hilaire, Discours de M. Dumas. In this thesis the son's name will be used in full to avoid confusion with his father.

105. Dumas' background in chemistry, discussed earlier, would have precluded attendance at more basic lectures such as those given at the Sorbonne, and advanced courses at other institutions such as the Ecole Polytechnique were closed to him.

the Academy of Sciences (106). On 18 August Dumas read the memoir they had written on "The Phenomena Accompanying Muscle Fibre Contraction" (107). It was the first of many that he would read to the Academy (108). In reviewing it for the Société Philomatique, Audouin brought out two points of interest to this thesis:

> "M. Prevost and Dumas, to whom physiology already owes many important observations, and who are credited with opening an immense field for discovery in wresting microscopic research from oblivion and even from disdain, have turned their attention to a study of the phenomena of muscular contraction in the memoir in which we are going to offer only the principal results.
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> It is easy to see in reviewing this work that the authors have followed scrupulously the logical and rigorous method that sticks to the observation of facts first, and then seeks to relate them with one another from an advanced point of view to draw legitimate conclusions.

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106. The Academy was notified of their findings on 19 May, the memoir was read 26 May and it was published in June with the following note added: "... The sensitivity of the kidney is the part which occupied us most since reading [the memoir] to the Academy; and thanks to the kind interest of M. Geoffroy de Saint Hilaire, we have found, in the delightful buildings of the Botanical Garden, the resources for experiments that would be unavailable to us as individuals." Ann. Chim. Phys., 23 (June 1823), 202-08 (208). The method involved reduction of the size of the stones until they were excreted. It worked in some cases but not where the stones contained a high proportion of uric acid. The memoir was also printed in Magendie's recently inaugurated quarterly Journal de Physiologie Expérimentale et Pathologique, 3 (1823), 217-24.

107. At the next meeting on Tuesday, 26 August, he read an addition. A Commission was assigned to examine the work, but no report was ever given, probably because it was entered into the Montyon competition. The memoir was published in J. Physiol. Expér., 4 (1823), 301-38, followed by the addition 339-44.

108. At the conclusion of the reading, the Marquis Pierre Simon de La Place (1749-1827), who had done physiological work with Antoine Laurent de Lavoisier (1743-1794) and had maintained an interest in the topic, invited Dumas to dine with him. A cordial relationship developed, to which Hofmann, op.cit.(1-6), p. viii, ascribes the beginnings of "those feelings of affectionate reverence, bordering on worship" that Dumas always had for Lavoisier.

> Those which they have drawn from their results offer a very powerful and completely new interest, because they permit us to represent rigorously all the known phenomena of muscular contraction by means of a few very clear and well defined physical principles." (109)

It is evident that Dumas had already formulated the approach to scientific research which he would follow for the rest of his life: Devise new methods for attacking a problem, or, as in this case, perfect disused ones, observe carefully, relate the facts observed and draw conclusions which would suggest new directions for research. In fact within a short time Humboldt had made new observations on nerves "that related perfectly to the remarkable work of MM. Prevost and Dumas" (110).

The fate of the ~~memoirs~~ research on generation has already been traced (111), but where was it to be published? It was an enormous work, well beyond the limits of Magendie's journal. Furthermore Dumas had prepared numerous drawings with which to illustrate it. The journal of the Société d'Histoire Naturelle would not have printed the whole since it had not been read to that group. In any event Dumas was interested in a different type of journal, one that published articles on natural science rather than natural history, where a priori statements would be replaced by careful observation, especially with a microscope, and the empirical methods that had been used so successfully in the physical sciences. Furthermore, he saw that it should not be limited to one branch of the natural sciences, as Magendie had done. He began to talk about it with his friends. Audouin responded, as did Adolphe Brongniart. Both loved doing research. While

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109. Bull. Soc. Philom., 1823, 139-43.

110. Ibid., 157-58. This was the next issue, and the summary of Humboldt's work was probably given by Audouin but not initialled.

111. Chapter 2, p. 66-67.

they had a broad general knowledge of natural history, their interest in zoology and botany respectively complemented Dumas' knowledge of physiology (112). They had discussed the possibility for several months before the conversation became serious in September 1823 (113). Audouin wrote a long letter to Alexandre Brongniart (1770-1847), father of Adolphe, describing their plans for the journal (114). The elder Brongniart sought to dissuade them at first (115), but eventually gave them his support and a contract was drawn up with the bookseller-publisher Béchet (116) for a monthly publication, the Annales des Sciences Naturelles, of about 125 pages in a format similar to that of the Annales de Chimie et de Physique. Apparently there was a

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112. Audouin's investigations were in entymology, those of Adolphe Brongniart in palaeobotany.

113. It is unlikely that any firm decision was made prior to Dumas' agreement to publish his August memoir in Magendie's journal.

114. Audouin had accepted a position with Alexandre, a geologist, as caretaker for his geological collection in June 1817, and within a short time had become 'one of the family'. Jean Victor Audouin, Journal d'un Etudiant (1817-18), Ed. J. Théodorides, Extracts from the monthly Histoire de la Médecine (1958-59), Paris (Edition Histoire de la Médecine) 1959, p. 32-33.

115. Alexandre was probably on an expedition at the time. In his diary an undated notation reads: "Audouin. Long letter of 6 pages on the Journal of the Natural Sciences. I must dissuade him from placing his name in it and above all that of Adolphe." Quoted in Launay, Louis de, Une Grande Famille des Savants - Les Brongniarts, Paris (G. Rapilly), 1940, p.157. The capitals for the journal are Launay's (Brongniart's?). Alexandre was probably not well acquainted with Dumas at this time. Certainly he was afraid that the others, on the brink of promising careers, would become bogged down in the tedious and time-consuming job of editing a journal. Furthermore, many journals during the Restoration were disappearing as fast as they came into existence, and the prospect of such a failure was not pleasant for a concerned father.

116. Jean Charles Béchet, surnamed the younger to distinguish him from his father Charles, also a bookseller-publisher, was given a patent dated 20 June 1820 to replace Desain at Place de l'Ecole de Médecine, No. 4. Since there will be no reason to refer to his father, the simple reference Béchet will be used.

revenue from this endeavour, though it was probably not large (117). From the point of view of content, the journal was a success from the start. From Geneva De Candolle wrote to Ad. Brongniart:

> "Some time ago I received your first number which I have read with much interest; if you continue in this way, I have no doubt that you will enjoy perfect success and I really want this both for science and for all of you, in whom I take a very sincere interest." (118)

Geoffroy Saint Hilaire contributed many articles for a time. Dumas' memoir on generation with Prevost occupied 69 pages in the first volume, 42 in the second and 36 in the third, including the article on the "Développement du Coeur et formation du Sang" which had appeared earlier and was modified only slightly (119). In the fourth volume Dumas

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117. Towards the end of 1825 Béchet ceded publication to Crochard, Bookseller-Publisher, Cloître Saint Benoit, No. 16 and Rue de Sorbonne, No. 3 and a new contract was signed. Al. Brogniart wrote in his diary: "17 October 1825. Dumas spoke to me about the new arrangements that were being proposed for the Annales des Sciences Naturelles. I find them good; but I am afraid that this small revenue may prevent Adolphe from choosing a profession." Launay, op.cit.(2-115), p.158. By 1828 when this contract was renewed, Arch. Acad. Sci., Fonds Dumas, Carton 1, the journal was well established and Crochard agreed to pay to the three editors a total of 8 francs a year for each copy sold until it was found necessary to print 750 copies at which time new arrangements would be worked out. Assuming 500 copies were sold, Dumas would have received 1333 francs per year for his efforts.

118. Bibl. du Muséum, Correspondance Adolphe Brongniart, Ms 1969. De Candolle expressed pleasure that they were asking for notes since he did not have time to write long memoirs. On a quick visit through Paris in 1825 he "left in the hands of brave Guillemin a memoir in plant physiology which Dumas had undertaken to see printed in your annals." Ibid., Letter of 13 January 1825.

119. In the earlier version the authors acknowledged gratefully that Dr. William Frédéric Edwards (1776-1842) had "arrived at the same conclusions regarding liver function from other considerations". Bull. Soc. Philom., 1823, 166. The manuscript of this note was signed by Dumas. Arch. Acad. Sci., Fonds Dumas, Carton 3. In both versions the authors pointed out that "In placing the function of making blood in the liver ... we attribute to it ... the importance of its action for the maintenance of health." Ibid. and Ann. Sci. Nat., 3 (1824), 106. No doubt the French owe to Prevost and Dumas the emphasis traditionally placed on this relationship!

published a "Note on the Changes in Weight which Eggs Undergo during Incubation", work done earlier with Prevost (120), in which they established that the weight loss experienced by eggs during incubation was due to the evaporation of water only and that as time went on, this loss in weight gradually decreased. In the course of their observations, the authors found that numerous factors had to be taken into account, so that they found themselves studying the foetus itself as it developed. In concluding the memoir they expressed their intention to read another in the future devoted to the latter topic:

> "In our next memoir we will give the stages of development for the first five days, and it will be seen that the characteristics of the foetus can be used to determine its age without difficulty." (121)

Since it is evident that most of the material had been gathered already, it would come as a surprise that two years passed before the work appeared (122), were it not that Dumas himself clarified the matter. They had simply not been able to complete it. Prevost had taken on duties in Geneva that made it impossible for him to undertake an extensive leave. In Paris Dumas had become very active in chemical education and research. Whether or not it was by preference, events seem to have led him

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120. Ann. Sci. Nat., 4 (1825), 47-56. The memoir began: "It has been known for a long time that eggs lose weight during incubation, but it does not seem that this question was properly treated until it was investigated by M. Geoffroy de Saint Hilaire ["Des différents états de pésanteur des oeufs au commencement et à la fin de l'incubation", Memoir read to the Academy of Sciences on 28 August 1820] ... Our work had already been completed when that of M. de Saint Hilaire appeared." Ibid., 47. The authors had done research at periods in between the beginning and end of incubation as well. Publication at the time would have been out of the question.

121. Ibid., 56.

122. "Mémoire sur le développement du poulet dans l'oeuf". Ibid., 12 (1827), 415-43.

inexorably in that direction. Their progress will be examined in Chapter 3.

CHAPTER 3

THE 'TWENTIES' IN PARIS

"Several years ago the administrators of the Athénée royal de Paris invited me to replace M. Robiquet as the professor of chemistry in that institution. ... Still too young to expect that a course similiar to one given by such a capable teacher would compare favourably, ... I chose a point of view differing from his, and changed the order in which the facts were presented. ... Beginning with my second course, I no longer limited myself to general chemistry but added chemistry applied to the arts. This course lasted three years. The research I had undertaken because of it and the interest in it, apparently inspired by the theme, led several persons to the belief that its publication would be of some value." (1)

Dumas' physiological research on reproduction appeared to be taking him even further away from chemistry than the studies on blood, despite the continued interest in that most important body fluid that was evident in his investigation of the development of the heart in a foetus. He was well aware that little was known of its chemical constitution and he continued to improve his methods for isolating, purifying and analysing organic compounds while working with Pelletier on the pharmaceutically active plant alkalis. But late in 1823 he still intended to continue his work in physiology for he invited Audouin and Brongniart to join him in initiating the Annales des Sciences Naturelles. The project was already well under way when suddenly Dumas was plunged into activities related to chemistry by two unexpected appointments. Towards the end of the year he became professor of chemistry at the Athénée Royal de Paris (2), where his subsequent involvement with the industrial aspects of the science led eventually to the foundation of the Ecole Centrale des Arts et Manufactures (referred to hereafter as the Ecole Centrale). Very early the next year he was made répétiteur in the Ecole Polytechnique. There for the first time he was able to set up his own research laboratory, where he carried out experiments whose practical and theoretical importance earned a permanent niche for him in the history of chemistry. The background necessary for a discussion of this research, and the events leading to the founding of the Ecole Centrale will be examined in this chapter.

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1. Traité, Preface, vii. The professor Dumas replaced was Pierre Jean Robiquet (1780-1840).

2. There were several Athénées in Paris at this time, but since there will be no occasion to refer to the others, which played no part in Dumas' life or activities, the Athénée Royal de Paris will be designated simply as the Athénée throughout my thesis.

As a pharmacy student Dumas was aware of the existence of the plant alkalis (alkaloids) (3), but it was not until after his visit to Paris in 1822 that he became seriously interested in their composition. Subsequent events suggest strongly that this interest may be traced to a meeting with Pelletier as has been mentioned already (4). Dumas analysed several of these compounds when he returned to Geneva (5), collecting his results in a memoir entitled "Extrait de la Statique Chimique de matières végétales et animales" (6). Though uncompleted, it contained brief descriptions and quantitative analyses of seven compounds (7). In none of them had he detected the presence of nitrogen (8).

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3. Partington, op.cit.(2-17), p.240, claimed that Dumas introduced the term alkaloid and used it in place of the term plant alkali. Partington referred to the Traité, Vol. 5 (1835), p.724, where Dumas said: "A class of compounds containing, in general, carbon, hydrogen, oxygen and nitrogen is designated by the name plant alkalis, organic alkalis, alcaloïdes." He called them organic alkalis in the rest of his discussion.

4. See Chapter 2, pp. ~~81-82~~ 75-76.

5. Arch. Acad. Sci., Fonds Dumas, Carton 3, contains a manuscript notebook giving the results of experiments done in Geneva (it will be referred to as Notebook A). It has many dated pages, but a lacuna in dating exists between 23 November 1821 and 24 July 1822, during which time he analysed quinine and morphine, very probably some time after the beginning of May.

6. Ibid. Unpublished manuscript bearing the title indicated. Dumas' use of the term statique chimique may be traced to Berthollet's Essai de Statique Chimique which the young man had read several times.

7. Brucine, strychnine, cinchonine, quinine, morphine, solanine and the principle of olive oil. The word picrotoxine appeared at the top of an otherwise blank page.

8. Until that time the only quantitative analysis published for any plant alkali was a very bad set of values for morphine given by Thomson. Dumas mentioned that Antoine Alexandre Brutus Bussy (1794-1882), then préparateur at the Ecole de Pharmacie had "published very recently a good analysis of morphine in which he had found nitrogen" (Ann. Chim. Phys., 24 (1823), 184) but does not indicate the date, or whether he had worked under Pelletier's direction, which seems very likely. Pelletier rarely included his name with that of his students over articles written by them on work done under his direction. Among those who had given qualitative analyses had been Pelletier and one of his students, Joseph Bienaimé Caventou (1795-1877). They had not found nitrogen in any of these substances. For example, in a report read to the Academy of Sciences on 19 July 1819, Thenard was able to say: MM. Pelletier and Caventou are convinced by experiments which seem to us to be decisive that this alkaline substance [brucine] contains absolutely no nitrogen." PVAS, Vol. 6, p.489. See also note 12.

Some time after 16 August 1822, however, he analysed narcotine, a compound found associated with morphine in opium that had been studied by Robiquet (9), and found that it contained over 7% nitrogen in addition to the carbon, hydrogen and oxygen present (10). On 28 November he reported this in a note read to the Société de Philosophie, the student group in Geneva (11). It is significant for several reasons:

1. Apparently it was the first plant alkali (Dumas did not classify it as such at the time) (12), in which nitrogen was discovered.

2. Following the established pattern, he ignored the 'negligible' amount of nitrogen which frequently remained after the absorption of carbon dioxide during an analysis (13).

3. He was still thinking in terms of a career in pharmacy.

The summary began:

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9. Ann. Chim. Phys., 5 (1817), 275-288.

10. Arch. Acad. Sci., Fonds Dumas, Carton 3, Notebook A. The page preceding the analysis was dated 16 August 1822, unfortunately the last date in the notebook. A more detailed study of his work on narcotine will be left to Chapter 4.

11. This unpublished reading was summarised by the secretary. Bibl. de Genève, Procès Verbaux de la Société de Philosophie, Ms. fr. 1679, Cahier 1, pp. 43-46. Analyses were given for brucine, cinchonine, quinine, morphine, narcotine, solanine and emetine.

12. It had no effect on litmus, nor was he able to react it with acids. By 1835, however, 'salts' of narcotine (they were in fact analogues of hydrates) had been prepared, and on that basis he was able to classify it with the plant alkalis. Traité, Vol. 5, p.785. See Bussy, J. Pharm., 8 (1822), 580-86, for his paper on the first plant alkali containing nitrogen.

13. Its presence was attributed to incomplete expulsion of atmospheric nitrogen from the system. All of his analyses added up to 98 or 99% which could be suggestive. To appreciate the problem involved, one must be aware that only compounds containing an N:C ratio (in modern terms) of 1:1 or 2:1 were known, i.e., cyanides, cyanates, urea. The N:C ratio in the plant alkalis mentioned, assuming that they were pure, lay between 1:10 and 1:30, not negligible, but very low indeed by comparison!

> "Mr. Dumas read a note on a part of chemistry that is little known, the analysis of plants, which is particularly directed towards the purpose of looking for and knowing exactly the active principle of plants that serves as a remedy. ... When it is found, perhaps we will learn how to bypass the plant to make the remedy directly." (14)

Shortly after his arrival in Paris, no longer pressed to finish the memoir on generation, Dumas contacted Pelletier, eager to continue the analyses of plant alkalis that he had begun in Geneva. Disquieted by a theory that dismissed small quantities of nitrogen always observed in analyses of these substances, they decided to eliminate all atmospheric nitrogen from the system so that even if the compound being examined did have a low nitrogen content, it could be determined quantitatively. Working together in Pelletier's laboratory, they developed a means of doing this and found that nitrogen was an integral part of nine compounds which they called organic salt-producing bases in a memoir read to the Academy of Sciences on 5 May 1823 by Pelletier (15).

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14. Loc.cit.(3-11), p. 43-44.

15. "Recherches sur la Composition élémentaire et sur quelques propriétés caractéristiques des bases salifiables organiques", Ann. Chim. Phys., 24 (1823), 163-91. The opening lines of the memoir make it clear that they worked together: "We were occupied, one of us in Geneva, the other in Paris, on some investigations into the elemental composition of plant alkalis, and since our work was not yet finished, we thought that it would be convenient to come together to review all the parts". In his oration at Pelletier's funeral, Dumas indicated that he had worked in the pharmacist's laboratory: "It is impossible for me to tear myself away from the memory of those happy times, made possible by the affection of our much regretted colleague, when I had no means for research and he made his laboratory available to me, when I had as yet no future, and with such great concern he tried to carve one out for me in the midst of his own." Acad. Sci., Funérailles de M. Pelletier, Discours de M. Dumas, Vice-Président de l'Académie, le 22 juillet 1842, p. 2-3. The laboratory to which he referred may have been in the Ecole de Pharmacie on the rue d'Arbelète, where Pelletier had been assistant professor from December 1814, but it is much more probable that he spoke of one adjoining Pelletier's pharmacy.

The authors gave a general description of their analytical methods, discussed the analysis of each compound and attempted to provide a relational framework for their observations which would explain the alkaline character of the compounds they had studied. While no attempt will be made to evaluate their particular analyses, some attention must be given to three modifications introduced into the basic procedures used earlier by Dumas (16). Pierre Louis Dulong (1785-1838) singled these out for comment when he read his report on the memoir to the Academy of Sciences (17):

1. Since the small amount of nitrogen in the sample was to be measured as nitrogen gas, removal of air from the system was essential. This was accomplished by placing two accurately weighed samples in the generating tube, separated by powdered glass, heating one to sweep the air from the system and replace it with a gas having the same composition as that to be analysed, then heating the second sample and collecting the gases produced. In this way the gas in the system could be ignored. Apparently Dumas later abandoned this modification (18), which Dulong described without comment.

2. Because hydrogen is an important part of all but a very few organic compounds, water is nearly always formed when they are oxidised. Two methods of determining the weight of hydrogen present in these compounds were known from the time of Lavoisier, an indirect method, in which the

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16. See Chapter 2, p.13.

17. After the memoir had been read to the Academy of Sciences, Dulong and Vauquelin were appointed to examine it. Their report was read by Dulong on 18 August 1823. PVAS, Vol. 7, p. 527-29.

18. A single sample was specified when Dumas described the procedures he was using in 1831 in a letter to Gay-Lussac, "Sur les Procédés de l'analyse organique", Ann. Chim. Phys., 47 (1831), 198-213.

weight of oxygen was determined and that of hydrogen calculated by subtraction, and one that was more direct in which the water formed was weighed to find the weight of hydrogen and that of oxygen was calculated by subtraction (19). French analysts had been content with the first method, striving always to obtain greater accuracy in their determination of the weight of oxygen involved (20). Aware, as was Lavoisier, that greater accuracy could be expected from the second, Berzelius devised an apparatus in which water condensed in a glass bulb that had been carefully weighed (21). Apparently Pelletier and Dumas were the first simply to collect the water in a weighed calcium chloride tube and use the weight thus obtained to find the weight of the hydrogen present in the compound. Dulong's comment on this procedure is worth noting:

> "The proportion of hydrogen is deduced ordinarily from the difference in weight of the apparatus taken at the beginning and end of the analysis, taking into account the carbonic acid and nitrogen released (22). The

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19. Lavoisier used the first method in his analyses, but he observed: "Although this method seems certain, nevertheless it is not as satisfying as one in which the water could be weighed directly and exactly." Mem. Acad. Sci., 1784, 593-608 (602).

20. Michel Eugène Chevreul (1786-1889) in his fundamental research on animal fats preferred this method as late as 1823, even though he used the weight of water formed (obtained by using a calcium chloride tube) to verify approximately the amount of hydrogen obtained: "If the amount of hydrogen obtained by experiment differs too much from that calculated, the combustion must be begun again ... this time taking every precaution possible to dry completely the inside of the tube and to put the mixture into it quickly ... "Recherches chimiques sur les corps gras d'origine animale, Paris, 1823, p. 14.

21. He attached a calcium chloride tube to the bulb, but its sole purpose was to ensure that no water escaped. In describing the process, Berzelius, after indicating that he had obtained the weight of water by drying the bulb, said: "Then I weighed the tube containing the calcium chloride, which never gained more than 0.1 grains and often less." Ann. Chim., 94 (1815), 5-33 (20). He mentioned that "one grain troy = 64.74 mg." Ibid., 17.

22. This was the first method.

> authors desired a means of verification. For that reason they collected the water formed in a tube full of calcium chloride fitted to the end of their apparatus. This precaution can only give greater certitude to their results." (23)

Whether Dulong was led into error by attachment to the first method or a simple misreading of the memoir, it is abundantly evident from the authors' own words that the reverse was true:

> "After the amounts of carbonic acid and nitrogen have been determined, the calcium chloride tube is weighed to obtain the weight of water produced; and since the water deposited comes from the decomposition of two samples of the substance, a quite considerable quantity is generally collected. The amount of oxygen contained in the substance can be obtained from these values by subtracting the weight of carbon, nitrogen and hydrogen (which the water represents) from the weight of the sample." (24)

Indeed, it was the weight of oxygen, not hydrogen for which they sought verification, as is evident from what immediately followed the quotation just given:

> "Nevertheless, it seemed convenient to submit this determination to a verification that would be close enough to allow the value for the oxygen to be used to accept or reject the values for the other substances." (25)

This gave rise to their third modification.

3. The authors recognised the danger in simply subtracting the weights of carbon, nitrogen and hydrogen from the weight of the sample in order to obtain the weight of any oxygen that might be present in the compound. While it is true that simple weighing could serve to determine the weight of oxygen given up by the copper oxide during the analysis, they preferred to verify this value, and consequently those of the other elements, by

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23. PVAS, Vol. 7, p.528.

24. Ann. Chim. Phys., 24 (1823), 166.

25. Ibid.

comparing the amount of hydrogen needed to reduce a pure sample of copper oxide with the amount of hydrogen required to reduce the copper oxide remaining after the sample being analysed had been completely oxidised (26).

Before terminating this discussion of the memoir on plant alkalis, a few remarks on the theoretical conclusions derived by the authors would not be out of order. The plant alkalis had been grouped together on the basis of similarities in properties, particularly their alkalinity, which was unique among organic compounds. The authors had shown that they all contained nitrogen. It seemed natural to relate these two characteristics. Their efforts to do so, however led to the rejection of such a hypothesis, as they reported:

> "It cannot be supposed that the alkalinity of these substances is essentially related to the existence of nitrogen, whether it be accepted that this principle is found in the state of ammonia, or thought that the property of alkalinity is determined in them by some other method of combination unknown to us." (27)

They mentioned, almost in passing, that a relationship existed between the oxygen in the plant alkalis and that in the sulphuric acid used to

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26. It is not surprising that Dulong could not see that this added anything to the accuracy of the measurement. Nevertheless, Dumas continued to use it, principally to avoid errors due to hygrometric water in the copper oxide, and developed two other methods to circumvent this source of error. Ibid., 47 (1831), 201-03.

27. Ibid., 24 (1823), 189. They based their statement, which depended on the underlying assumption that all of the nitrogen in the compound acted in the same way, on the following observations: "Morphine and veratrine contain about the same quantities of nitrogen, but in forming its sulfate, the former absorbs 12.465 of acid and the second 6.644; and the former is neutral while the second is still acid. Quinine, brucine and strychnine contain more nitrogen, yet form neutral salts with smaller quantities of acid than that found in the salts of morphine." Ibid., 189-90. In fact the assumption is not quite true, and the alkalinity of the compounds is largely related to the nitrogen present, but a discussion of the extremely complex phenomenon of basicity in organic compounds would be necessary to explain their observations, and it is evidently beyond the scope of this thesis.

neutralise them, but made no attempt to relate their alkalinity to the oxygen content (28), undoubtedly convinced that some relationship existed between the nitrogen and alkalinity whatever it might be. In any case the search for it led the authors to a volume relationship between the carbon dioxide and nitrogen released during analysis, and this in turn suggested that it would be fruitful to express their results in numbers of atoms of each of the elements present at a time when such a practice had fallen into disfavour (29). It was a measure of their faith in the accuracy of the analyses they had made, a conviction that was not greatly misplaced (30).

While Dumas was occupied with this research, there is reason to believe that he continued his apprenticeship in pharmacy with Pelletier as well, and did so for the rest of the year (31). Pelletier's interest

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28. "In the salts which the bases can form, the oxygen of the acid appears to us to be a multiple or fraction of that of the base." Ibid., 189.

29. The few organic compounds whose compositions were known were far more complex than the many mineral substances that had already been given formulas involving small whole numbers. Even chemists who were willing to accept the atomic theory could not bring themselves to take into account such small quantities of elements let alone express them when analytical procedures gave percentages of questionable accuracy.

30. Dumas did not use formulas at this stage. The relative numbers of atoms were given and were of an order similar to that of emetine: C - 30, H - 24, N - 1, O - 3, where the atomic weights used were C= 38.218, H=6.244, N=88.518 and O=100.00. The modern formula is $C_{29}H_{40}N_2O_4$. It can be obtained from Dumas' values (except for one atom of carbon) by doubling all of his numbers except carbon (he used C=6 on the modern scale of atomic weights) and removing 4 H_2O (water of crystallisation). The difference in carbon was due to an error in the generally accepted value for its atomic weight which persisted for nearly 20 years. Dumas' other results were not quite this accurate, but were excellent considering the state of the science. The influence of this work on Dumas' ideas of atomic theory will be considered in Chapter 4.

31. Reference was made in note 15 to the assistance given by Pelletier to Dumas in the "carving out of a future".

seems to have extended even further. Shortly after Robiquet had become professor of a course in the Natural History of Medicaments at the Ecole de Pharmacie in 1814, Pelletier was appointed to replace him as assistant professor for the same course. Both directed their own pharmacy, although Robiquet had gone a step further in taking a particular interest in the manufacture of chemicals. For several years he had also been giving lectures in chemistry at the Athénée. It is not difficult to see Pelletier's hand in the appearance of Dumas as préparateur for this chemistry course shortly after his arrival in Paris (32). The importance of this position for Dumas' future in Paris must be underlined. He had never obtained the diploma of baccalaureate. He was fully aware that without it there was virtually no hope that he would ever become a professor in a government school (33). On the other hand teaching positions

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32. It is surprising that this position has never been mentioned by Dumas' biographers. Evidence that he was indeed préparateur at the Athénée can be found on several small sheets spread throughout Arch. Acad. Sci., Fonds Dumas, Carton 7, in Dumas' handwriting, all of similar format, all bearing small diagrams of apparatus generally on the right hand side. One of these sheets is labelled: "Athénée, 20 Janvier 1823, note des préparations." The others carry similar references. Each sheet lists the equipment necessary for demonstrations during a particular lecture. The date 13 January on one of them indicates the latest date on which he could have begun his duties. Yet another, undated, includes the following information: "Athénée. Sulphur. Note concerning Preparations. Sulphur in natural crystals and on gangue. See M. Pelletier. Crystallise sulphur during the lecture."

33. The programme at the Ecole Normale had developed to such a degree from the time of its foundation in 1808 that agrégation, only envisaged at that time, had become a necessary step, subsequent to the baccalaureate and licence, on the way to becoming a professor, by decree of the Conseil Royal de l'Instruction Publique, 6 February, 1821. Despite the events surrounding the closing, then reopening of the school on a limited basis during the next decade, the law was never changed. Following a decree of 30 October 1830 agrégation became the primary goal of the Ecole Normale. It may be argued that the Grandes Ecoles maintained a certain independence from the University system in this regard, but one would hardly expect them to accept lower standards.

were available in private 'schools' which did not require such credentials. Among these the Athénée was the most widely recognised and enjoyed the greatest prestige. It had been founded in 1781 as a private society whose primary goal was the popularisation of science (34). This was accomplished by providing financial support for courses given principally by prominent scientists who emphasised the relationship between science and daily living. As the number of those exposed to a science education had increased over the years, subtle changes had occurred in this aim until Colladon, who attended lectures in the mid-1820s was able to say: "It was an institution where evening courses were given on new developments for those who wished to remain abreast of the progress of science and literature." (35) Those interested in attending lectures registered at the secretariat of the Society at 2 rue de Valois, across from the Palais Royal (36). The lectures were apparently given in the Palais beginning at 8.00 p.m.

Dumas' duties as préparateur, a position unique to science courses, included the assembling of equipment and chemicals that were to be used during the demonstrations that accompanied the lectures, preparing any solutions necessary, writing notes and drawing diagrams on the blackboard

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34. Called the Musée originally, it became the Lycée until that name was reserved for the secondary schools founded in 1802, when it became the Athénée. See Smeaton, W. A., "The Early Years of the Lycée and the Lycée des Arts. A Chapter in the Lives of A. L. Lavoisier and A. F. de Fourcroy.", Annals of Science, 11 (1955), 257-67 and 309-19. For later information see De Job, C., L'Instruction Publique en France et en Italie au dix-neuvième siècle, Paris, 1894.

35. Colladon, op.cit.(1-65), p.187.

36. "The registration fee is 120 francs for men, 60 francs for women and students." Le Moniteur Universel, 1824, No. 336, (1 December), p. 1556.

in advance, to which the professor would refer, assisting in the demonstrations, in general facilitating in every way possible the smooth presentation of the lecture. Since it seems that no laboratory or stockroom was connected with the hall in which Robiquet lectured, Dumas was probably responsible for transporting the materials needed each week from Robiquet's pharmacy on the rue des Francs Bourgeois-St. Michel (37) where Dumas prepared the demonstrations, to the Palais Royal, about a mile away. But Dumas' energies were not limited to the performance of these routine tasks. He applied himself diligently, enthusiastically to mastering the entire teaching situation, for, as he saw it, the Athénée would be the centre of his life in Paris. If he received a small sum for his work well and good; but the promise of Robiquet's early retirement because of the stress of other duties was a far more cogent reason for applying himself. It may be that he was given the opportunity to substitute for Robiquet on occasion as lecturer. One can well imagine his reaction when suddenly he was advised that he had been chosen to give the lectures for 1824. Though the chain of events is not clear, one may assume that Robiquet, satisfied with the progress that Dumas had made, suggested to Ampère, who was among those concerned with choosing the professors for the coming year, that Dumas ought to be given the position. As Hofmann remarked: "Ampère succeeded in procuring the appointment for Dumas without having spoken to him on the topic." (38) Shortly afterward the Courrier Français listed Dumas

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37. De Saussure referred to "Robiquet, Boyveau et Pelletier, fabricants de produits chimiques, rue des Francs Bourgeois-St. Michel No. 8 à Paris." Bibl. de Genève, Correspondance de Th. de Saussure, Letter of 25 March 1836.

38. Hofmann, op.cit.(1-6), p. ix.

among those who would lecture in the Athénée during the year 1823-24 (39). He probably attended the opening meeting of the year, a literary evening held on Saturday 29 November (40), and the following week began a series of lectures on general chemistry. In 1828 he wrote:

> "Still too young to expect that a similar course would stand up favourably in comparison with that of such a capable teacher [Robiquet], I thought it necessary to avoid any such possibility. Consequently I chose a point of view different from the one he had used, and changed the order in which the facts were presented. Moreover, I learned quickly that in an establishment where nearly all of those attending continued to come from year to year, it was necessary for the professor to change his topic. Consequently, beginning with my second course, I no longer limited myself to general chemistry but added chemistry applied to the arts." (41)

In view of the emphasis that Robiquet undoubtedly placed upon descriptive chemistry, not at all unusual at this time, the changes Dumas mentioned certainly would have involved the introduction of much more theory, especially that having to do with atoms and the classification of the elements. It must have been his ideas on the latter that led him to change the order in which the course was presented. If the originality of his approach, added to his diligence and enthusiasm, was sufficient to satisfy the administration and assure his position, it is worth noting that his style of teaching left something to be desired at this time, for he wrote to Prevost frankly of his fear that he was boring his listeners.

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39. The other science professors listed were: Magendie, physiology; Louis Benjamin Francoeur (1773-1849), astronomy; Claude Servais Mathias Marie Roland Pouillet (1790-1868), physics. Dumas may have made time to attend the popular course given by François Auguste Alexis Mignet (1796-1884) on the History of England. Mignet, an editor of the Courrier Français, was at the beginning of a noteworthy career as an historian.

40. The programme was published in Le Moniteur Universel, 1823, No. 333 (29 November), p.1392.

41. Traité, Preface, p. vii.

Prevost replied:

> "I am very glad that you have 'bored your listeners' a little as you have said, because that will show you that your delivery is really tedious. During our discussions together, listening to you tried my patience, simply because you were so slow in expressing your ideas. Correct yourself now and you will become a very capable professor." (42)

He accomplished both eventually, at the expense of great effort.

Before the further ramifications of Dumas' assignment to teach at the Athénée are considered, a second appointment, at least as important, must be studied in some detail, for it too directed him unfailingly towards a career in chemistry (43). In 1823, Gaultier de Claubry resigned his position as répétiteur for Thenard's first year chemistry course at the Ecole Polytechnique. Thenard and Gay-Lussac, professor of the second year course, discussed the matter of his successor with Arago, a member of the Administrative Council of the school, and it was agreed that Arago should submit Dumas' name to the Council (44). Dumas became répétiteur

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42. This letter from Geneva, dated 1 January 1824 was cited by Gén. Dumas op.cit.(1-3), p.47. An exposition of this aspect of Dumas' life was given disproportionate emphasis by the author of his biography in LaRousse, P., Ed., Grand Dictionnaire Universel du XIX^{e} Siècle, Paris, Vol. 6 (1870), p.1377. The following description formed only a small part of his commentary: "... his beginnings at the Athénée were not those of a man destined in the future to charm large and demanding audiences in more important surroundings. His involved, laborious, dull and incorrect speech was not in the least attractive. Unlike so many savants who neglect this powerful mode of action, this talent which brilliantly enhances all others, M. Dumas resolved to learn the art of speaking."

43. It should be recalled that both of these appointments came after the contract founding the Annales des Sciences Naturelles had been signed and work on the first issue had progressed almost to the point of publication.

44. Arago and Gay-Lussac were the editors of Annales de Chimie et de Physique, in which several articles by Dumas had appeared by this time. One of his memoirs had weathered severe criticism by the editors. Dumas had proved the value of Gay-Lussac's method of analysis, indeed had enhanced its value by the simplified determination of water he had introduced. He may have been working in Gay-Lussac's laboratory (cont.)

officially on 27 January 1824 (45), at 23 years of age the youngest of those teaching at the school by four years, quite amazing considering that he was not a graduate of the Ecole, lacked even the degree baccalaureate in letters, and finally had not sought the position! Thus to a not inconsiderable salary at the Athénée (46) was added 1500 francs per year, more than enough to support a young, unmarried man at the beginning of his career. It was probably at this time that Dumas finally gave up all thoughts of a career in pharmacy (47), confident of a future in teaching, though both of his positions were temporary appointments, renewable annually.

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44. (cont.) in the latter part of 1823. R. Blunck, Justus von Liebig, die Lebensgeschichte eines Chemikers, Berlin (Wilhelm Limpert-Verlag), 1938, p.57, wrote: "From now [summer 1823] on Liebig worked in Gay-Lussac's laboratory in the Arsenal, with him and the young Jean Baptiste André Dumas from Geneva, who was also a discovery of Humboldt."

45. He was elected unanimously by the Council, Chatelain, op.cit.(1-6), col. 129, and named officially by an Arrêté of the Minister of the Interior, Jacques Joseph Guillaume François Pierre le Comte de Corbière (1767-1853), Archives de l'Ecole Polytechnique (hereafter AEP), Carton 1824 (1).

46. Apparently there was a relationship between the number of those attending lectures and salary, but it is not clear whether the salary was guaranteed or depended on the number attending an individual professor's lectures.

47. There is no evidence that he was examined or received as a pharmacist in Paris. Bouvet, M., "Berthollet, Fourcroy, J. B. Dumas et Wurtz, etaient-ils Pharmaciens?", Revue d'Histoire de Pharmacie, 14 (1945-49), 147-52, carefully avoided a direct answer to the question, though he implied that Dumas did not become a pharmacist. Perhaps the most important evidence in favour of this opinion is the appearance of Dumas' name in the list of associate members of the Société de Pharmacie de Paris for the first time in 1838. J. Pharm. Chim., 2e Sér, 24 (1838), 484. Certainly he never practised pharmacy as such, and his election to the Society was undoubtedly due to his appointment as a professor of organic and pharmaceutical chemistry at the Ecole de Médecine.

The Ecole Polytechnique was founded in 1794 to prepare young men for careers in public services as officers, consultants, directors, or other positions of responsibility that demanded a knowledge of mathematics and science. Most graduates pursued military or naval careers because of the particular needs of the time. After 1815, however, increasing numbers continued their studies at advanced schools, especially the Ecole des Ponts et Chaussées and the Ecole des Mines, in preparation for civil careers. Candidates usually applied at the age of 16 or 17. Difficult examinations reduced their number significantly, thereby generating an elite student population. The prospectus for 1823-24, Dumas' initial year at the school, indicated that the Second Division students (first year) would attend lectures in five courses: Mechanics and mathematical analysis; descriptive geometry; physics; chemistry; literature and history. These courses were continued in the First Division (second year), except for that in descriptive geometry, which was replaced by courses in astronomy, geodesy and physical geography; machines; and architecture. The weekly lectures in chemistry, given by Thenard in the Second Division and Gay-Lussac in the First Division, were one and one-half hours in duration. These lectures were not limited to theoretical and descriptive chemistry. The outline for Thenard's course included the following statement:

> "Moreover, in speaking of each substance, the arts which depend on its properties will be considered. Thus in the discussion of the action of oxides on one another, the art of glass-making will be studied; the art of the brick-maker, potter and that of making porcelain; the preparation of mortars, cements and concrete." (48)

An additional half-hour was devoted to pre-laboratory discussion. The

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48. "Programme du Cours de Chimie", AEP, Livre des Cours, 1823-24, p. 35-41 (36).

professors were expected to question students from time to time and give examinations at the end of the first two of the three annual terms. Formal public examinations, held at the end of the year, were conducted orally by the inspector of studies and a group of examiners.

In Geneva, Dumas had guided several pharmacy students who had requested instruction in experimental techniques but he had never faced large numbers of students in a formal setting in which laboratory exercises were part of a required course. Since guidance in the laboratory and testing after experiments occupied much of his time as a répétiteur at the Ecole Polytechnique, his duties in this position will be described within the context of a discussion of laboratory instruction at the school. The long recognised need for improved quarters for the student chemistry laboratories (49) was met for the most part with the construction of a separate building consisting of eight rooms in a line, each with bench space for 16 students working in pairs (50), so that 128 students could

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49. From the time that the school had moved from the Palais Bourbon to the present site in what was then the disused Collège de Navarre, the student chemistry laboratories had been housed on the ground floor of what had been the chapel. The interior had been rebuilt to include the school library and cabinet de physique on the newly constructed first floor as well as the chemistry amphitheatre on the ground floor with its preparations laboratory. In a long report to the Conseil des Batimens civils dated 24 April 1820, AEP, Carton 1820 (Carton 1830 also contains a copy), Léon Marie Dieudonné Biet (1785-1856), discussed the plans for a new chemistry laboratory. In it he referred to the existing quarters: "Until now they have been housed in rooms below the library, in half the necessary space. Apart from this unsuitable placement, the laboratories lack completely any air flow, and its three chimneys are incapable of receiving all the vapours from 40 furnaces (fourneaux) lit at the same time. More than once the health of many students has been compromised."

50. Biet described the architect's plans: "... there will be ten rooms separated from each other by partitions against which chimneys will be placed back to back. These rooms will be open at the top of the partitions to provide an air flow; entry will be from the side facing the main courtyard. A covered porch in the centre of the building, (cont.)

do their laboratory exercises at the same time. Further expansion occurred, probably in 1826 because of a report made that year on the need to accommodate 300 students (51). Places for 50-60 students working in

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50. (cont.) precisely on the main axis of the institution, will serve as a passageway. The building will be covered by a roof having two gutters and a ceiling immediately beneath its framework to avoid reducing the space inside." Ibid. Because Biet saw what he believed to be flaws in the plans, more details of the construction were recorded: "1°. It is possible that each of the rooms is not large enough to permit the use of 8 furnaces at once. Each room is nearly square with an inside measurement of 6 metres. The furnaces are so placed that there will be only 1½ metres in between them, too restricted, I believe, for spreading apparatus. 2°. Placing the chimneys opposite one another could prevent them from drawing air properly. 3°. The chimney mantle only projects one metre. This is not sufficient should certain noxious gases be released." Ibid. Small undated detailed architect's drawings exist that fit this description exactly. AEP, Registre des Plans et Croquis. They include 8 laboratories and a large parlour, the latter, in view of the original emplacement, dividing the entrance courtyard from that of the students. On 5 May the project was approved by Comte Joseph Jérôme Siméon (1749-1842) the Ministre Secrétaire d'Etat, who forwarded Biet's report to the Council of the Ecole. After studying the report, the Council advised Siméon on 27 July that they agreed with Biet and would build the laboratories in the Acacia Garden at the other end of the main axis, the site that had been their first choice before they had tried to economise. The consequent elimination of the parlour left a building of the same type with only eight rooms. Plans of the school for 1821 and 1837 show that the dimensions of the building are exactly those of the original design after excision of the parlour, which would lead one to believe that the interior design remained essentially the same.

51. Included among the needs reported: "... the chemistry laboratories are not extensive enough. ... The construction of a large chemistry amphitheatre behind the student laboratories has long been projected." AEP, Carton 1825. A sheet bearing the pencilled date 1825, AEP, Carton 1830 was more specific: "Chemistry. Amphitheatre for 150 students with its laboratory. Student laboratories for 50 furnaces (later 25 more). Room for storing chemicals. Shop for apparatus. Cabinet for the professors. Two small cabinets with two small laboratories for the répétiteurs. Cabinet of mineralogy. Place for the Galvanic Pile. [This was crossed out with pencil also.] Coal Cellar." The pencilled portions were very likely added in 1830 when some of these needs were finally met.

pairs were added (52). Dumas presided over these laboratories with César Mansuète Despretz (1791-1863) who had been Gay-Lussac's répétiteur since 1819. Their duties, as drawn up in 1827, include the following:

> "MM. the répétiteurs share between themselves the direction of students in their chemical operations. They will move about the laboratories frequently, providing the students with useful explanations.
> For the First Division each of them must supervise four laboratories, for the 2e five laboratories. ...
> After examining the products and report provided by the two students working together, the répétiteur will assign a mark to each of them. In this evaluation he will take into account the care and assiduity he has observed and made note of during the experiment.
> During the week following the laboratory period the two notebooks of marks will be directed by the good offices of the répétiteur of the Division to the Inspector of Studies after allowing the professor of the same Division to have access to them. ..." (53)

The difficulty of presiding over four or five separate laboratories (54), with 16 students working in each, must have been enormous, and it could only have been offset by the strict military discipline observed in the school (55). Laboratory periods, held weekly, were two hours in length.

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52. It seems probable that the two new laboratory wings were added in 1826, but not later than 1831, when a large increase in the student population occurred. One wing contained 16 furnaces, the other was shaped to another building in back which reduced the number.

53. AEP, Carton 1827. "Surveillance des manipulations chimiques par MM. les répétiteurs", 1 March 1827. In a meeting of the Council of Instruction of 3 June 1824: "The Assistant Governor recalled that the two répétiteurs of chemistry must both be present during all laboratory periods ..." AEP, Registres du Conseil d'Instruction, 15 mai 1821 - 6 decembre 1827.

54. Since the only entrance to the laboratories was from the courtyard each was, in effect, an isolated unit.

55. A concept of the character of this discipline can be gleaned from the regulations drawn up 28 June 1832 by the Minister of War, AEP, Carton 1832. Included among them were: "44. A profound silence must be observed in the amphitheatres. All conversation, even on topics of the lecture or the questions asked, is forbidden. ... 46. Students must not enter the enclosure of the chemistry amphitheatre reserved to professors (cont.)

The threefold purpose of the experiments was given in the course outline:

> " ... to give examples of every kind of synthesis and analysis and of the various chemical changes [known] ... to confirm the theories exposed in the course ... to give the students a more precise knowledge of the procedures and materials employed in the arts relating to the services to which they are called." (56)

Although emphasis in the experiments in both divisions was placed on mineral chemistry, some attention was given to the preparation and analysis of organic compounds in those of the First Division. In addition to fulfilling his duties in connection with the laboratories, Dumas was expected to spend two periods each week examining the Second Division students orally on Thenard's lectures, a total of five hours when he first arrived but reduced to four in 1826. Finally, he and Despretz were to be available during scheduled study periods to give assistance to their students.

Dumas' interest in the school did not end here. In 1825 a project was undertaken, which he probably initiated, whose purpose was indicated in a letter that he wrote to Monseigneur Denis Le Comte de Frayssinous (1765-1841), Grand Master of the University of France:

> "At the request of the professors of chemistry of the Ecole (57), the conseil d'Instruction is interested in completing the cabinet intended for examination by the students. It is to contain samples of all chemical products and some art objects pertaining to applied chemistry, to be found among the establishments dependent on the Ministry of the

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55. (cont.) and répétiteurs. They may not touch the instruments and other objects placed on the professor's desk and on the mercury trough without authorisation from the professors and répétiteurs. If it is given, and after they have examined these objects, they will replace them with the greatest care."

56. AEP, Programme du Cours de Chimie 1823-24.

57. Dumas' original words: "At the request of MM. Thenard and Gay-Lussac, professors of chemistry at the Ecole Polytechnique" were changed by a different hand, probably Thenard's, to read as indicated. Several other small changes were made.

> _Maison du Roi_ - the Sèvres factory, the Gobelins works and that of the Mint, all using procedures and materials to which the professors of chemistry have often attracted the attention of their students in a special manner. They would like very much to have these objects in hand when they are talking about them. ... To avoid duplication of effort, it would be better if the directors would deal directly with M. Dumas, who has been assigned to complete the existing _cabinet_, and who will indicate the objects missing and choose them according to the order of topics in the lectures. ..." (58)

The results were gratifying, and correspondence involving the donations continued for many years. That Dumas made use of these samples in his future research is evident from the references made to substances obtained from these establishments in many of his journal articles.

Another of the duties of a _répétiteur_ was the preparation of an annual inventory, which was more complete and in greater detail when one of them offered his resignation. Such an inventory was required in 1823. One of the five lists of chemicals and equipment drawn up gave the contents of Gaultier de Claubry's laboratory, and bears his signature (59). It was in two parts, the second dated 10 October 1823 cataloguing the weights of the 1200 chemicals in the laboratory (60). It was countersigned by Dumas, who wrote: "I have received and verified the present

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58. AEP, _Carton 1825_. Copies of the initial letters written by Dumas to each of the establishments mentioned are also in the Carton, as well as those to the Powder and Saltpeter Factory, Royal Printer, Botanical Garden, School of Mines, Veterinary School at Alfort and the _Conservatoire des Arts et Métiers_. If there were others they were not preserved.

59. AEP, _Carton 1823_. The other lists included the chemicals and equipment in the _cabinet_ and laboratory of Gay-Lussac; those of Thenard; the laboratory of Despretz; and the common stockroom.

60. The individual weights for about 75% of these chemicals was less than 100 grams, for a few only half a gram. The fifteen with weights of one kilogram or more included sulphuric acid, which is hardly surprising. What is worth noting is the presence at that time of three kilograms of bismuth!

inventory on 15 June 1824." (61) The first part, consisting of only two folio pages, dated 24 January 1822, listed the apparatus, and was apparently not rechecked in 1823. Judging from the types and quantities of the various pieces (62), this equipment was clearly for the use of the répétiteur in preparing materials for demonstrations and the student laboratory periods. It was not intended to be a research laboratory. No doubt Hofmann's disparaging comments (63) had some justification, but the government was supporting a school not a research establishment, and that in difficult financial conditions. In this light, his statement: "The famous laboratories which had witnessed the grand experiments on potassium and sodium, and the researches published in the two volumes of Gay-Lussac and Thenard were no longer in existence" (64), suggests a magnificence which is somewhat doubtful, even in the time of Napoleon, when removal to makeshift quarters in the Collège de Navarre occurred. If Dumas was "sorely disappointed" (65), it was because he had become accustomed to the

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61. Ibid., Inventory by Gaultier de Claubry, final page. Certainly Dumas would not have had an earlier opportunity to carry out this verification. Some time during November 1824 he rechecked the inventory of Thenard's cabinet and laboratory, and kept both lists current thereafter.

62. Over 1200 bottles were catalogued, but this number and the fact that just over 1000 of them were of 6 ounce capacity (about 150 ml.) would lead one to believe that these were the containers for the chemicals listed.

63. "All the répétiteur had at his disposal was a sort of kitchen for the preparation of the lectures, and a little room without a fire-place, furnished with cupboards for the specimens. ... There was neither balance nor barometer, no thermometers, no graduated tubes and vessels, in fact, no instrument of precision for research. The whole stock of the laboratory consisted in the apparatus and preparations used for the manipulations and demonstrations in a course of general chemistry." Hofmann, op.cit.(1-6), p. ix.

64. Ibid.

65. Ibid.

very good accommodations which he had enjoyed in the Genevan laboratories. It was, however, a place in which he could do research, and very quickly he began to build up a supply of the necessary equipment (66). By 1825 the authorities duly noted the need for other accommodation for the répétiteurs (67). Some action may have been taken, but it was not until 1832 that Dumas was able to set up a proper research laboratory in an annex of the school (68). He had begun to do serious research in his "kitchen" long before, as early as 1825. The results were published in the Bulletin of the Société Philomatique. Dumas became a member of the Society in 1825.

The Société Philomatique was founded in 1788 by a group of young men with a thirst for studying the sciences and a desire to communicate to others what they had learned (69). Their meetings, marked by a friendly, informal character from the beginning, were the forum for discussing recent

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66. Several items from Berthollet's cabinet of physics and chemistry, which the school had purchased from his widow in 1823 for the sum of 6848 francs, AEP, Carton 1823, were assigned to his laboratory. The manoeuvring of funds that was necessary to make the purchase of this equipment possible serves as a measure of the penury of the times. Dumas added other items to his inventory from the stockroom from time to time, certainly with Thenard's acquiescence. For example, on 23 June 1825 he transferred to his inventory: "a platinum crucible, a metal mortar and pestle, a small copper suction pump with stopcock, a small bell-jar mounted on a copper base with double adjustment, an apparatus for the analysis of plant substances using potassium chlorate." AEP, Carton 1824.

67. See Chapter 3, note 51.

68. Gén. Dumas, op.cit.(1-3), p. 93. The exact location of this laboratory is unknown.

69. Two of the six founding members, Alexandre Brongniart and Baron Augustin François de Silvestre (1762-1851), were still associated with the Société in 1825. A lengthy study of the Society must be left to others. Crosland, op.cit.(1-28), p. 169-79, has given an interesting perspective of its early history. The Bulletin of the Society, published from 1791 to 1836 is a valuable source for information concerning its activities.

discoveries of general interest as well as reading their own studies and research. When the Academy of Sciences was suppressed in 1793, its members could have formed their own private society, which was quite permissible, but many elected to join the Société Philomatique. While this gave the group a certain prestige, it also imprinted upon it a somewhat different character which in turn gradually germinated a form and set of regulations strongly similar to those of the First Class of the Institute (the Academy reborn two years after its demise). Indeed membership provided young men with a training and proving ground on which to prepare for possible election to the Institute (70). It was a desire to maintain this youthful character that led to the drafting of a different and perhaps unique regulation requiring resignation after a certain period of time (71). Those who were affected by this ruling were encouraged to continue their association with the Society somewhat passively as Associés Libres (72). Vacancies in the seven sections (73), normally occurring as

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70. Only two of the 23 who were Associés Libres in 1825 never became members of the Institute. Among the 49 members, 14 were already in the Institute and all but four of those remaining were elected at a later date. A list of members and Associés Libres was given in the Annuaire de Sociétés Savantes de la France et de l'Etranger publié sous les auspices du Ministère de l'Instruction Publique, Paris, 1846, p.344. It will be referred to hereafter as Ann. Soc. Sav.

71. Initially age was the determining factor, then length of time as a member. In 1846 one was allowed to become an Associé Libre after 10 years as a member, and was required to resign at the end of 15 years.

72. In this role they continued to enjoy all the rights of membership without the obligations such as payment of fees (an annual fee set each year plus a standing weekly fee of 1.25 francs in 1846). Ibid., p.343. Clearly these men had many other outlets for their creative ability, but their presence at meetings provided encouragement and inspiration as well as a certain amount of guidance and criticism.

73. These were: Mathematics, Astronomy and Geography; General Physics and Applied Mechanics; Chemistry and Chemical Arts; Mineralogy, Geology and Mining Arts; Botany, Plant Physics and Agriculture; Zoology, Anatomy and Physiology; Medicine, Surgery and Veterinary Arts. Nouveau Bull. Soc. Philom., 1825, unpaginated. The interest in the applied aspects of science is evident.

a result of such resignations, were filled by a candidate "chosen from among those recognised as savants by their writings and have indicated the desire to be accepted into the Society either directly or through a member" (74).

Dumas' continued interest in the study of science would undoubtedly have led him to attend most of the meetings of the Society in 1823 and 1824 (75), and certainly he would have expressed the desire to join. His publications, his work at the Athénée and Ecole Polytechnique qualified him as a savant in the sense in which the term was used. Thus he became a leading candidate for the vacancy created when Thenard, who had been a member since 1803, decided to resign. Quite possibly Thenard, having had ample time to evaluate the qualities of his répétiteur, chose to become an Associé Libre at this time to make a place for him. Dumas was elected on 29 January 1825 (76) and straightway was appointed to replace Pelletier as the representative of the Chemistry Section on the Editorial Committee for the Bulletin. In this capacity he was able to read no fewer than five notes describing research that he had completed at the Ecole Polytechnique before a decision was made towards the end of

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74. "Règlements de la Société Philomatique", No. 34. Ann. Soc. Sav., p.342.

75. It was not unusual for non-members to be invited, even on a regular basis. The author of a brief history of the Society remarked: " ... a select audience was admitted to its meetings" Ibid., p.340. Almost weekly during 1817-18 Audouin entered a note in his diary that he was going to a meeting of the Society or had been to one and mentioned the topics discussed, even though he did not become a member until 1821. Audouin, op.cit.(2-114).

76. The procedure involved paralleled that of election to the Academy which will be discussed fully in a later chapter.

1826 to discontinue publication of the Bulletin (77). Though his interest led him to continue his membership (78), there is no evidence to suggest a further direct influence of one on the other. Yet belonging to the Society was important for one aspiring to membership in the Institute, an ambition that Dumas had had from his youth in Geneva.

At some time during 1823 Dumas began to move in the scientific social circles (79). Several of the members of the Institute who were so inclined held weekly soirées to entertain their friends and associates as well as foreign visitors (80). Both undue burden and conflicting dates were avoided by designating a certain day of the week on which one would entertain. Except in unusual circumstances, the Thenards were 'at home' to those invited on Tuesday only, the Cuviers on Saturday, the Brongniarts on Sunday (81). Launay wrote:

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77. Though the Bulletin had served a purpose during the interval following its foundation in 1791, a great many specialised journals had begun to appear due to the freedom of publication granted by the Restoration government. Although many were short-lived, enough had become solidly founded by 1826 to satisfy the major goals set by the founders of the Bulletin. No doubt the birth of Annales des Sciences Naturelles, which had filled a real need for the natural sciences, contributed considerably to the demise of the Bulletin.

78. He was listed as an Associé Libre in 1846. Ann. Soc. Sav., p.344.

79. It was probably after his invitation to dine at the home of LaPlace in August. See Chapter 2, Note 108.

80. During the Restoration period, "social life was no longer centred around the Tuileries but in the Paris Salons. ... The material simplicity that governed these receptions allowed everyone to have them." G. de Berthier de Sauvigny, La Restauration, Paris (Flammarion) 3rd Edition 1974, p.261. Normally these soirées were built around recitals, concerts, games or just conversation that frequently turned to politics.

81. Launay, op.cit.(2-115) p.141; Thenard, Paul, Un Grand Français: Le Chimiste Thenard, 1777-1857, Dijon, 1950, pp. 171-72.

> "Towards the end of 1823, Dumas is seen appearing in the weekly receptions [at the Brongniart home] on the rue Saint Dominique, or meeting with the Brongniarts in a social evening at the Thenards, or a concert given by Madame Orfila." (82)

Dumas' interest in being with the Brongniarts went beyond the contract he had made with Adolphe and Audouin to edit a new journal. He had acquired a more than passing interest in Adolphe's sister Herminie Caroline Brongniart (1803-1890) and joined Audouin as a regular visitor to the Brongniart home (83). Launay has provided interesting details on this aspect of Dumas' life:

> "On 10 November 1824, Brongniart noted [in his diary] a conversation concerning his daughter Herminie that he had had with Dumas. The first question raised was a wholly material one. He endeavoured to discover how the young couple expected to live without any income apart from the poorly paid positions of the young man and a dowry of 40,000 francs belonging to the young lady. In any case, whatever good opinion Brongniart may have had of Dumas, whether his own or that of his son, whom he knew to be serious and prudent in matters concerning his sister, as a father he felt the necessity of going still farther by fulfilling a natural wish to learn more about the life of her suitor while he was in Geneva; consequently on 4 December 1824 he wrote to De Candolle for information about 'a young _savant_ of generally recognised merit and even having a pretty good reputation as a chemist and physiologist.' Satisfied by De Candolle's response, he gave Dumas permission to court his daughter. On 2 February 1825, Brongniart's wedding anniversary, Dumas and Audouin presented a _vaudeville_ for the children of the household, repeating it for their mother. Finally, and not without some delay, the wedding date was set for 2 May. It was nearly a year before it eventually did take place on 18 February 1826. During this time Brongniart attended a lecture given by his future son-in-law at the _Athénée_ on atomic theory. On the evening (84) of the

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82. Launay, _op.cit.(2-115)_, p.146. Mateo (Matthieu) José Buenaventura Orfila (1787-1853) made toxicology into a science. The Orfilas and Thenards were close friends.

83. In 1827 Audouin married Mathilde Brongniart, another sister.

84. "soir".

> wedding, Madame Brongniart helped the newlyweds to put their new home at the Muséum in order." (85)

The lodgings to which Launay referred belonged to Alexandre Brongniart as successor of the Abbé René Just Haüy (1743-1822) in the Chair of Mineralogy. They were on the first floor of the present administration building above those of Achille Valenciennes (1794-1865). Although these quarters may have been useful for Brongniart at times, he had no real need for them, since he also had a residence at the Sèvres Porcelain Factory of which he was director in addition to his home at 3 rue Saint Dominique (86). On 26 February 1827 Charles Ernest Jean Baptiste Dumas was born, and a few years later on 25 December 1831 he was joined by a sister, Nöele Jean Baptiste Dumas (87). Dumas was soon joined at the Museum by his brother-in-law, Adolphe, and Audouin, each with a residence in his own right as a professor.

This chapter in Dumas' life cannot be closed without considering one further aspect of his early life in Paris - his interest in applied chemistry. Born during De la Rive's lectures, it had remained dormant while he worked with Prevost but was quickly reawakened by the Paris Industrial Exposition held in the vast rooms of the Palais du Louvre in the summer of 1823. There, perhaps for the first time, he became aware

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85. Ibid., p. 146-47.

86. "Nevertheless Brongniart had a foot in the door there, and we owe memories of his children and grandchildren to this triple existence lasting 25 years: Sèvres, the Museum and his home on the rue Saint Dominique." Ibid., p.140. He had organised his activities so that he would be able to spend Sunday to Wednesday in Paris and Thursday to Saturday in Sèvres.

87. Ernest, father of Général Dumas, author of the life of Dumas, one of the sources to which reference has been made, died 24 February 1890, Nöele 19 December 1928. They were buried next to their father in a plot near the southwest corner of the Cimetière du Sud (Montparnasse) in Paris.

of the gap in thinking between research chemists making rapid advances in theoretical and descriptive chemistry and those who controlled production, often oblivious to these findings, disinterested or even disdainful. For the latter Dumas saw the need of a bridge-building course, designed to show that an understanding of theory could provide a rational basis for improving industrial processes. His appointment as a professor in the Athénée provided him with the opportunity to do something about it. But would such a course appeal to those who had attended Robiquet's lectures, limited largely to descriptive chemistry? Dumas decided that both he and his students would profit from an interim course during the year 1823-24, in which he would introduce chemical theory as a foundation for his discussion of the descriptive material and reorganise the latter using a method of classification that he had devised (88). While he taught this general course (89), avoiding the introduction of applied chemistry for the most part, he made preparations for the more ambitious, more original set of lectures. His teaching techniques needed improvement, but it was even more important to extend his knowledge of industrial chemistry. This he accomplished by voluminous reading, particularly in the Annales des Mines, and attendance at a course given by Nicolas Clément-Desormes (1779-1841) at the Conservatoire des Arts et Métiers (90). During the forty

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88. "I chose a point of view different from his [Robiquet] and I presented the facts in a different order." Traité, Preface, p. vii.

89. Ibid.

90. Le Moniteur Universel, 1823, No. 333 (29 November), p.1392, reported that the opening of courses at the Conservatoire would take place that day, and listed the courses being offered. Among them: "Cours de chimie appliquée aux arts. Professor, M. Clément-Desormes. Mondays and Thursdays each week precisely at half-two." Dumas was one of several hundred attending. Clément (the name by which he was more commonly known) had given similar lectures since 1819. This course was also useful for his work as répétiteur at the Ecole Polytechnique.

lectures he wrote lengthy notes, including with them careful sketches from blackboard diagrams to which Clément referred during his discussions of industrial equipment (91). No doubt Dumas was aware before he began the course that the lectures would incorporate necessary descriptive chemistry and not much chemical theory (92), otherwise there would have been little point in designing the programme that he had in mind. It was an ambitious one, intended to continue over a period of three years. The final preparation that occupied his time during the year consisted in outlining this course and detailing the early lectures.

By the end of the first year it had become evident to his friends that his approach was sufficiently original and interesting to warrant the publication of his course notes. In 1828 Dumas wrote in retrospect:

> "Since several persons thought that there would be some value in publishing the course because of the research that I had done and the interest that the topic had generated, I entered upon a contract to do so." (93)

This contract, signed 2 August 1825, was again with Béchet, this time for a work on industrial chemistry to be published in four volumes, each of

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91. These dated notes occupy 189 pages in a folio notebook, Arch. Acad. Sci., Fonds Dumas, Carton 11. The notes on topics of particular interest to Dumas were generally much longer, e.g.: the nature, properties and uses of fuels; glasses; porcelains.

92. His important lectures on boilers, containing the rudiments of a thermodynamic principle specified later by Nicolas Léonard Sadi Carnot (1796-1832) were an exception. A preliminary examination of Clément's contributions to early thermodynamic studies has been undertaken by J. Payen, "Deux Nouveaux Documents sur Nicolas Clément", Revue d'histoire des sciences et de leurs applications, 24 (1971), 45-60.

93. Traité, Preface, p. vii.

700-800 pages (94). At that time Dumas planned to subdivide it into 8 tomes. He drew up an outline to indicate the approximate number of pages to be assigned to each topic. For example, in Tome 1 he considered only non-metallic elements and their compounds with each other. Even a cursory comparison of the Table of Contents (Table 1) (95), with the

TABLE 3-1. Proposed Table of Contents for Tome 1 of Dumas' Industrial Chemistry Textbook, with the Number of Pages Projected.

Hydrogen	6	Diamond	10
Sulphur	15	Wood charcoal	14
Sulphurous acid	20	Animal charcoal	8
Sulphuric acid		C^2H^4; safety lamps	10
monohydrate of		Wood	9
Nordhausen	38	Carbonisation	38
Phosphorus	11	Peat and charcoal	
Nitric acid	5	from peat	11
Arsenious acid		Combustible minerals	
and its sulphides	5	crude and carbonised	40
Boric acid	3	Gas lighting	48
Silicic acid	14	Total pages	305

94. This contract was referred to in a later agreement made with Thenard, who had written a popular chemistry textbook which had gone through six editions, the last in 1836. The last volume of Dumas' Traité appeared in 1846. On 30 April 1849 "at Dumas' request", a contract was drawn up in triplicate to combine the two. It was never honoured, for on 7 May Dumas was elected to the legislative assembly. In it the following statement was included: "A past agreement between M. Dumas and M. Béchet on the second of August 1825, by which the former ceded to the latter the property of his work on chemistry, had established that that work could be divided into two distinct texts, the one on general chemistry, the other on chemistry applied to the arts and to agriculture only, each forming 4 vol. in 8° of 700-800 pages; had this division taken place, 4000 copies of each treatise could have been printed and 7500 fr paid for each volume which would be advertised at 9 fr and sold at 8 fr." All three copies of the 1849 contract are in Arch. Acad. Sci., Doss. Thenard (Fonds Dumas) (This method will be used to designate the marked papers that have been transferred from the Fonds Dumas to other dossiers in the archives.) Concerning the number of volumes, however, it should be noted that the Bibliographie de la France, ou Journal Général de l'Imprimerie et de la Librairie, 1828, No. 43 (25 October), 779 gave the following information: "Traité de Chimie Appliquée aux Arts, Vol. 1 ... this work should consist of (doit avoir) four volumes in 8°, each accompanied by an atlas in 4°. Price of each volume 8-0, atlas 2-50."

95. Arch. Acad. Sci., Fonds Dumas, Carton 8, Dossier "Notes d'expériences / Analyses de Z. Delalande / Sulfovinate de barite / Ether sulfurique / Chimie industrielle (tables des tomes)". Z. Delalande (1818-1839) was a student of Dumas.

published version (96), shows that Dumas added a large quantity of pure chemistry, more than doubling the length of this tome to 689 pages. There had been no discussion of oxygen or the halogens (97) in his original draft, nor had he mentioned selenium or its compounds to which he devoted 16 pages later. To the topic phosphorus he added 15 subtopics on phosphorus compounds. His early emphasis on elements or compounds of known industrial importance was replaced by a system built around a classification of the known non-metallic elements into families, using analogies based on their properties. Thus it became necessary to change the title of his work from "Industrial Chemistry" to "Chemistry Applied to the Arts". Evidently the 80 page introduction in which Dumas presented his approach to chemical theory was not mentioned in the first draft. Needless to say, similar changes were made in other tomes, particularly volume five devoted to pure organic chemistry for the most part.

The interest that he had shown in industrial chemistry by teaching the course had another important consequence. Although it is very unlikely that Dumas would have become a subscribing member of the Société d'Encouragement pour l'Industrie Nationale (98) before 1823, he was

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96. Traité. There were 22 topics and 110 subtopics.

97. A very brief discussion of bleaching was to be included in Chapter 6. Bromine had not yet been recognised as an element and fluorine had not been prepared, nor had its compounds been linked to those of chlorine or iodine. The latter element had only been studied carefully a decade before and the sole use that had been found for iodine or its compounds was the treatment for goitre already discussed.

98. The Société d'Encouragement, as it will be designated in this thesis, was founded in 1801 by a group of 23 men - among them Berthollet, Chaptal, De Candolle and Silvestre - who were interested in fostering industrial improvements. In the statutes, approved by a Royal Order dated 21 April 1824, the means to be used to achieve this goal were outlined: "1. Awarding of prizes, medals and incentives for discoveries and developments in the useful arts; 2. Experimentation and testing to evaluate new methods and resolve industrial problems; 3. Publication of a monthly bulletin [Bull. Soc. d'Encouragement] distributed to members of the Society and containing a descriptive announcement of useful industrial discoveries made in France and abroad." Ann. Soc. Sav., p.168.

elected member of the Comité des Arts Chimiques, a part of the administrative council, in the general meeting of the Society held in the autumn of 1825 (99). He joined the ten other members of the committee (100) in the task of examining new or improved equipment and processes relating to the chemical industry that were submitted for the council's approval and helped to prepare the reports that would be read before the council. While general meetings were held only twice each year (101), members of the administrative body met every other Wednesday at 7.30 p.m. "to hear the reports on objets presented to the Society for its approval"(102). Since this approval was dependent on the reports for the most part, the significance of the committees' work had increased as the reputation of the Society had grown, for approval included publication in the Bulletin and improved marketing value for devices or processes involved. Thus Dumas became part of another important professional milieu, expanded a little further the circle of his friends and acquaintances. In addition, he gained early access to more unpublished research and another outlet for

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99. Dumas was first listed as a committee member in November 1825. Bull. Soc. d'Encouragement, 24 (1825), 427. Anyone (French or foreign) who was nominated by a member and paid the fees could become a subscribing member, but the limited membership of the administrative council was determined by election: officers annually, committee members every three years (a third each year). Since re-election was allowed, a member could remain in office or on a committee as long as he was active. During the period 1802-84 there were only three presidents: Chaptal, Thenard and Dumas!

100. Most of them Dumas had already come to know: D'Arcet, Despretz, Pelletier, Robiquet, Thenard and Vauquelin. There were also three assistants on this committee: P. F. G. Boullay, Gaultier de Claubry and Anselme Payen (1795-1871).

101. The spring meeting was devoted to awarding prizes: Society business was conducted in the autumn meeting: annual elections, reading of annual reports of various kinds, etc.

102. Ann. Soc. Sav., p.169.

the publication of his own ideas became available (103). His active membership on the committee continued until he was elected to office. When Thenard was forced by ill health to resign from the presidency in 1845, Dumas was elected as his successor. He was re-elected annually for the rest of his life.

In 1826 Dumas' involvement in industrial chemistry took on a more personal character when his elder brother opened a dye works in Puteaux, a suburb of Paris. Dumas had been interested in dyes and dyeing from the time he had arrived in Geneva - lectures to the student society, a memoir on indigo published with Le Royer, notebooks containing analyses of several dyes. The third part of his course at the Athénée, which he was about to begin, included a section on this topic. No doubt he was pleased to have his brother nearby and was anxious to assist him in any way possible, including arranging for any financial backing that might have been necessary (104). Perhaps he hoped to gain a better insight into the practical problems of dyeing, and even to have the opportunity to do some industrial research. The factory was in full operation and all seemed to be running smoothly when a tragic accident on 6 June 1827 brought an end to the enterprise. The following report appeared in Le Moniteur:

> "A steam engine in the shop of M. Dumas' dye works in Puteaux near the Neuilly bridge exploded on Wednesday

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103. Although none of Dumas' work was published in the Bulletin before 1841 except a report (1837) that had already appeared in the Comptes Rendus of the Academy of Sciences, during the next 43 years (except 1851-53) he contributed several items annually, some rather extended. In 1865 no fewer than 18 items were indexed! While there were reports, some of the work was his own research and much represented a creative response to problems that prepared the way for research or action.

104. References for a loan for example. My sparse information about Dumas' brother precludes any serious discussion of his background, even with respect to the financing of the project.

> about six o'clock in the evening. The boiler was torn loose, overturned, went through a very thick wall and ended up in the garden of the establishment located on the bank of the Seine. The boilerman was killed, his body horribly mutilated. Though M. Dumas suffered no external injuries, he died the next day from the effects of concussion alone. The noise of the explosion was as loud as that of an artillery piece of 36. The two victims left no children; the worker was married. The books and other effects have been sealed. The damage is limited to about what has been reported." (105)

As heir to the factory and a large debt that remained (106) Dumas decided to repair the damages and resume operations. He seems to have retained ownership until some time in 1831. On the occasion of his candidacy for the Academy in 1832, he included with the credentials that he sent to the members a printed letter responding to "allegations being spread that were untrue":

> "I had the misfortune in 1827 of losing an older brother who had founded a factory in Puteaux. Taking over his business was burdensome, but I accepted it without restriction to do justice to my name and to his memory (107). I directed the factory for one year and in 1828 I handed it over (108) to the person who is still running it successfully (109).
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> I no longer own the factory, I have no interest in its operations nor in those of any other factory or commercial society whatever.

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105. <u>Le Moniteur Universel</u>, 1827, No. 161 (10 June), 931.

106. The factory would not have been open long enough to allow repayment of any considerable portion of the loan.

107. He could have declared bankruptcy, but this failure could have dogged him for the rest of his life.

108. "cedée". The exact nature of the agreement is not clear, but Dumas retained ownership, and therefore responsibility, until 1831.

109. It will become evident that the "person" referred to was the same Francillon who had assisted Dumas in his experiments with phosphorus done at the <u>Ecole Polytechnique</u>. "... Francillon, who gladly assisted me in the delicate research involved and facilitated its accomplishment by his zeal and wisdom." <u>Ann. Chim. Phys.</u>, <u>31</u> (1826), 154. Francillon was probably a student of Dumas at the <u>Athénée</u> and may well have worked with Dumas' brother.

> Moreover, I hereby solemnly declare, no matter what has been said, and without fear of suffering the slightest contradiction:
> 1°. That all business done during my administration has been transacted by cash payment or paid off at term;
> 2°. That all matters concerning my brother's estate are settled, without exception." (110)

Launay (111), who has examined Brongniart's personal papers, has painted a somewhat different picture:

> "Dumas ... thrown brusquely into an encumbered business, led by an imprudent associate to give his signature (112), was forced to admit to his father-in-law gnawing debts whose appalling figures never ceased to mount for four years, until the day when he finally acknowledged on 19 August 1831 liabilities of 224,000 francs without any liquid assets (113). ... Thus Brongniart felt obliged to take over the contract for the factory (114) and after several years sold it to the associate, M. Francillon." (115)

Whatever the case may be, these events shed some light on efforts made by Dumas and on his behalf during these few years to find other sources for revenue. In 1827 Thenard invited him to teach in the Collège de France (116). After the death of his brother, Dumas continued to

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110. Silvestre's copy of this letter, the only one that I have been able to locate, may be found in the library of the Muséum.

111. Launay, op.cit.(2-115), p.147.

112. Launay did not indicate what Dumas had signed.

113. In Brongniart's notes Launay found frequent exclamations of the following type: "For a young, spiritually-minded man, orderly, knowledgeable, of good moral character to be thrown into such an abyss! Isn't it a dream, a nightmare? For a man who has nothing to have incurred such debts, a man of good sense and of spirit!"

114. "dut se porter adjudicataire de l'usine". There was no question of bankruptcy.

115. Ibid. The information necessary to reconcile these points of view is unavailable to me at the present time.

116. Dumas, lecturing there in 1836 said to his students: "This viewpoint ... was set forth *here* in a first attempt at a chemical philosophy, to which I devoted several lectures in 1827." Leçons, p.350 (my italics).

to replace Thenard for part or all of every year until 1832 (117). He gave courses there on two other occasions because Thenard had become too ill to lecture, but during the period 1827-32 this new source of income (118) was a welcome addition to the salary he received from positions at

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117. Since it is generally believed that Dumas only lectured here during the summer of 1836, a complete listing of his presence from 1827 to 1832 has been drawn up, based for the most part on documents in the Archives du Collège de France (ACF). By his own admission Dumas had taught there in 1827, probably in the second semester of 1826-27. ACF, Affiches Générales, D-I-b, indicated that the second semester of the following year would open 9 April 1828: "En cas d'absence, il [Thenard] sera remplacé par M. Dumas." Dumas stated that he had done so. Traité, Vol. 5, p.417. In 1828-29, ACF, Registres des Procès Verbaux d'Assemblés, G-11-4, p.33 indicated that he had replaced Thenard. In 1829-30, ACF, Registre de Présence, C-VII-d.210, indicated that Dumas, giving three lectures a week, signed 48 times from the date that the registers began (January 1830), and since ACF, Etat de Traitemens dus aux Professeurs, C-VII-c, indicated that he had given 55 lectures, it must be assumed that he gave seven lectures in December 1829, i.e., that Thenard gave only the opening lecture. In 1830-31, ACF, Registre de Présence indicated that Dumas gave all lectures except the opening lecture, three each week, 74 in all. It was at the end of this course that Dumas advised Brongniart of the extent of his debts, and that his father-in-law took over the contract, allowing Dumas to pursue studies for a medical degree (Chapter 9). Not until he had completed this work did he replace Thenard again, from 2 June to 7 July 1832 (10 days). Ibid. During that year there were only two lectures each week. It should be noted that the number of lectures to be given by a professor was variable, depending on an agreement with the administration at the beginning of each year.

118. Dumas received part of Thenard's salary as his replacement. In 1832-33, now that Dumas had been relieved of his burden, Thenard taught the course himself. Ibid. In 1833-34, Dumas taught there during the second semester only (30 April-18 June). Ibid. In 1834-35, F-II-b.35 indicates that all lectures were suspended by the Minister of Public Instruction at the request of the professors because new buildings were being constructed. In 1835-36, ACF, Registre de Présence shows that Dumas lectured throughout the year, beginning 22 December. There were 34 lectures in all. The last eleven, given once a week, were published as his Leçons de Philosophie Chimique. Despite the description he gave of a course that he would give the following year in organic chemistry, when Dumas signed his name to ACF, Registre de Présence, on 25 June, he wrote "Dernière leçon", which neither he nor anyone else had done before that time. From December 1836 it was Pelouze who replaced Thenard.

the *Athénée* and the *Ecole Polytechnique*. To this were added earnings from the *Annales des Sciences Naturelles* (119) and an industrial journal, founded in 1827, which owed its existence largely to Dumas' efforts (120). He became a principal founder of an industrial school, the *Ecole Centrale des Arts et Manufactures*, which should have increased his income, but had the opposite effect at the very time when he was most in need. An attempt to obtain a Chair at the *Muséum* failed (121), though it eventually led to his appointment as assistant professor in the Faculty of Sciences. During this period the publication of the first three volumes of his textbook also helped.

This great occupation with other activities drastically reduced Dumas' time for research. His work on ethers with Félix Polydore Boullay (1806-1835) was completed before the end of 1827. He published no memoirs or articles in 1828 or 1829. Though their value must not be underestimated, few of the thirteen that appeared during the next two years extended beyond two or three pages and none were longer than fifteen pages (122). However, in 1832 the clouds finally began to lift (123).

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119. The contract was renewed in 1828. Dumas continued as editor until 1833, when he was replaced by Guillemin and Milne Edwards.

120. This journal will be discussed in Chapter 5.

121. Candidatures for high positions in the *Bureau de Garantie* and the St. Gobain factories, one of the largest in France, were also unsuccessful. Launay, *op.cit.(2-115)*, 148-49.

122. In contrast, articles published during later two-year periods were generally longer and more numerous, and he was also required to give reports to the Academy of Sciences on the work of others, which were sometimes quite long and time consuming.

123. When Brongniart took over the contract, Dumas was freed of financial responsibility in the affair. Launay, *op.cit.(2-115)*, p.147, ended it on a positive note: "The outcome was better than could have been expected. Though Dumas had never interrupted his research, he was able to continue it more peacefully." Apparently Dumas inherited some obligations when Brongniart died in 1847, however, for Launay added: "It was thirty years before he was completely free." *Ibid.*

Before the end of the year he was a member of the Academy of Sciences, had teaching positions in several of the major educational institutions in Paris and was an active member of three societies. He had been editor of two journals and accomplished important research in physiology and chemistry.

CHAPTER 4

DUMAS AND THE ATOMIC THEORY

"I am convinced that the equivalents of chemists, those of Wenzel, of Mitscherlich, what we call atoms, are nothing more than molecular groups. If I were master, I would remove the word atom from science, persuaded that it goes beyond experience; and in chemistry we should never go beyond experience.

Doubtless the forces of nature have their limits, but will there be a time when we will be able to say: The limits assigned to the forces of nature by an infinite wisdom are at a particular point?" (1)

Dumas made this statement during one of his lectures on chemical philosophy at the Collège de France in 1836, ten years after he had announced a significant contribution to its development. It was made the focal point of a case study whose purpose was to distinguish scientific assertions, doubts and denials, on the phenomenological level from those on the epistemological level. The author wrote:

> "I want to consider this matter in the historical context of chemical theoretical developments of the last century, in particular the sceptical conclusions on atomic theory reached by the famous French chemist J. B. Dumas and others, conclusions which were sufficient to shake the confidence of chemists in Avogadro's hypothesis and the atomic theory in general." (2)

Since Dumas never wavered in his belief in the existence of ultimate particles, it is clear that a definition of terms is necessary before this claim can be fully appreciated. This is a difficult task because words seem to change their meaning over a period of time. The problem is further complicated by the fact that these terms were used within the context of three different vantage points from which Dumas looked at the atomic theory. To each of them he devoted long periods of his life: The calculation of atomic volumes and their use in the classification of the elements; the measurement of vapour densities as a means of determining atomic weights; the development of very exacting quantitative methods for establishing accurately the atomic weights of the elements, so that he could test the attractive hypothesis suggested by William Prout (1785-1850) that the atomic weights of all elements are integral multiples of the weight for

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1. Leçons, Lecture 7, 28 May 1836, pp. 258-90 (290) (Dumas' italics). Dumas referred to Carl Friedrich Wenzel (1740-1793) who had carried out studies of chemical affinity.

2. Buchdahl, G., "Sources of Scepticism in Atomic Theory", British Journal for the Philosophy of Science, 10 (1959-60), 120-34.

hydrogen. In this chapter an effort will be made to show the development of Dumas' attitudes towards the atomic theory from each of these vantage points(3).

Dalton's Atomic Theory before 1819. The discussion of Dumas' views on the atomic theory cannot be undertaken without a review of the ideas presented by John Dalton (1766-1844) and the extent to which they were accepted by his contemporaries before 1819 when Dumas first began to study the theory seriously. The principal tenets of Dalton's hypothesis can be summarised in the traditional manner as follows(4):

1. All chemical elements are composed of very small indivisible globular particles called atoms (5).

2. Atoms of the same elements have the same weight and volume; they are the same in every other way.

3. Atoms of different elements differ in all of these properties.

4. Chemical combination consists in the union of the atoms of elements in simple numerical ratios to form compound atoms with weights equal to the sum of the weights of their simple atoms.

But Dalton added a further dimension which must be mentioned because he defended it vigorously and it did not stand the test of time:

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3. The importance of putting modern conceptions to the back of one's mind can hardly be overemphasised.

4. For greater details see Partington, op.cit.(2-17), Vol. 3, pp. 784-86.

5. My italics. An appreciation of Dalton's emphasis on indivisibility is essential to an understanding of Dumas' thought. In 1810 Dalton said: "I have chosen the word *atom* to signify these ultimate particles in preference to *particle*, *molecule* or any other diminutive term, because I conceive it much more expressive; it includes in itself the notion of *indivisible*, which the other terms do not. It may perhaps be said that I extend the application of it too far when I speak of *compound atoms*; for instance, I call an ultimate particle of *carbonic acid* a *compound atom*. Now, though this atom may be divided, yet it ceases to be carbonic acid, being resolved by such division into charcoal and oxygen." Dalton's notes for the 18th of his lectures given at the Royal Institution in 1810, quoted by Nash, L. K., *The Atomic-Molecular Theory*, Cambridge, U.S.A. (Harvard Univ. Press), 1967, p.22 (Dalton's italics).

5. Equal volumes of different gases at the same temperature and pressure cannot contain the same number of ultimate particles, since water vapour, the particle of which must contain at least one atom of oxygen, is lighter than oxygen gas." (6)

These points all appeared in Dalton's notes by 1803 (7), but were not published until 1807, when Thomas Thomson (1773-1852), one of the most enthusiastic supporters of the theory included it in the third edition of his System of Chemistry (8). He wrote many articles on the topic, and in 1813 drew up a chart of atomic weights in which oxygen was given a weight of 1 unit (9). The only other chemist in England who gave Dalton his unqualified support at this time was his friend William Henry (1774-1836). William Hyde Wollaston (1766-1828) had many reservations, which led him to draw up a list of equivalents for elements and compounds (O=10) rather than atomic weights (10).

Strangely, Dalton's ideas entered France through Berthollet, the one person most likely to oppose them, and with the most influence to do so effectively. Berthollet had arranged for the translation of the third edition of Thomson's System of Chemistry (11). Since the French chemist

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6. Loc.cit.(4-4), p.786.

7. Ibid., p.784.

8. Thomson, T., A System of Chemistry, Third Edition, 5 Vols., Edinburgh, 1807.

9. Ann. Phil., 2 (1813), 42, 46-47.

10. Phil. Trans., 104 (1814), 18-22.

11. Thomson, T., Système de Chimie, Précédé d'une Introduction de M. C. L. Berthollet, 9 Vols., Paris, 1809. Crosland has observed that Berthollet had the first part of Dalton's New System in hand in August 1808 while Thomson's work was being translated. Cardwell, D. S. L., Ed., John Dalton and the Progress of Science, Manchester (Manchester Univ. Press), 1968, p.279.

had rejected for many years the idea that elements combine in constant proportions (12), it is not surprising that his long introduction contained arguments and warnings against the atomic theory with which those ideas had become so intimately intermingled. Most of the outstanding young French chemists were members of the Society of Arcueil at the time and on this issue they were not inclined to oppose their mentors, Berthollet and La Place, founders of the Society, who had both rejected the concept. Dalton did not help his cause in France when he attacked Gay-Lussac's law of combining volumes because it contravened his fifth point. Gay-Lussac in his memoir on the law had suggested: "The many results which I have revealed in this memoir are also very favourable to [Dalton's] theory." (13). The only member of the Society who showed any enthusiasm for the theory was Dulong (14). In 1819, working with Alexis Thérèse Petit (1791-1820), Dulong showed that solids, not gases, act in accordance with the following rule formulated by Dalton: "The quantity of heat belonging to the ultimate particles of all elastic fluids must be the same at the same pressure and temperature." (15)

German chemists had hardly been touched by the theory in 1819 but the same cannot be said for their Swedish counterparts for Berzelius had accepted it as an important conceptual tool. By 1818 he was able to

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12. This concept was proposed in 1797 by Louis Joseph Proust (1754-1826). Berthollet's opposition stemmed from his studies of reactions in solution.

13. Gay-Lussac, J. L., "Mémoire sur la combinaison des substances gazeuses les unes avec les autres", Mémoires de la Société d'Arcueil, 2 (1809), 207-33 (231).

14. Crosland, op.cit.(1-28), p.418.

15. Dalton, J., A New System of Chemical Philosophy, Manchester, Vol. 1, 1808, Part 1, p.70. Dulong and Petit listed 13 solid elements for which the product of specific heat and atomic weight was a constant.

publish a chart in his chemistry textbook (16) listing the latin name, chemical formula, atomic weight and percentage composition of over 2,000 compounds derived from 45 of the 49 known elements (17). These were the result of thousands of analyses made for the most part by Berzelius himself. They provided the grist for the mill of his theoretical considerations. Working from the point of view adopted by Jeremias Benjamin Richter (1762-1807) and the theory of constant proportions, he was able to recognise the important step forward that had been taken by Dalton, although he saw a need for certain modifications of the theory that he made in 1813 (18). From this time he referred to his corpuscular theory rather than the atomic theory, despite the inclusion of many concepts originated by Dalton. He missed the real value in Gay-Lussac's volume theory by equating combining volumes with atoms (19), but was favourable to it. It was this supposed equivalence that led him to reject Avogadro's hypothesis.

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16. Berzelius, J. J., Lärbok i Kemien, 8 Vols., Stockholm, Vol. 3, 1818. The part of this volume that contained an account of the atomic theory, the determination of atomic weights and his electrochemical theory was published separately as an Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité. Traduit du Suédois, ~~sur~~ les yeux de l'Auteur et publiée par lui-même, Paris 1819. It was translated into German in 1820.

17. Jorpes, J. E., Jac Berzelius, His Life and Work, Transl. from the Swedish by B. Steele, Stockholm (Almquist and Wiksell), 1966, p.46.

18. Two of these are mentioned because they will be considered again in my thesis and were specifically rejected by Dalton: Electro-chemical dualism and the view that all atoms have the same volume.

19. He noted: "Hence there is no difference between the theory of atoms and that of volumes, than that the one represents bodies in a solid form, the other in a gaseous form. It is clear, that what in the one theory is called an atom, is in the other theory a volume. ... In the theory of volumes we can figure to ourselves a demi-volume, while in the theory of atoms a demi-~~volume~~ atom is an absurdity." Quoted by Partington, op.cit.(2-17), p.161.

Amadeo Avogadro (1776-1856) and Ampère both scrupulously avoided the use of the term atom in their independently derived versions of the hypothesis that equal volumes of gases at the same temperature and pressure contain the same number of molecules (20). Nevertheless, not only was this concept essential for the development and acceptance of the atomic theory, but it assumed a central position in this part of Dumas' research from 1826 to 1836. The approaches used by Ampère and Avogadro will be examined in greater detail when Dumas' views are studied.

Atomic Volumes. Dumas became interested in the atomic theory while he was attending the chemistry lectures given by De la Rive in Geneva (21). Not long after he had completed the course, he obtained a copy of the work by Berzelius on this topic, which contained a long table of atomic weights for elements and compounds (22). In it he also found the statement that all atoms are the same size, which seemed to him to be highly improbable, even from the simplest of calculations. Since many atomic weights were available, he imagined a way of testing the statement. He had only to find the atomic densities of several different elements and compounds. As he wrote later:

> "The question came down to finding a procedure for obtaining the density of the integrant molecule of a substance so that this value, combined with the weight

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20. No attempt will be made at this point to define the word molecule.

21. It seems reasonable to assume that Dumas concentrated on fundamental chemistry textbooks in his early years in Geneva. Those he studied first, the works of Lavoisier and Berthollet, were written before Dalton's atomic theory had been published.

22. Berzelius had supervised publication of his Essai sur la théorie des proportions chimiques in Paris and undoubtedly took copies of the work with him to Geneva when he visited friends there on the way back to Sweden in the summer of 1819.

> accepted by chemists for the same molecule would give its volume." (23)

Since there was no way to find the density of a single integrant molecule, Dumas had to assume that in the solid state all atoms were touching one another, that there were no spaces between them, so that the density of an integrant molecule was the same as the density of a large mass of the substance (24). As he noted: "nearly every well-known _physicien_ had studied the density of substances" (25), yet no one had found a simple relationship among the values that had been obtained for the many elements and compounds known. Nor had one been found to relate atomic weights. He hoped that the atomic volumes of elements and compounds would provide data which would make a natural classification of these substances possible.

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23. _J. Phys._, _92_ (1821), 401-02. For a brief discussion of this paper see T. M. Cole, Jr., "Early Atomic Speculations of Marc Antoine Gaudin: Avogadro's Hypothesis and the Periodic System", _Isis_, _66_ (1975), 334-60 (335). Since this was Dumas' first venture into particle studies, understanding his use of the terminology involved is essential. A close study shows that Dumas used the term _integrant molecule_, or simply _molecule_, only to describe the ultimate particle of an element or compound (he used the term particle once in this sense), while the term _atom_ referred to a large number of such molecules, namely the weight in grams equal to the atomic weight given by Berzelius (O=100). For example, one atom of oxygen weighed 100 grams, so one atom of copper would have weighed 791.39 grams. The volume of this weight was the atomic volume and the unit of volume used (e.g., millilitres) in determining the density became the unit of atomic volume. Thus the atomic volume of copper was 87.9 millilitres because the density of copper was 9 grams per millilitre. Throughout the article Dumas used a unit only once (it was a general practice not to use units in calculations), an experimental weight of 100 grams for sulphur, but he did base his results on the density of water as unity, therefore one gram per millilitre. Since he wanted to apply the numerical values to both atoms and integrant molecules, avoiding the use of units was useful.

24. In his words: "... plusieurs molécules juxta-posées de manière à n'offrir aucun interstice probable entre elles." _Loc.cit.(4-23)_, 402. Though Dumas used the term, absolute atomic densities could not be determined precisely without knowing how the "molecules" were packed, but acceptable relative densities could have been obtained for the elements as long as the spheres were touching. Dumas was aware of the large decrease in density resulting when water solidified, but apparently did not see this as a problem.

25. _Ibid._, 401.

Working alone at first, then with Le Royer (26), Dumas sought to obtain greater precision in density determinations (27). He studied twenty elements and seventeen compounds. By making small adjustments he was able to show that the atomic volumes of the compounds were almost all small, whole-number multiples of the value for ice. The volumes for the elements were seen to be even-number multiples of the value for a hypothetical element, suggesting to him that they could be arranged in an arithmetic series. Thus both seemed to have predictive value. Unfortunately, he was hampered by errors in the weights given by Berzelius and by insufficient information (28).

By the time the first volume of Dumas' Traité appeared in 1828, Berzelius had corrected many of his atomic weights on the basis of the specific heats of Dulong and Petit and the theory of isomorphism advanced by Mitscherlich (29). Dumas altered his atomic volumes accordingly and added some new values. He also changed the emphasis in his interpretation

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26. See Chapter 1, pp. 29-31 and 42.

27. Standard methods were used (either hydrostatic weighing or liquid displacement), but great care was taken to purify the samples and to remove air trapped when they were placed in the liquid, thus obviating the two greatest sources of error.

28. Many of the atomic weights listed by Berzelius in 1819 were higher than currently accepted values by a factor of two. Dumas limited his choice of compounds to oxides and their compounds with each other. His choice was qualitatively excellent, but weak quantitatively. His data for the elements, which could have been useful, suffered both ways. He was unable to include data for light metals and non-metals whose volumes in the solid state were considerably higher and might have suggested that he organise the results in a different manner.

29. Isomorphism exists where elements can replace other elements in a crystalline substance with no significant change in the crystalline form. Though Mitscherlich read a paper on the topic in 1819, his more important article did not appear until 1822, well after Dumas had published his article with Le Royer.

to groups of elements having approximately the same atomic volume, using isomorphism as a guide. There were a few exceptions, but this was a minor problem compared to the conceptual difficulty that Berzelius had raised in his criticism of the 1821 memoir on atomic volumes (30). Since all 'molecules' of the same element carried the same electrical charge, mutual repulsion made contact impossible and spaces must exist in a sample of an element. This was supported by the fact that different elements expand differently when heated. As for compounds, different crystalline forms suggest the existence of spaces that could not be compared. Since Dumas had accepted Berzelius' electro-chemical theory, he was obliged to lay aside any interpretation of his observations on atomic volumes for the time. As he wrote:

> "Certainly the molecules of substances do not touch; consequently the density of a solid is never absolute and does not in any way represent the true density of the molecules that constitute it, but only the average density of the solid molecules and the empty space left between them." (31)

Polydore Boullay, who had assisted Dumas in other work to be discussed later, chose to be satisfied with this average density in carrying out one of the two thesis investigations required to obtain the degree Doctor ès Sciences (32). Using these values, he found that the atomic volumes

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30. Jahres-Bericht über die Fortschritte der physischen Wissenschaften, 2 (1823), 40-41. Reference given in Cole, op.cit.(4-23), 336.

31. Traité, Vol. 1, pp. xlvii-xlvii.

32. Boullay, Polydore, Dissertation sur le volume des atomes et sur les modifications qu'il subit dans les combinaisons chimiques, Paris, s.d. (Submitted 20 February 1830). Because of his experience with atomic volumes Dumas was eminently qualified to direct Boullay, son of the pharmacist P. F. G. Boullay, and Polydore may be regarded as Dumas' first research student. Certainly the general theme of his research came from Dumas, either personally or through his Traité, since no one else had been following this line of investigation. Polydore's work was discussed briefly in Cole, op.cit.(4-23), 336-37.

of elements changed when they combined, some contracting, others expanding. Suspecting a relationship between atomic volumes and cohesion, he listed the elements as Dumas had done in 1821 from smallest atomic volume (carbon) to largest (sodium and potassium) (33) and found a parallel in hardness. With some variations, he grouped them as Dumas had in the Traité.

Boullay was not the only student of Dumas who investigated relationships between atomic volumes and the properties of the elements. In 1827 Dumas began giving a course in chemical philosophy at the Collège de France (34). Fully aware of his capabilities and interests, Thenard gave him a free hand in these lectures. Among the students who attended his initial course in the second semester of 1826-1827 should be included Marc Antoine Augustin Gaudin (1804-1880) (35) who suggested a new way of considering atomic volumes and used it to support a hypothesis that became a cornerstone of chemical thought in other hands (36). Because there had been a subtle shift in emphasis from the particles of which elements were composed to the spaces between them, Gaudin attempted to re-establish the original perspective by introducing a new term, what he called 'atomic number', to denote a relative value representing the number of

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33. Boullay was the first to refer to the values for sodium and potassium.

34. See Chapter 3, p.123.

35. Gaudin indicated that he had been a student of Dumas in his memoir: "Recherches sur la Structure intime des Corps inorganiques définis", Ann. Chim. Phys., 52 (1833), 113-33 (115). Since he had attended Ampère's lectures at the Collège de France at about the same time, it seems quite proper to assume that he attended Dumas' lectures there, rather than at the Athénée.

36. Since Cole, loc.cit.(4-23), has studied Gaudin's work in some detail, my discussion will be brief. Furthermore, Gaudin's thought has entered the mainstream of scientific development rather slowly, and only through the efforts of others. The reasons for this are outside the scope of my thesis.

atoms (37) contained in a fixed volume of the element. This he obtained from the formula 10,000Δ/P where Δ was the density of the element compared to that of water, and P its atomic weight (38). Though one of his efforts to find a relationship between 'atomic numbers' and the properties of elements seemed useful at first sight, it was not as valuable as he believed it would be (39). The other was far more general, indeed it was the first attempt to identify periodicity as a general characteristic of

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37. Gaudin, M. A., "Note sur quelques Propriétés des Atomes", Bibl. Univ., Science et Arts, 52 (1833), 127-41. Cole, loc.cit.(4-23), 345, has discussed the fate of this article, received on 7 November 1831 by the Academy of Sciences in Paris. Gaudin limited his use of the term atom to mean an ultimate particle. His use of the term 'atomic number' has no relationship whatsoever to its modern use.

38. This formula is the inverse of the one devised by Dumas to find atomic volume. Gaudin used the factor 10,000 to convert decimals to integers. Since atomic volume was the volume of a particle or group of particles, inverting it gave the number of particles in a fixed volume. Because densities were referred to water (grams/millilitre) and atomic weights could be expressed in grams/particle, 'atomic numbers' represented the number of particles in a millilitre. Thus any problem connected with Dumas' system was also part of Gaudin's. Because atomic volumes could not be determined absolutely, neither could 'atomic numbers'. Thus without knowing the distance between the particles, even the relative values could have been virtually meaningless. Gaudin did not bring out this point (nor did Cole).

39. There were several elements whose densities in the solid or liquid state were known whose atomic volumes Dumas had either avoided discussing altogether or did not mention after 1821. In examining three sets of elements whose properties were analogous within a set, Gaudin found 'atomic numbers' that were either the same or simple multiples of some value within the group: chlorine 60, bromine 63, iodine 64; phosphorus 90, arsenic 177 and antimony 83; sodium 33, potassium 17. The density he used for arsenic had already been corrected by Dumas in his Traité (from 8.3 (1821) to 5.75), and further correction gave a value close to that of other members of the group. The density of lithium was not known until after 1850 and when rubidium and cesium were discovered about the same time, determination of their atomic volumes showed that the only relation existing was an increase with weight which involved no special proportionality.

the elements. It was based on atomic weights and his 'atomic numbers' (40). After listing the elements vertically according to atomic weights (41), he drew lines at hydrogen and each of the halogens, noting that these were the elements whose particles had the greatest "mobility" (42). They were also elements whose 'atomic numbers' had a minimum value (i.e., their atomic volumes had a maximum value. Both the "mobilities" and the atomic volumes decreased to minima about half way between hydrogen and fluorine, fluorine and chlorine, etc. Gaudin used this chart to associate other properties of the elements with their atomic weights and 'numbers': colour, magnetic character, conductivity of heat and electricity and the refraction and polarisation of light. It was many years before chemists accepted this point of view, and Gaudin played almost no part in the developments that led eventually to the publication of a periodic table in 1869 by Dmitri Ivanovich Mendeléeff (1834-1907). In 1873 Gaudin summarised his lifetime of research on the structure of matter in a publication which included the following aknowledgement: "I must point out that I have received valuable words of encouragement in France; M. Dumas has never refrained from spurring me on ..." (43). Certainly it was Dumas who initiated the

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40. Elements had been grouped by analogies by others, among them Dumas whose Traité was organised on the basis of such groups, but no one had tried to group all of the elements to show a periodic recurrence of properties according to weight.

41. Cole, loc.cit.(4-23), 355, claimed that Gaudin was the first to do so, anticipating John Hall Gladstone (1827-1902) whom Partington, op.cit. (2-17), p.885, suggests was the first to do so.

42. Gaudin used this phrase to describe substances that were "gaseous, in the form of vapour, liquid, volatile or very fusible." Quoted by Cole, loc.cit.(4-23), 353.

43. Gaudin, M. A., L'Architecture du Monde des Atomes, Paris, 1873, p.215. In 1873 the work was of more value historically than scientifically.

work on atomic volumes that became an integral part of Gaudin's thought (44) and Dumas maintained his interest in research done on the topic.

Vapour Densities, Atomic Weights and Chemical Equations. In 1821 Dumas believed that his studies on the structure of solids would be more useful than gas density measurements in determining atomic weights and classifying the elements (45). By that time his analysis of urea had shown him that percentage composition could be found by determining gas densities. The value of this approach became even more evident during his investigation of plant alkalis with Pelletier. As early as 1822 he had found that the volumes of carbonic acid gas and nitrogen gas measured in the normal analyses of nitrogen-containing organic compounds could be used

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44. In 1840 Hermann Franz Moritz Kopp (1817-1892) wrote an article concerned with the topic, "Thoughts on Atomic Volume, Isomorphism and Specific Gravity", Ann. Chim. Phys., 75 (1840), 406-36, without acknowledging Dumas' earlier work. Boussingault, who had just become an editor of the journal, added the following note: "The first thoughts on atomic volumes were due to M. Dumas, who published them 20 years ago in the Journal de Physique. These ideas, reproduced in the first volume of his Traité de Chimie appliquée aux arts, were also developed in the 'Chemical Philosophy' section at the end of the last edition of Thenard's Chemistry ..." Ibid., 435. Boussingault referred to Thenard, L.J., Traité de Chimie élémentaire, théorique et pratique, Paris, 6e Ed. (1836), Vol. 5, pp. 409-519 (435-36). The importance of comparing solid densities near the point of fusion, and liquid densities at the boiling point was mentioned. This essay had not appeared in any of the previous five editions of Thenard's work. Grimaux has said: "M. Wurtz told me that this part of Thenard's Traité de Chimie was due entirely to Bineau." C. Gerhardt, Junr. and E. Grimaux, Charles Gerhardt, sa Vie, son Oeuvre, sa Correspondance, Paris, 1900. This is possible. Bineau was preparing his notes of Dumas 1836 lectures for publication at the time. It would also explain the frequent appearance of Dumas' name in Thenard's essay.

45. Relatively few gases were known. In his memoir with Le Royer Dumas noted that Gay-Lussac's research on combining volumes was unrelated to his own. Moreover, Gay-Lussac "had tested a few cases to establish the concepts, but apparently had given up speculating on them, or at least had not followed them up since his initial work on the topic was published in the Mémoires de la Société d'Arcueil." J.Phys., 92 (1821), 411.

for more than simply calculating the percentage of carbon and nitrogen present. In August of that year he had detected a small but measurable quantity of nitrogen in narcotine (46), and soon afterward in other plant alkalis. It seemed probable that the alkalinity of these compounds was due to their nitrogen content since alkalinity could be associated with nitrogen as well as with oxygen. Examination of carbon to nitrogen weight ratios revealed no simple relationship, but comparing the carbonic acid and nitrogen produced during analysis led him to say: "These volume relationships are remarkable by their simplicity, even though the carbon and nitrogen are represented by very different absolute quantities." (47) Dumas had observed this in August and very quickly arrived at the conclusion that the elemental composition of the compounds could be given not only in terms of percentages but also in terms of the number of atoms of each element contained in the compound (48). On 5 May 1823, eight months

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46. Notebook A. (See Chapter 3, note ~~240~~ 10).

47. Ann. Chim. Phys., 24 (1823), 189 (my italics). The values have been reproduced by Kapoor, op.cit.(1-101), 30.

48. In Notebook A Dumas gave the following set of figures which show clearly how he made this change. The information has been put in tabular form for convenience:

	1	2	3	4	5	6	7
carbon	55.57	3/4	945	10	764.36	68.54	69.48
nitrogen	5.82	1/15	84	1	88.518	7.93	7.27
hydrogen	4.10	2/3	840	10	62.44	5.60	5.12
oxygen	14.51	1/7	180	2	200.00	17.93	18.13
	80.00				1115.318	100.00	100.00

He used a sample of narcotine weighing 80.00 centigrams, from which he obtained the weights of each element present (col. 1). These he divided by the respective atomic weights (carbon - 76.436; nitrogen - 88.518; hydrogen - 6.244; oxygen - 100.000), rounding off the fraction to obtain the relative number of atoms (col. 2) which he converted into whole numbers (col. 3) by multiplying by the common denominator 1260. These numbers he then reduced to smaller integers (col. 4) which he changed into total atomic weights (col. 5). From these values he calculated the theoretical percentage composition of a compound containing the number of atoms of the various elements shown in col. 4, and verified this composition by comparison with the percentage composition (col. 7) obtained from the experimentally determined weights (col. 1).

later, Pelletier read their memoir to the Academy of Sciences. In it they gave the number of atoms of each element contained in nine plant alkalis (49). Despite a cautious statement included about the value of such considerations (50), it must be said that a certain boldness was necessary to publish compositions like that for strychnine (carbon - 60 atoms (51); nitrogen - 3 atoms; hydrogen - 30 atoms; oxygen - 2 atoms), at a time when the atomic theory was far from being generally accepted.

Long before undertaking the research with Pelletier Dumas had adopted many of the ideas that Berzelius had put forward in his Essai. In 1823 the Swedish chemist had observed that the atomic volumes of solids could not be usefully compared because all the atoms of the same element or compound had the same charge, thus the atoms could not be in contact because they repelled one another. While this seemed to create difficulties for his theory that elements and compounds could be classified on the basis of their solid atomic volumes, Dumas was now led to consider that gas densities might be the key to a natural classification of the elements. He may have begun experiments that year, but if the events of late 1823 and early 1824 (52) are taken into account, it is more likely that he waited until the summer. In the meantime, as répétiteur at the Ecole

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49. Ann. Chim. Phys., 24 (1823), 163-91 (191). They also gave the percentage composition. Kapoor, op.cit.(1-101), 31, has listed the alkalis and their composition in terms of numbers of atoms.

50. "We think that these calculations will offer some advantage as a means for comparison, and we only present them from that point of view, persuaded that it would be premature to attach too much importance to this kind of consideration." Ann. Chim. Phys., 24 (1823), 189.

51. For the atomic weight of carbon Dumas used 37.66 (O=100) following Gay-Lussac as did most of the French chemists, whereas he had used 75.31 during his work in Geneva. This may have been because Gay-Lussac was an editor of the journal.

52. See Chapters 2 and 3.

Polytechnique he was obliged to master Gay-Lussac's techniques for determining gas and vapour (53) densities by collection over mercury. The limitations of this procedure led him to devise a new method that summer in which a known volume of vapour was weighed (54). By 1825 he had perfected the apparatus involved and had begun making measurements that led to the publication of several journal articles in 1826, culminating in his "Memoir on Some Points Concerning Atomic Theory" (55), one of Dumas' most important publications. In it he described his procedure:

> "After several attempts I arrived at the following method. I am sure that it will become quite standard in laboratories because of its simplicity and its applicability to all substances that will boil at a temperature below the melting point of glass.
>
> In general, it consists in filling a glass bulb of known capacity with the vapour to be studied, at atmospheric pressure and a predetermined temperature, necessarily higher than the boiling point of the substance. These conditions are obtained by placing an excess of the substance in a bulb with a tapered neck and raising the temperature to a suitable level. At the conclusion of the experiment the mouth of the bulb is closed by means of a blowpipe. The temperature of the bulb and the atmospheric pressure are observed; both the weight and volume of the substance remaining in the container are determined. These values are sufficient to make the calculation of the density possible." (56)

The temperature was stabilised by immersing the bulb in a suitable bath: water, sulphuric acid or a fusible metal alloy, depending on the

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53. The term vapour was and is used to describe a substance in the gaseous state that is a solid or liquid at room temperature.

54. Gay-Lussac's method involved finding the volume of a given vapour whose weight had been measured in the solid or liquid state. The procedure was described by Biot, op.cit. (1-69), pp. 291-99.

55. "Mémoire sur quelques points de la théorie atomistique", Ann. Chim. Phys., 33 (1826) 337-91. It was read before the Academy of Sciences on 9 October 1826. In this chapter it will be referred to as the October Memoir (Oct. Mem. in footnotes).

56. Ibid., 341-42.

temperature desired. To test the precision of his apparatus, Dumas determined the vapour density of iodine which had been found in two ways by Gay-Lussac: From the vapour density of hydrogen iodide (8.7879) and from the atomic weight of iodine (8.6118). Dumas' calculation from direct measurement of weight and volume was 8.716 (57), and he could conclude that the method was satisfactory.

An understanding of the problems that arose almost immediately, requires a knowledge of the relationship between vapour densities and atomic weights. Long before Dumas' time two internally consistent systems (density and specific gravity) had been devised to link two basic properties of all substances, weight and volume. Density was based on defined units (weight in grams and volume in millilitres) while specific gravity involved comparing the densities of all compounds to that for a reference compound. When the density of water at 4° Centigrade became 1.0000 grams per millilitre because those two units had been defined in terms of the properties of water, the specific gravity of mercury became 13.6, because one millilitre of mercury weighed 13.6 grams (i.e., mercury was 13.6 times as dense as water). Comparing solids and liquids to the density of liquid water was convenient, but it was more convenient for several reasons to compare the density of gases to air. But air could not be given a unit density, as water had been, without assigning new units of weight and volume. Thus the system of specific gravity for gases was complicated slightly because it was necessary to find the absolute density of air (0.0012991 grams per millilitre or 1.2991 grams per litre). The absolute

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57. The atomic weights were, respectively, 127.5, 125.0 and 126.5 (O=16). In 1832 Dumas was able to say: "New experiments done by M. Berzelius have confirmed my determination, correcting the atomic weight accepted earlier for this substance." Ann. Chim. Phys., 50 (1832), 172. The modern value is 126.9.

density of oxygen was 1.4324 grams per litre. The specific gravity of oxygen on an air standard, then, was 1.1026 (58). Frequently the term vapour density was used for the latter value, causing some confusion. Fortunately Dumas, by reporting both the weight of a litre of vapour and its vapour density (i.e., specific gravity), forestalled possible errors of interpretation (59).

The concept of vapour density had taken on new significance when Gay-Lussac discovered that gases combine in small whole-number ratios by volume. Very quickly Avogadro had realised how this law could be integrated with Dalton's atomic hypothesis (60). He made three simplifying assumptions:

1. The molecules constituting gases are far apart relative to their size and thus essentially independent of one another.

2. In equal volumes of gases (at the same temperature and pressure) there are an equal number of molecules. It was this concept that became known as Avogadro's hypothesis.

3. The molecules of gaseous elements must be divisible. While he had indicated that in all the elements he had studied "the molecules must be divided into two parts", he had added "but it is possible that in other

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58. Dumas used the specific gravity values determined by Berzelius and Dulong, Ann. Chim. Phys., 15 (1820), 386-95. A table of values was given, ibid., 395, in which they were called densities erroneously. They were the latest of several such determinations. Dumas and Boussingault gave an improved figure for oxygen twenty years later, 1.1057. Ibid., 3 (1841), 257.

59. The term vapour density will always be used in this thesis in the same sense as specific gravity, unless otherwise indicated.

60. Avogadro, A., "Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps ...", J. Phys., 73 (1811), 58-76. "Basically our hypothesis is only Dalton's system strengthened by a new means of precision, the link we have found with the general fact established by M. Gay-Lussac." Ibid., 76.

cases division could be into four parts, eight, etc." (61)

In these principles were to be found a means for calculating a relative set of atomic weights. For if equal volumes of gases contained equal numbers of molecules, then the weights of those molecules were in the same ratio as the weights of the volumes indicated. That is to say, the weights of the molecules were directly proportional to the vapour densities (62) which could be easily obtained using the methods devised by Gay-Lussac and Dumas. The crux of the method, however, lay in the third principle. As long as the molecules of all gases contained the same number of ultimate particles (Avogadro's "integrant molecules"), the real number of these was unimportant, although it had to be an even number to satisfy the law of combining volumes. But if even one element contained a different number, then the number in every elemental gas or vapour had to be known to be able to establish an internally consistent set of atomic weights by this method, which is precisely what Dumas set out to do:

> "I resolved to perform a series of experiments to obtain the atomic weights of a large number of substances from their density in the gaseous or vapour state. In that case there will be only one hypothesis to make, and all physicists agree on it. It consists in supposing that in all elastic fluids at the same conditions, molecules are placed at equal distances from one another, that is, the same number are present." (63)

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61. Ibid., 61. Avogadro did not mean to exclude the possibility that a molecule of hydrogen or oxygen could be divided into four or eight parts, only that division into two was sufficient. Ampère's three dimensional particles all consisted of at least four molecules. Ann. Chim. Phys., 90 (1814), 43-86 (45).

62. For O=100, atomic weight/100 = vapour density/1.1026 (i.e., v.d.= 0.01026 x a.w., or a.w. = 90.694 x v.d. It must be remembered that the vapour density indicated is based on that of air, not on the weight of a litre of the gas.

63. Ann. Chim. Phys., 33 (1826), 337-38 (my italics). Dumas went on to say that no chemist had accepted the practical consequences of this, not even Gay-Lussac: "... mais il ne paraît avoir encore été admis dans la pratique par aucun chimiste, si ce n'est par M. Gay-Lussac." Ibid.

This point has not been emphasised sufficiently in discussions surrounding the acceptance of Avogadro's hypothesis. I believe that Dumas fully appreciated the problem, and that it was precisely for this reason that he did everything in his power to integrate any apparent exception. While he admitted that he could not specify how many ultimate particles there were in the molecule of an element (64), in practice he assumed that all molecules were divisible into two equal parts, the simplest assumption allowable by Avogadro's hypothesis.

When Dumas began his research in 1825, he expected that he would be making a number of routine measurements to give greater precision to the atomic weights listed by others (65). Almost immediately an anomaly appeared. The weight he obtained for mercury was $\frac{1}{4}$ of the value assigned to it by Berzelius, and remained anomalous even though the Swedish chemist halved his value the following year (66). The result for sulphur was so bizarre that he avoided publishing it for over six years while he studied the element more fully. Of greater interest to my thesis was his struggle with the weight of phosphorus (and hence with its analogue, arsenic). It will be used as the framework for a presentation of the problems associated with Dumas' use of vapour densities as a means of determining atomic weights.

In 1814 Berzelius had assigned an atomic weight of 167.5 to elemental phosphorus, but after a careful analysis of its oxides he revised

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64. Ann. Chim. Phys., 33 (1826), 338.

65. "At the time when I devised a simple, exact and convenient procedure for obtaining any vapour density, I thought more of applying it to elements as a means of verification than as a method for discovering new properties." Ibid., 50 (1832), 172.

66. As late as 1832 Dumas still hoped that his value would be accepted, because mercury was so different physically and chemically from any other metal. Ibid., 172-73.

his figure drastically four years later to 392.3 (67). Dumas tried to verify this value by direct vapour density determinations but in spite of many attempts, success had eluded him because of the difficulties involved. In the meantime, he found the vapour densities of two hydrides of the element which he used to obtain its atomic weight indirectly. Secure in the belief that the results were satisfactory, he decided not to wait for direct data, and on 9 January 1826 he read a long paper to the Academy of Sciences on the topic (68). After giving additional evidence in favour of a 5 to 3 ratio for the oxygen in the two acids of phosphorus (69), he concentrated on the hydrides (70).

Gay-Lussac had shown in 1815 that the oxidation of one volume of prussic acid yielded one half-volume each of nitrogen and water and one volume of carbonic acid (71). To be able to express the composition of the acid in volumes required only one assumption: that one volume of carbonic acid was formed from one volume of carbon vapour. Since carbon had

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67. Berzelius gave the two acids the formulas PO_3 and PO_5 which showed half as much phosphorus as the modern formulas.

68. "Mémoire sur les combinaisons du phosphore, et particulièrement sur celles de ce corps avec l'hydrogène", Ann. Chim. Phys., 31 (1826), 113-54. In this chapter it will be referred to as the January memoir (Jan. mem. in footnotes).

69. Thomson and Sir Humphry Davy (1778-1829) had proposed a 2 to 1 ratio, while Berzelius and Dulong had favoured 5 to 3.

70. The two hydrides were easily distinguishable because only one of them burned spontaneously in contact with air. Dumas had learned of this in Geneva when he assisted Le Royer in the recovery of alcohol contaminated by Museum specimens that had been kept in it for some time. The flaming gas had been given off from a syrupy residue formed during distillation with calcium chloride. Dumas commented on the presence of relatively large amounts of phosphorus in brain matter. Traité, Vol. 1, pp. 266-67.

71. Ann. Chim. Phys., 95 (1815) 136-231. The modern equation is:

$$HCN + 5/2\ CuO = CO_2 + \tfrac{1}{2} N_2 + \tfrac{1}{2} H_2O + 5/2\ Cu$$

never been vapourised, Gay-Lussac calculated its vapour density indirectly (72) and found that adding it to half the vapour densities of nitrogen and hydrogen gave a value that was within one percent of that determined directly for prussic acid. Thus it appeared that the calculated vapour density for carbon was its real value, and Gay-Lussac could say: "It seems evident to me that prussic acid is composed of 1 volume of carbon vapour, ½ volume of hydrogen and ½ volume of nitrogen condensed into one." (73). Since it could be shown from Avogadro's hypothesis that vapour densities were proportional to atomic weights, the resulting equivalence of volumes and atoms allowed rewriting this statement: one atom of carbon and one demi-atom each of nitrogen and water were condensed into one of prussic acid. But this required that the atomic weight of carbon be 6 rather than the weight that had been assigned by Berzelius, 12. Thus the Swedish chemist who had begun with a lively interest in the volume theory gradually turned away from it.

But Dumas accepted, with all its consequences, the principle that Berzelius had rejected, and prepared for the criticism that would surely follow. In the October memoir he state unequivocally:

> "In the system adopted by Berzelius, for the formation of compounds a general plan has been followed which consists in representing their atoms as though they were formed from simple atoms combined, always in whole numbers. Thus in this system, water results from two atoms of hydrogen and one atom of oxygen, hydrochloric acid gas from one atom of chlorine and one atom of hydrogen, while to be consistent with the ideas put forward on the constitution of gases it is necessary to represent water by one atom of hydrogen and a half-atom of oxygen, hydrochloric acid gas by a half-atom of chlorine and a half-atom of hydrogen.

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72. Given the values for the vapour density of oxygen and carbonic acid, he was able to calculate the vapour density of carbon (0.4160) from the equation carbon + oxygen = carbonic acid.

73. Ibid., 155.

The formula of a compound must always represent what enters into one volume of that substance taken in the gaseous state." (74)

There is some question whether his commitment had been complete in January. He had found that both hydrides of phosphorus contained 1½ volumes of hydrogen and had also measured their vapour densities. From this information he had been able to find the weight of phosphorus used. The values may be summarised as follows:

	Hydride A	Hydride B
Weight of 1 litre of the gas	1.761	1.214
Weight of 1½ litres of hydrogen	0.103	0.103
Weight of phosphorus	1.658	1.111

The atomic weight of phosphorus could then be obtained by means of a proportion involving the weights of phosphorus and hydrogen. Because Dumas was only interested at this time in showing that his method could be used validly to obtain a value that was in accord with one established by other means, he treated his data in a somewhat different way from the manner in which it would normally be used. He assumed that the 'order' of the weight given by Berzelius was correct and from this approximated the ratio of P:H atoms in the two compounds which turned out to be 1:4 for hydride A and 1:6 for hydride B. He then calculated the exact values for 4 and 6 atoms of hydrogen respectively and put these (24.87 and 37.40) back into the algebraic equation to obtain the atomic weight found by his method:

Hydride A: $\frac{1.658}{0.103} = \frac{a.w.}{24.87}$; Hydride B: $\frac{1.111}{0.103} = \frac{a.w.}{37.40}$

74. Oct. mem., 339 (my italics).

The values obtained were 400.33 and 402.3 (75), which allowed Dumas to write about hydride B: "This gas contains 1½ volumes of hydrogen and is composed of 6 atoms of hydrogen and 1 atom of phosphorus." (76) This is a surprising statement since it asserted that one volume of hydrogen contained four atoms. On the other hand, until he had more data, it was better to show agreement with the weight assigned by Berzelius, for whom he had great respect.

By October he had collected enough data to challenge not only the atomic weight of phosphorus but those of several other elements (77). In his memoir he wrote:

> "In considering <u>hydrogène proto-phosphoré</u> (phosphine) as a compound of 3 volumes of hydrogen and 1 volume of phosphorus vapour condensed into 2, one finds:
>
> 1.213 x 2 = 2.426 = 2 vol. phosphine
> 0.0687 x 3 = 0.2061 = 3 vol. hydrogen
> 2.2199 density of phosphorus vapour" (78)

from which he was able to obtain an atomic weight of 201.3 (though he rounded this off to 200). This he verified by drawing upon the vapour density of the <u>proto-chlorure de phosphore</u> (phosphorus trichloride) whose density he found to be 4.8750:

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75. <u>Jan. mem.</u>, 151. Dumas' density values were all referred to air, i.e., specific gravities. Thus 0.103 = 1½ x 0.0687, the specific gravity of hydrogen. He used 6.22 and 6.23 respectively for the atomic weight of hydrogen and his arithmetic was not perfect, although it improved over the years as will become evident. His weights were a little high compared to that of Berzelius (392.3). He noted: "For a long time I have examined the experiments of M. Berzelius and my own; I have tried to locate the source of error in both methods and I must say I remain uncertain." He decided to defer to the older chemist. <u>Ibid</u>.

76. <u>Ibid.</u>, 153.

77. Arsenic, mercury, silicon, boron, tin, titanium.

78. <u>Oct. mem.</u>, 353-54.

"But we know without doubt that the proto-chlorure de phosphore is formed from 3 volumes of chlorine and 1 volume of phosphorus vapour; therefore:

$$\begin{array}{llll} 2.470 \times 3 & = & 7.410 & = 3 \text{ vol. chlorine} \\ & & \underline{2.2052} & = 1 \text{ vol. phosphorus} \quad [P = 200] \\ & & \dfrac{9.6152}{2} & = 4.8076 \end{array}$$

That is to say, 3 volumes of chlorine, 1 volume of phosphorus condensed into 2 volumes." (79)

It was a tidy picture and seemed to be substantiated when Berzelius reduced his own figure for phosphorus to 196.155 while preparing a revised version of this textbook the same year (80). In the October memoir Dumas made the change in weight of phosphorus without mention of his previous paper. Indeed it was not until he had completed his perfectly analogous analyses of the hydride of arsenic (arsine) and the halides of arsenic that he was sure that he could safely reduce the combining ratios, simplify the relationships and, most important, maintain an internally consistent system by halving the atomic weight. Thus it was unimportant that 1 atom of arsenic might theoretically be able to react with 6 of hydrogen to form 4 of arsine; but it was necessary that 1 atom be able to react with 3 to form 2 (81). After carefully describing how he could obtain Berzelius' atomic

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79. Ibid., 354

80. The new German edition was published 1825-31. He completely revised the section on atomic theory and published it as Part 1 of Volume 3 (1827). Only his new table of atomic weights of the elements and their oxides was published in France (Ann. Chim. Phys., 38 (1828), 426-32) in which he introduced his barred symbols for double atomic weights and dots representing oxygen atoms (e.g., water became $\dot{\overline{\mathrm{H}}}$). He took into account specific heats and isomorphism in recalculating atomic weights, but it is not unlikely that he liked the analogies used by Dumas and halved his own atomic weight, as a consequence, for phosphorus and arsenic. He reduced mercury by $\frac{1}{2}$ not $\frac{1}{4}$ for other reasons, but did not change the others.

81. To use modern terminology, arsenic could theoretically be tetratomic but it could not be less than diatomic, and had to be diatomic for his system to be consistent.

weight by examining the volume relationships involved in forming a substance having the formula AsH^6 (82), he showed that much simpler volume ratios were equally possible and exactly the same as in existing reactions of hydrogen with phosphorus to form phosphine and with nitrogen to form ammonia. He said:

> "In the formula AsH^6, 1 vol. of arsenic vapour and 6 vol. of hydrogen condense into four, a result which is not very compatible with the usual simplicity of gaseous combinations and condensations. Therefore it is better to divide the atom of arsenic given by M. Berzelius by two, and to represent the gas arsine by AsH^3. In that event, 3 vol. of hydrogen and 1 vol. of arsenic condense into 2, a situation absolutely similar to that in which phosphine is formed." (83)

Thus to oxygen, hydrogen, nitrogen, carbon and the halogens could be added phosphorus and arsenic, all apparently having the same type of fundamental particle, divisible into two on combination. There were still no exceptions.

When he wrote the first volume of his Traité Dumas took full advantage of this fact and made an important change in his approach. Before its effect can be appreciated, a cardinal point must be understood concerning the role of oxygen as a standard for atomic weights (84) and it is best to use modern terminology for this. Because the notion of atoms as ultimate chemical particles is now accepted, it is also recognised that oxygen gas consists of diatomic molecules. But whenever the gas reacts,

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82. From 1826 Dumas normally used formulas in his articles. For a time he was the exception rather than the rule in this regard. He obtained 940.24 for the atomic weight of arsenic. He pointed out that Berzelius had made an error in arithmetic in giving 940.77, that the value should have been 940.23 using Berzelius' figures.

83. Oct. mem., 359.

84. Berzelius chose oxygen as a reference element for his table of weights because it formed one or more binary compounds with almost every known element.

these molecules divide and the resulting atoms unite with atoms of the reacting element. In his determination of atomic weights Berzelius had no reason to be concerned with oxygen gas (i.e. oxygen molecules) since his measurements were made on compounds that contained oxygen atoms. Since the law of combining volumes was derived from chemical reactions, attention was focused on this aspect of chemistry. Numerical relationships between the molecules of elements and compounds that were used and produced in a reaction added another quantitative dimension to the established concept that molecules were composed of set numbers of atoms. Although there were not many reactions in which all of the components were in the gaseous state, there were a surprising number in which gases were used or produced along with substances that were in the other states. Had all elemental gases been monatomic there would have been no problem. That they were not was evident from the law. While Berzelius was able to refer all weights to O=100, it was to monatomic oxygen. When the weight of a volume of gas was involved, it could only be compared to diatomic oxygen (O=200). No one understood this at the time.

When Dumas began his work, no anomalies had been recognised among the substances that entered into reactions as gases. Indeed even though it was not a gas, carbon had been added to the list of 'diatomic' elements despite the difference of opinion created concerning its atomic weight. In his January memoir Dumas wrote that one atom of phosphorus had united with 6 of hydrogen to form 4 of phosphine, which would have introduced an anomaly, as has been shown. In the October memoir he amended the equation. By this time he was writing the first volume of his textbook and he had decided to make atoms its framework. This included equations for hundreds of reactions (85). There were several reasons for not writing these in terms of volumes:

1. Many reactions involved compounds that were not gases or whose vapour densities were unknown, so that he could not reasonably present them in that manner.

2. Using volumes only where those known appeared could cause inconsistency, confusion and perhaps even error.

3. His textbook was intended for manufacturers or those intending to pursue that career. Their interest was in weight relationships for the most part, not volumes, even where gases were concerned.

In his Traité, he changed all volumes to atoms.

Equations were used in the first chapter where he discussed the chemistry of hydrogen (86). After describing its preparation he wrote: "By means of the atomic theory the numerical relationship between the materials used and the products can be established in the following manner ... (87)". The context leaves no doubt about the practical rather than theoretical interpretation of the term atom that he expects from his readers. He is referring to parcels of weight rather than ultimate particles.

Dumas' equation for the preparation of phosphine will give an insight into the manner in which he wrote them at this time and also into

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85. There were 119 equations in the first volume alone! The first book was divided into chapters devoted to non-metallic elements and their non-metallic compounds. To avoid repetition only the compounds of the elements that had been previously considered were discussed and these were mostly binary. The numbers in each chapter were: H - 2; O - 6; Cl - 5; Br - 2; I - 5; F - 3; S - 13; Se - 7; P - 11; N - 13; As - 12; B - 6; Si - 6; C - 28.

86. Traité, Vol. 1, p.5. The text proper was preceded by a long discussion of chemical theory. Ibid., pp. i-lxxx.

87. Ibid., p.5.

the problem that he created by doing so:

"Atoms Used		Atoms Produced	
4 at. phosphorous acid	2769.20	3 at. phosphoric acid	2676.90
6 at. water	337.46	4 at. phosphine	429.76
	3106.66		3106.66" (88)

While they do not seem to be equations in the modern sense of the term at first sight, they give the same information. Even the constitution of the compounds can be deduced from the data. An atom of phosphorous acid is 2769.20/4 or 692.30. In his atomic weight chart (89) he lists phosphorus as 196.15 and oxygen as 100 from which the only formula possible is P_2O_3. Similarly the formula for phosphoric acid must be P_2O_5. Turning to the water used, we find the weight to be 56.24 or one-half that to be expected given the weights of hydrogen and oxygen, but this problem can be resolved by examining a relevant passage in Dumas' discussion of the composition of water:

> "Recent experiments by MM. Berzelius and Dulong (90) have provided numbers for its composition which have been adopted by all chemists. According to them, it is formed from
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> | | | | |
> |---|---|---|---|
> | oxygen | 88.90 or | 100 | 1 atom of oxygen |
> | hydrogen | 11.10 or | 12.48 | 2 atoms of hydrogen |
> | water | 100 | 112.48 | 1 atom of water |
>
> ... M. Gay-Lussac determined the density of water vapour by his own procedure and found that this density, reduced by hypothesis to 0° and 0.76m to make it comparable to that of gases, was represented by 0.625. But in taking
>
> the density of hydrogen = 0.0687
> half the density of oxygen = 0.5513
> the density of water vapour = 0.6200
>
> which confirms the preceding data and in addition teaches us that the volume of water vapour is composed of a half-volume of oxygen and one volume of hydrogen, information

88. Ibid., p.262.

89. Ibid., pp. 1-li.

90. Loc.cit.(4-58).

which we will use constantly throughout this work." (91)

The importance of this declaration cannot be overestimated for it influenced the course of Dumas' thought and the direction which theoretical organic chemistry took for nearly half a century. Dumas had a very limited commitment to the atomic theory, despite the opening statement of his October memoir:

> "Since the creation of the atomic theory, the results deduced from this admirable concept have acquired new importance every day and have become the basis for all chemical research which needs some precision." (92)

He went on to point out that all of the various methods devised to establish an internally consistent set of atomic weights suffered from their limitations. On the other hand, he believed that the measurement of vapour densities would provide a uniform set of data by which weights could be assigned to all of the elements, thus doing away with these limitations. His hope rested on the knowledge that gaseous and volatile compounds of several metals existed (93) and the expectation that such compounds would be found for all the elements. It was this hope that led him to accept completely the consequences of the volume theory. It is important to see exactly what he rejected because of this. Dumas believed in the existence of ultimate particles. Particles were absolutely necessary for the volume theory and it was unthinkable that they could be composed of anything but other particles. But he believed that the latter were grouped <u>even in solids</u> and that all measurements of atomic weight had

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91. Traité, pp. 33-34 (my italics). This is the premise that he had accepted in the October memoir.

92. Oct. mem., 337.

93. He discussed those of silicon, boron, tin and titanium in the memoir, and was able to include in his Traité a volatile chloride of manganese that he had discovered. Ann. Chim. Phys., 36 (1827), 81.

been made on these groups. Thus he said:

> "The most immediate consequence [of Avogadro's hypothesis] consists in considering that molecules of elemental gases are susceptible of further division, division which is produced at the moment of combination and which varies according to the nature of the compound. Even though this consequence has not yet been generally accepted, it is impossible to avoid when one regards as true the preceding supposition on the constitution of gaseous substances. When the question is considered from this point of view, it soon becomes evident that the determination of true atoms (94) from gases or vapours offers insurmountable obstacles in the present state of the science. Indeed if the molecules (95) of an element, in passing into the gaseous state, <u>still remain grouped in a definite number</u>, we can easily compare these substances in the conditions in which they contain the same number of groups; but for the moment it is impossible to determine how many elementary molecules (96) exist in each of them." (97)

Dumas believed that the grouping in solids did continue in the gaseous state, because he used artificial vapour densities with the firm conviction that they could be compared with directly determined vapour densities in a meaningful way as Gay-Lussac had done with carbon. He had done this already in his January memoir where he had "determined" the atomic weight of phosphorus. In the October memoir he applied this principle to the revision of the atomic weights for phosphorus and several other elements. Once this was done, he was able to write the equations necessary to make quantitative information available in concise, intelligible form to those who would use the textbook to apply chemical principles to industrial processes.

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94. Read "atomic weights".

95. Dumas abridged Avogadro's term "constituent molecule", that is a group of atoms of the element.

96. Read "atom". Dumas' use of the phrase was the same as that of Avogadro, i.e., as an ultimate particle.

97. <u>Oct. mem.</u>, 338 (my italics).

No doubt he would have preferred using formulas in these equations rather than words. Apart from the fact that they would have been less intelligible to those who would use the book, he had not experimented sufficiently with this approach, nor had anyone else. He had written three of them in the October memoir (98) to clarify difficult points, but in his discussion of all three he had carefully avoided any reference to volume relationships. He had mentioned earlier in the memoir that "the formula for a compound must always represent what enters into one volume of that substance taken in the gaseous state" (99). When it came to writing a formula, however, problems with fractions arose. For example, it would have been necessary to write $HO^{\frac{1}{2}}$ as the formula for water (100). In two of the three equations mentioned water was involved. Perhaps to avoid criticism, he indicated that he was using "the notation of M. Berzelius" (101), which allowed him to write the formula for an atom of water ($\dot{H}2$) rather than a volume ($HO^{\frac{1}{2}}$). He continued to express the composition of water in atoms in his "Memoir on the Formation of Sulphuric

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98. Dumas referred to them as formulas. To avoid confusion the term equations will be used.

99. Oct. mem., 339.

100. Two volumes of hydrogen combined with one of oxygen to form two of water vapour. The only way to write an equation for this reaction without implying that there were a certain number of particles in a molecule of the elemental gases was to do so in terms of $HO^{\frac{1}{2}}$ as the formula for water. Thus for example:

$$2\ H + O \longrightarrow 2\ HO^{\frac{1}{2}}$$ or dividing the coefficients by 2: $$H + \tfrac{1}{2}O \longrightarrow HO^{\frac{1}{2}}$$

In fact Dumas did use this formula on one occasion but referred to it as a half-atom of water. Ann. Chim. Phys., 37 (1828), 48. In writing formulas Dumas used numbers, to represent number of 'atoms', that were smaller than the letters and centred, but he soon raised them slightly in the manner of Berzelius. They will be raised throughout my thesis.

101. Ibid., 366.

Ether (102) but wrote $\dot{H}H$ rather than $\dot{H}_2$. For example, sulphuric ether was given the formula $2C_2H_2 + \frac{1}{2}\dot{H}H$, a slight variation from that of Berzelius. This formula, which could also have been written $2C_2H_2 + HO^{\frac{1}{2}}$ to emphasise the volume aspect, was a one-volume formula. Since volume formulas were used by Dumas and most organic chemists from this time until late in the century, this term needs explanation.

Because vapour densities were proportional to atomic weights, it was evident to those who accepted Gay-Lussac's law and Avogadro's hypothesis that the vapour density of a compound depended on its formula. Conversely, it could be regarded as a means for obtaining its formula or a simple multiple thereof in terms of either weight or volume. In order to standardise this determination as far as volume was concerned, the formula derived from its measured vapour density was referred to as a one volume formula. It has been shown that vapour densities could be calculated also. Thus the vapour density for water can be found by substituting vapour densities for hydrogen and oxygen in the equation $H + \frac{1}{2}O = HO^{\frac{1}{2}}$: $0.0687 + \frac{1}{2}(1.1026) = 0.6200$. The measured value for water vapour referred to standard conditions of temperature and pressure was 0.6133. Therefore $HO^{\frac{1}{2}}$ was a one-volume formula. In a similar manner the value for C_2H_2 (Bicarboned hydrogen) (103) was calculated from

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102. Ann. Chim. Phys., 36 (August 1827), 294-310. In my thesis it will be referred to as the August memoir.

103. Since C^2H^2 will be referred to frequently in my thesis, it is necessary to justify the use of the English term 'bicarboned hydrogen', the literal translation of the French hydrogène bicarboné introduced by Dumas. In his Traité, Vol. 1, p.463, he had indicated: "As the naming of the carbures d'hydrogène is far from being related to their composition, we think it necessary to give a list of them here that will direct us in our study of them." There were eleven, three of which had been referred to in England as carburets: Light carburetted hydrogen (methane), heavy carburetted hydrogen (ethylene) (cont.)

2C + 2H, i.e., 2(0.414) + 2(0.0687) = 0.9652 (C=6). The measured value was 0.9852, and again this was a one-volume formula. Finally the value for sulphuric ether (as written above) would be 2(0.9652) + 0.6200 = 2.5504. From the measured value, 2.5832, it was evident that this too was a one-volume formula. Examination of a number of these formulas showed Dumas that fractions could be removed by using two-volume formulas. Thus the substances referred to could be written: H^2O, C^4H^4 and $C^8H^8.H^2O$. The real strength of the ether theory lay in the manner in which he wrote his formulas, and this forced him to use four-volume formulas in most cases (104). Unfortunately, as will become evident in a later chapter, his inconsistency in this matter caused much confusion (105).

A review of the equation for the reaction of phosphorous acid with water (page 156) now reveals that Dumas used one volume formulas to

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103. (cont.) and bicarburet of hydrogen (benzene, given that name by Faraday in 1825 when he discovered it). To distinguish marsh gas from olefiant gas Dumas used the terms <u>hydrogène demicarboné</u> and <u>hydrogène carboné</u> respectively in the first volume of his textbook. In the August memoir, however, he gave the name <u>hydrogène bicarboné</u> to the latter. In terms of theory, marsh gas was a forgotten compound, but presumably was given the name <u>hydrogène carboné</u>. The reason for the change lay in his desire to give them names in conformity with their one-volume formulas C^2H^2 and CH^2 respectively. The term ethylene came into use much later, bicarburet of hydrogen had already been used for another compound so there seems to be no reasonable alternative to a literal translation.

104. "In the article already cited (487) [<u>Traité</u>, Vol. 1, pp. 482-83], where the properties of bicarboned hydrogen were discussed, the quantity corresponding to a single volume has been taken as the atom, but in taking four volumes, as one has done here, we will simplify many formulas." <u>Ibid</u>., Vol. 5, p.452.

105. E.g., for a time he did not use H^4O^2 to represent water, and even when he did so he did not hesitate to use H^2O in formulas for other compounds rather than represent them by eight volume formulas. It was also convenient to use a two-volume formula for ether $C^8H^8.H^2O$ to compare it with its 'hydrate', alcohol, whose four volume formula was $C^8H^8.2H^2O$.

indicate the number of atoms of water and phosphine in the equation so that he would have been obliged to write it:

$$4\ P^2O^3 + 6\ HO^{\frac{1}{2}} = 3\ P^2O^5 + 4\ P^{\frac{1}{2}}H^{1\frac{1}{2}}$$

whereas two-volume formulas for these substances would have given a simpler and more acceptable equation:

$$4\ P^2O^3 + 3\ H^2O = 3\ P^2O^5 + 2\ PH^3$$

However, this would have been contrary to the principle that he had put forward in 1826 that all formulas should be written as one-volume formulas. His memoirs on ethers changed everything of course, but then it was too late. Not until volume five of the Traité, in his study of organic reactions did he use chemical equations of the modern type. They were the fruit of research during the intervening years and will be discussed in later chapters of the present work.

Dumas had not been able to measure the vapour density of phosphorus before volume one of the Traité was published. It is easy to imagine his chagrin when he finally succeeded, only to find that the vapour density was 4.35, close to the value he had initially assigned, then halved to bring it into agreement with the accepted weight. Hoping that some explanation would be found, he did not reveal the results immediately. In February 1832 Mitscherlich, visiting Dumas in Paris, asked the French chemist to demonstrate his techniques for determining vapour densities. (105a) Dumas chose to re-examine sulphur and phosphorus and the astonished Mitscherlich urged him to publish the anomalous results. In a short article at the back of the February 1832 issue of the Annales de Chimie et de Physique he described the special difficulties connected with measuring the vapour density of phosphorus and gave the value that he had

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105a. Arch. Acad. Sci., Fonds Dumas, Carton 8, Notebook labelled "Laboratoire de M. Dumas 1832".

obtained (106). Then, a few months later, his doctoral thesis was published (107). After reviewing briefly the various attempts tha t had been made to apply the atomic theory to practical chemistry, he discussed the anomalies: mercury, phosphorus, arsenic and sulphur. While he could still hope that his value for mercury might be accepted because this element was so different from the other metals, it had now become clear that phosphorus, and probably also arsenic, was divided into four parts when it combined rather than two as were the particles of all gaseous elements, so that its atomic weight was twice the accepted value. The consequences of this did not escape Dumas, and are evident in his comments:

> "Thus a discussion initiated in the memoir on the atomic theory that I published several years ago is almost finished. In that memoir I limited myself to the application of rules, generally accepted for compounds of gaseous substances, to the volatile compounds of phosphorus, arsenic, boron, silicon, titanium and tin. I could not suppose then that those compounds could contain a third or a quarter of the volume of the vapour of the elements that I have cited, and I had considered as very probable that the atomic weight of these substances should be reduced. ... Indeed, if a quarter volume of phosphorus can enter into gaseous combination, what is to stop tin, titanium, boron and silicon from entering in by thirds or still smaller numbers? Considerations drawn from the law of composition of salts formed from the acids that these substances can produce take on all their force again, and the original opinions of M. Berzelius retain all their authority with regard to boron and silicon, whose atomic weights cannot be determined by vapour density and whose specific heat has not been measured." (108).

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106. Ann. Chim. Phys., 49 (1832), 210-14.

107. "Dissertation sur la densité de la vapeur de quelques corps simples", Ibid., 50 (1832), 170-78. In his report on it, Thenard noted: "He [Dumas] had the occasion of repeating his experiments for M. Mitscherlich recently, and had obtained the same results, so he believed that it was necessary to communicate his results to the Academy, for chemists to evaluate." Ibid., 179.

108. Ibid., 174-75.

In adopting the volume theory he had hoped that no exception would be found in applying it by means of Avogadro's hypothesis to the determination of atomic weights. From 1826 sulphur had shown itself to be resistant to incorporation into the system. He had made a thorough study of the curious physical changes that the yellow solid underwent when it was heated until it boiled a second time but had not determined its vapour density when it boiled at the lower temperature, so there was still a possibility that at 107° it might have the expected vapour density (109). Furthermore he had not yet determined the vapour density of arsenic directly and no other element but phosphorus was a clear exception. Yet the door was all but closed. It was four years before he finally closed it in a series of eleven lectures that he gave at the Collège de France in 1836, the last that he gave there in replacement of Thenard. In these lectures he expressed the general scepticism concerning the atomic theory that had spread to most chemists of the time. Before they are examined, however, a study of his use of terms is necessary.

In his course at the Athénée, Dumas had seen that an emphasis on the quantitative aspects of chemical processes would be invaluable for a manufacturer. To study his problems intelligently required an understanding of chemical equations, an approach to chemistry that had remained

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109. Ibid., 175-78. Dumas was fully aware of the possibility that sulphur atoms could be grouped. He noted: "Would there have been a moment for sulphur when, after liquefaction its molecules grouped themselves in such a manner as to form compound atoms capable of resisting passage into the gaseous state thereafter; in such a way that if its vapour density had been taken around 107° this density could have been three times less than in the case that I studied? ... In the present state of things, one cay say that its vapour is three times too dense, or even that its [heat] capacity is three times too large, a result that reveals the existence of some molecular modification, new and worthy of attention in that it bears on fundamental concepts within the atomic system." Ibid., 177.

almost undeveloped since Lavoisier had first used one in connection with his research on fermentation (110). The manufacturer could not limit his interest to the product which was the object of his principal concern; it was important for him to consider all of the reactants and products involved in the process from a quantitative point of view to make it financially viable. But a knowledge of the use of equations would depend on some understanding of chemical theory, particularly the part involving atoms. Thus Dumas found it necessary to introduce this theory into his course. He developed the theoretical aspects even further in another series of lectures at the Collège de France, and drew upon these resources in the preparation of a long introduction to his Traité published in 1828. During this time he was obliged to examine the atomic theory carefully so that he could present it not in the research milieu but to students who would be able to use it or develop it further.

He began his discussion by giving simple operational definitions for atoms in conformity with Dalton's theory:

> "The atom of an element is therefore the very small particle of this substance that undergoes no further change in chemical reactions.
>
> The atom of a compound in its turn is only the small group formed by the union of elemental atoms of which they are composed." (111)

It was important for his purpose that his descriptions should be as concrete as possible. He had prepared his students by explaining the notion of proportional numbers, that is the weight of an element needed to combine

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110. Lavoisier, op.cit.(1-69), p.140. Berthollet, op.cit.(1-69), had directed attention towards chemical reactions, but his rejection of the law of definite proportions made equations useless. Berthollet focused on the process rather than the compounds involved.

111. Traite, Vol. 1, xxxiv. Dumas did not mention Dalton, but he did say: "Such is the idea of atoms that was formed at first." Ibid.

with other elements. At this point he raised the question of how many atoms were represented by proportional numbers and this took him into a discussion of gases and Gay-Lussac's law of combining volumes. He could then bring in Avogadro's law showing its strong foundation in the laws of physics:

> "One accepts, and it is difficult to doubt it, that in a given gas all the molecules are placed at equal distances from one another. If then one imagined this distance to be different for the molecules of another gas, it would be difficult to explain why the influence of an external force produces identical results in both situations." (112)

Clearly he was referring to particles having physical existence. Whenever he mentioned particles of gases in the sense used by physicists he called them molecules or physical molecules. This had not changed. If it were assumed that these molecules were also Dalton's atoms, a direct relationship should have existed between vapour density and atomic weight. Application of this principle to gaseous reactions showed that this was not true (113), so he could advise his students: "It must be accepted that atoms of gaseous substances can be divided when they enter into compounds" (114). But a fraction of a Daltonian atom was out of the question as Berzelius had later pointed out (115) so Dumas now gave it a different

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112. Ibid., xxxv (my italics).

113. When one litre of chlorine reacted with one litre of hydrogen, two litres of hydrochloric acid gas were formed, not one. This meant that one atom of each element combined to form two atoms of compound and this was only possible if the atom of each element had divided into two parts. Dumas had already discussed this problem in the October memoir and had used the term half-atom. In doing so he had quite reasonably followed Avogadro (half-molecule) and Ampère (half-particle) who had suggested the hypothesis.

114. Ibid., xxxix.

115. Jahres Bericht, 7 (1828), 80.

name. Since he had accepted the equivalence between the terms atom and <u>physical</u> molecule, it was a simple matter to call the fractional atom a <u>chemical</u> molecule, and we find him saying to his students:

> "We will accept throughout this work ... that heat never divides physical [molecules] as far as they can be divided in chemical combination. All known phenomena indicate that the value for this chemical molecule cannot be known precisely; thus the physical molecule, given by gases, must do. ... [A physical molecule] is formed from a group of chemical molecules, represented by a whole number, probably even a very small number.
>
> We will call atoms, then, the groups of chemical molecules that exist isolated in gases.
>
> Atoms of gaseous elements always contain a certain number of molecules, which is unknown to us.
>
> Atoms of gaseous compounds are formed either from the combination of whole atoms with each other, or with simple fractions of other atoms, or from fractions of atoms combined with each other." (116)

It was the physical molecule that was the source of atomic weights. It was not a particle about which nothing could be known and it made much more sense to Dumas to assign the name atom to this particle rather than the chemical molecule, which could have a weight of half, quarter or smaller fractions of the value for the physical molecule. In so doing, however, he attached a quite different meaning to the term atom than that accepted by Dalton.

Since the vapour density method could not be used for finding the atomic weights of non-volatile substances, Dumas was obliged to relate the results obtained by his method with those found by using other established methods, such as that of Dulong and Petit in which the specific heats of elements were linked with their atomic weights. He could only make that relationship if the weight found from specific heats was that of the physical molecule, not the chemical molecule. This would be true if the

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116. <u>Traité</u>, Vol. 1, pp. xxxix-xl.

heat capacities of all gases were the same and friends in Geneva had found that they were (117). Dumas extended it to solids and was able to say:

> "Thus the law of Dulong and Petit will only provide the weights of molecular groups analogous to those of which gases are made and not at all the weight of chemical molecules. Nothing prevents fractions of atoms from entering into compounds, formed from solids in the same way as we have accepted for gases." (118)

Though Dumas maintained these ideas and terminology in his thesis (119), the anomalous results for phosphorus, arsenic and particularly sulphur had obviously been disconcerting and had led to many unsuccessful attempts to explain the anomalies.

Meanwhile, Gaudin had drawn together the pieces of information related to the problem. In an article published in 1833 he used Avogadro's hypothesis, simple geometric reasoning and the basic assumption that "it was necessary and sufficient" for molecules such as hydrogen and chlorine to be composed of only two atoms and showed that oxygen, nitrogen, bromine and iodine had also to be diatomic (120). Using Dumas' vapour density measurement for mercury, the smallest weight of mercury that would combine with oxygen and the assumption that oxygen gas was diatomic, he was able

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117. De la Rive, A. and F. Marcet, Bibl. Univ., 22 (1823), 265-282 (280) and Ann. Chim. Phys., 35 (1827), 5-34. Dumas refers to their recent experiments, "done with the greatest care". Loc.cit.(4-116), xli.

118. Traité, Vol. 1, p. xlii.

119. Ann. Chim. Phys., 50 (1832), 170-78.

120. It was only because no clear distinction had been made between the words atom and molecule, claimed Gaudin, that no one else had reached the same conclusions. "An atom will be for us a small, spheroidal, homogeneous object, or a material point, essentially indivisible, while a molecule will be an isolated group of atoms, in any number and of any kind." Gaudin, loc.cit.(4-35), 115. He then introduced the terms: "monatomic, diatomic, triatomic ... polyatomic" to identify the number. Ibid., 115-16. The definitions were clear and terms used in a modern sense.

to show that mercury could only be monatomic, that vapour density measurements were always to be referred to diatomic oxygen. Of the twenty elements that he listed, the only weight varying significantly from the modern values was that for potassium, which was twice what it should have been. He was concerned with errors by multiples, not errors in decimals:

> "We can accept atomic weights, in so far as only decimals are concerned, with closed eyes if we go to MM. Berzelius and Dumas; their consummate ability, their knowledge, their exactness and their openness are a sure guarantee for us of the truth." (121)

Apparently he was able to choose the best weights from among those given by Dumas and Berzelius. For example, he assigned correct weights for silicon (122) and carbon. Concerning carbonic acid he said "Neither more nor less than two atoms of oxygen for one atom of carbon is accepted for this substance." (123) This is a surprising statement if one considers that the French school followed Dumas and Gay-Lussac in accepting C^4O^4 as its formula, a one to one ratio. Gaudin's memoir appeared in the February issue. In the March issue, Dumas added the following footnote to his memoir on the "Composition of Pyrocitric Acid":

> "Many chemists, following the example of M. Berzelius, have adopted an atomic weight double that assigned to carbon by M. Gay-Lussac. I have retained M. Gay-Lussac's value here after some hesitancy. My own conviction would be a minor matter, but apart from it I have the certainty that the most able chemists in France consider the weight I have indicated here as more probable than the other." (124)

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121. Ibid., 114-15.

122. The weights assigned were such that for the same oxide of silicon Dumas wrote the formula SiO, Berzelius SiO^3 and Gaudin, correctly SiO_2.

123. Ibid., 123.

124. Ibid., 293-303 (299). French chemists used C=6 rather than C=12 for many years afterwards.

Of the anomalies that had been a thorn in Dumas' side, however, he said nothing, despite the fact that he was at least aware of Dumas' vapour density value for sulphur. Hindsight indicates that Gaudin had provided the way out of a dilemma. His ideas were not accepted at the time, nor is it likely that they could have been given serious consideration (125).

Preoccupied with organic chemistry, Dumas was unable to give his full attention to the anomalies that had sown the seeds of scepticism, not only in his own mind but in the thoughts of his fellow chemists. In 1835, however, he was again invited to replace Thenard at the Collège de France. The lectures given in the first semester were not particularly noteworthy, but he had already begun preparation for the important series, published the following year as Leçons sur la Philosophie chimique (126), on the origins of chemical theories and the problems associated with them. In his initial lecture he summarised the content of chemical philosophy:

> "Taken from the viewpoint of modern chemistry, it consists in the general study of the material particles that chemists call atoms and the forces that influence them. Thus it comprises the search for all the properties of atoms, the study of chemical activity, its effects, its cause and its various modifications; it seeks to sort out the similar and different

125. Several reasons may be suggested. S. H. Mauskopf, "The Atomic Structural Theories of Ampère and Gaudin", Isis, 60 (1969) 61-74, indicates that "Gaudin's ideas remained without influence" because "he was outside the French scientific establishment; he never held a teaching or research post ... he worked in isolation. ... No one seems to have taken his theory seriously." Ibid., 70. A deeper problem, the fact that "his assumptions, particularly his chemical assumptions, became more untenable as time progressed" (ibid.), is of no concern to this discussion. A reading of Gaudin's 1833 memoir suggests that the basic ideas were not new, nor were they based on new experimental work by the author, that his contribution was largely reorganisation using new terminology (clearer to a later generation perhaps, but not to those working in the 1830s).

126. The lectures were given once each week for eleven weeks. The normal schedule had been two, or even three a week.

relationships exhibited by natural substances and tries to find the causes for these relationships." (127)

Dumas combined a considerable amount of history with his chemical philosophy, but the purpose of his work must be borne in mind in judging the historical content: an exposition of the central role that particles had assumed in chemical theory. By the fifth lecture he had arrived at the theory of equivalents, an essential introduction to the atomic theory. The following week he began his review of the theory (128) only after he had pointed out that Dalton had posited atoms to 'explain' the laws of constant and multiple proportions, but had given no experimental proof for their existence (129). Moreover, Dalton had insisted that the indivisibility of chemical atoms was an essential feature. This led Dumas to comment:

> "Is it indispensable, after all, to have recourse to the supposition of atoms in order to explain the laws of quantitative chemistry? Is it necessary to accept the indivisibility of material particles between which chemical reactions take place? I answer this question without hesitation: No, that is not necessary; no, among all of the facts of chemistry there are none that oblige one to suppose that matter is formed of indivisible particles, none that give any certitude or even any probability to the statement that these particles are indivisible.

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127. Leçons, p.2.

128. In the last half of the lecture Dumas reviewed the history of the atom from the time of Democritus to that of Georges Louis Le Sage (1724-1803) of Geneva who wrote, Dumas noted: "the last work I know whose purpose it was to establish an atomic system without experimentation." Ibid., p.256. Dumas referred to Le Sage, G. L., Essai de Chimie mécanique, Geneva?, 1758. Dumas was probably introduced to Le Sage's work during P. Prévost's philosophy lectures in Geneva. Prévost had more than a passing interest in Le Sage.

129. Dumas observed: "The ease with which all phenomena of quantitative analysis has been explained or predicted starting with the principle that atoms exist has resulted in the general acceptance of Dalton's views; but the foundation upon which those views have been based has never been demonstrated." Ibid., p.233. He noted that empirical proofs from chemistry led one into a vicious circle, and those from physics were unconvincing. He ended a detailed discussion of the only serious attempt (by Wollaston from astronomical considerations) by dismissing it.

> Suppose that chemical reactions could only take place among masses of a certain order, divisible if one wishes by forces of another nature, it makes little difference; all chemical phenomena are just as easily explicable as they would be if indivisibility were accepted as an essential property of masses. Indeed, for explaining the data that depend on this science, what difference does it make whether or not they [the particles] are susceptible to infinite division, if one wishes, by non-chemical forces? May not the union, separation, replacement of these particles be conceived just as well? Do not all the concepts of chemists remain wholly intact apart from this further divisibility? (130)

Once he had freed his students from the restrictions that Dalton had imposed by establishing a necessary relationship between atoms and indivisibility, Dumas could discuss much more openly the anomalies that had appeared in other theories depending on that of Dalton. Thus, in his seventh lecture he reviewed the law of combining volumes and the consequences that Avogadro had drawn from it, reminding his students that reactions such as the one between hydrogen and chlorine could only be explained if the atoms of these elements were divisible. Dumas emphasised: "I accepted this ten years ago when I began writing on these questions, taking great care, moreover, to explain very carefully the sense in which I understood the word atom at that time." (131) At that time he had distinguished between atoms of elements that could only be divided by chemical means, not by physical means (i.e., molecules in modern terms) and those that could not even be divided by chemical means (i.e., atoms in in modern terms) (132). It is in this light that one must understand his statement: "In the case of chlorine and of hydrogen, chemistry divides

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130. Ibid., pp. 233-34 (Dumas' italics).

131. Ibid., p.263.

132. Later in the lecture Dumas called the former physical atoms and the latter chemical atoms.

atoms that physics cannot divide." (133) He then noted that a way around the problem had been suggested: "Restrict the general rule to the elemental gases. These, it is said, are all comparable among themselves and are not to be compared with gaseous compounds: they alone contain the same number of atoms in equal volumes." (134) After he had shown that this could be done successfully by limiting oneself to the elements oxygen, hydrogen, nitrogen, chlorine, bromine and iodine, he then discussed the anomalies, concluding:

> "It is necessary either to reject the most beautiful analogies of chemistry and the very interesting laws that will soon be discussed, or agree that phosphorus, arsenic and nitrogen do not contain the same number of atoms." (135)

Stated in this way, Dumas seemed to leave his students no choice, a suggestion that was reinforced when he said a little later: "Gases, even when they are elementary, do not contain in equal volumes the same number of atoms, at least the same number of <u>chemical atoms</u>." (136) He implied that the number of <u>physical atoms</u> was the same. Assuming this to be true, and accepting the correctness of the analogies, Dumas was able to say:

> "You will notice that in the three examples that we have used as a test, chemical atoms seem to be grouped; that the gaseous particles of phosphorus or arsenic contain twice as many as those of nitrogen; that the gaseous particles of sulphur contain three times as many chemical atoms as there are in the particles of oxygen gas." (137)

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133. <u>Ibid.</u>, p.265. Dumas said nothing about the further divisibility of the chemical atom. He did not want to close the door on the possibility that a chemical atom might be divisible by some means that was not known at the time.

134. <u>Ibid.</u> Dumas may have been referring to Gaudin's work.

135. <u>Ibid.</u>, pp. 266-67. As he indicated, the sulphur-oxygen analogy suffered to an even greater extent, since the weight given by vapour density measurements was triple that suggested by analogy.

136. <u>Ibid.</u>, p.268. Although he had already made a clear distinction between chemical atoms and physical atoms, this was the first time that he had used the adjective "chemical".

137. <u>Ibid.</u>

Thus the number of chemical atoms in equal volumes of gases was not the same. On the basis of empirical evidence, this was as far as he could go. He could have extended the theory as Gaudin had, but he did not believe that the evidence was clear enough to warrant such an extension. He had already pointed out to his students often enough that theories could easily lead them into serious error if they were not anchored in empirical foundations (138). He was not about to fall into that trap himself. Gaudin's diatomic molecule of oxygen, first hinted at by Avogadro, was a daring simplifying hypothesis it is true and time has shown it to be extremely useful. Nevertheless, it was gratuitous. Four years after it had been announced Dumas had seen no firm empirical evidence forthcoming, nor had the anomalies been removed, so he was obliged to conclude with respect to the latter: "You can say that chemical action divides these substances more than heat does, and that's all." (139)

He then discussed the problem of mercury. Chemical analogy with lead or silver suggested that the atomic weight for the liquid metal was 200 (O=16), while vapour density determinations indicated that it was only 100 on the same scale. This implied the existence of an atom that was smaller than the chemical atom, and he could not accept this (140). Had the vapour density data for any other metal been available, it is possible

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138. For example, in commenting on Le Sage's work, he said: "Thus it is evident that the influence of meditating on atoms is fatal to those who turn to it imprudently and without any empirical restraint." Ibid., p.188. This is only one of many such comments.

139. Ibid.

140. As Dumas noted: "Heat would have divided the particles of a substance to a greater extent than chemical action. ... if such a shocking anomaly exists." Ibid., p.269. This was incorrect of course.

that he would have seriously considered Gaudin's hypothesis. As it was, the existence of a legitimate chemical analogy between mercury and silver could be maintained by halving the atomic weight assigned to silver (141).

After listing some generalisations associated with Avogadro's hypothesis that could be derived directly from experimental studies of gases (142), Dumas summarised his views on their constitution:

> "For those who want to go beyond this, it can be added that gases seem to be formed of groups of molecules, more or less coalesced; that these groups sometimes contain the same number of other groups, chemical atoms, or sometimes double or triple that number; because it must be supposed not only that the physical atoms of gases are groups of small masses distinct from one another, but that this is also true for their chemical atoms." (143)

Thus if a chemical atom of oxygen contained two molecules (144), chemical analogy suggested that sulphur should also contain two and have a corresponding atomic weight. But the atomic weight of sulphur that was obtained from its vapour density was triple that value. If the number of particles (physical atoms) must be the same in all gases, then there were three times as many molecules in a sulphur particle as there should have been. This was why he distinguished between physical and chemical atoms. There were two molecules in a chemical atom of sulphur and six in a physical atom, or rather three chemical atoms in a physical atom. If this seems unnecessary from a modern viewpoint, one must bear in mind that the

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141. Dumas indicated that he was disposed to do this and that Rose had done so already. He probably referred to Heinrich Rose (1795-1864).

142. For example, "all gases are equally compressible". <u>Ibid</u>., p.270.

143. This was the only place in the lecture where he used the term physical atom, but he had made the distinction between physical and chemical atoms earlier without using the term.

144. Dumas always avoided this simple case, preferring to use 2000 or some such number to avoid implying that two was the magic number.

evidence upon which these ideas were built was quite limited. Dumas had already been faced with a weight for mercury obtained from its vapour density that was less than that obtained by analogy. Although it was only half as much and could be accounted for in a two-molecule-to-an-atom system, there was no reason to believe that an element would not be discovered having a vapour density that would lead to an atomic weight of 1/4 or 1/8 the weight assigned by analogy, and the whole system would tumble. For this reason, he was forced to admit that vapour densities could give no absolute information about atomic weights (145).

Dumas might be faulted for being a little too cautious if gases presented the only problem. Like Avogadro's hypothesis, the law of Dulong and Petit had shown great promise as a means of determining atomic weights (146), but there had been anomalies there as well, cobalt, tellurium and carbon to mention only three. Although the value for silver seemed to be only half that determined from chemical considerations, there was reason to question the latter (147). The value obtained for the weight of mercury was half that obtained from its vapour density. Furthermore a memoir describing new experiments on specific heats of gases, read to the SPHN de Genève on 17 June 1835 (148) had led De la Rive and Marcet to agree with Dulong's view that all gases did not have the same specific heats, which made the integration of the two systems difficult if not impossible.

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145. Ibid., p.269.

146. His interest in the law was evident in his long exposition of both the law itself and its application to the problem. Ibid., pp. 271-82.

147. Within a few years organic chemistry provided the chemical data needed to reduce the atomic weight to the value obtained from its atomic heat.

148. Ann. Chim. Phys., 75 (1840), 113-44. For a discussion of the problems associated with specific heats see Fox, R., The Caloric Theory of Gases from Lavoisier to Regnault, Oxford (Clarendon Press), 1971.

Thus Dumas was led to conclude that atomic heats could provide no better clue to atomic weights than Avogadro's hypothesis. He had encouraged his students to gather data as a means of sorting out the anomalies among vapours (149). He now drew their attention to the great need for experimental data on the specific heats of compounds as well as elements (150).

If hope for specifying atomic weights by these methods had been reduced considerably, there was still another possibility available, isomorphism. Dumas hinted at its usefulness by defining isomorphs:

> "Isomorphic substances are those which crystallise in the same manner, and later are capable of mixing with, or growing on a crystal without changing its form. As a consequence of these observations, M. Mitscherlich has accepted that, in general, isomorphic substances must be formed of the same number of atoms, united in the same way." (151)

To use isomorphs as a means of determining the atomic weights of elements two pieces of information were necessary: A reference substance, such as iron oxide (FeO), whose composition was known, and compounds of the same type (an oxide in this case) and same crystalline form. Since zinc oxide fulfilled both of these requirements, its formula could only be ZnO, from which the atomic weight of zinc could be found by reference to the weight of iron. Dumas believed that this was the most useful of the three methods (152). He summarised their relationship with the atomic theory:

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149. He invited students who were really interested in the hypothesis to determine vapour densities for both elements and compounds using accepted methods, or to devise modifications or completely new methods. <u>Leçons</u>, p.271. The gratifying response will be discussed later in this thesis.

150. <u>Ibid</u>., p.281. The law of Dulong and Petit had been extended to compounds by Franz Ernst Neumann (1798-1895), who measured values for several carbonates, sulphates and oxides and collated them. <u>Ann. Phys</u>., <u>23</u> (1831), 1-39.

151. <u>Leçons</u>, pp. 283-84.

152. Though he discussed polymorphism at length in the eighth lecture, Dumas did not raise it as a problem.

> "When the concept of atoms is incorporated, the study of gas or vapour densities, specific heats and crystalline forms gives rise to ideas of the greatest interest, though they are incomplete. For that reason alone, it can be said that the existence of atoms has appeared to be very probable, and perhaps if one is pressed to admit it, even if the word atom is understood in the way the ancients understood it." (153)

But the real problem had not been solved. Studies had shown that molecules were grouped to form atoms. Had these groups always contained the same number of atoms, then an internally consistent set of atomic weights would have been possible. They did not, nor had any way been found to integrate the three systems. Thus the atomic theory was on a foundation that was no firmer than it had been before any of the theories had been devised, and Dumas was obliged to comment:

> "It is certain that the density of gases does not give their atomic weight; it is probable that the heat capacity of substances does not give it either; equivalents of acids, bases or salts cannot make known [the weights of] elementary atoms; and all things considered, atomic theory would be a purely conjectural science if it were not supported by isomorphism. ... Thus isomorphism completes what neutrality and double decomposition have begun. It leads us to the discovery of equivalent binary compounds, and equivalent elements, and because of this its discovery constitutes one of the greatest services ever rendered to chemistry, to natural philosophy." (154)

By the eleventh and last lecture, Dumas had examined many important chemical theories, and it seemed to him that within ten years a theory had come into existence, was developed and had "passed into the science or was irrevocably rejected" (155). Significantly, the atomic theory was not among those that he mentioned at this point. It did not fit the pattern. In its 'modern' version it had been around since 1807 and still had not "passed into the science", nor had it been "rejected irrevocably". Though he had

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153. Ibid., p.286.

154. Ibid., pp. 288-89 (Dumas' italics).

155. Ibid., p.424

never accepted an atom that was indivisible, it must be said that his efforts to develop a consistent set of atomic weights had been unremitting, for he saw the enormous practical consequences of such a system. All the evidence seemed to point away from the possibility that chemical atoms were ultimate particles. He was convinced that they were molecular groups, and that one had to be content with equivalents. In drawing the lecture to a close he remarked:

> "It is my conviction that the equivalents of chemists, those of Wenzel, of Mitscherlich, what we call atoms, are none other than molecular groups. If I were master, I would remove the word atom from science, persuaded that it goes beyond experience; and in chemistry we should never go beyond experience." (156)

Though the second sentence has been used frequently to show that Dumas rejected the atomic theory, it might be more useful to ask whether he ever accepted it. Indeed the discussion in this chapter suggests that he did not. On the contrary, the attitude expressed in the first sentence is much closer to his acknowledged approach from the outset. This is not to say that he rejected the existence of an ultimate particle. Far from it. What he did reject was the notion that it had been identified, and so he did not want the term used since Dalton had gone out of his way to emphasise that the concept of indivisibility had to be associated with it. In the sentence quoted above he used the expression "molecular groups". In this lecture he did so on four other occasions, always to represent physical or chemical atoms. He did not use the word molecule once! Yet in the remaining lectures he used it frequently, either alone, when referring to ultimate particles, or in conjunction with other words, allowing him to discuss the concepts he had represented in this lecture by the expressions physical and chemical

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156. Ibid., p.290 (Dumas' italics).

atoms. The word atom crept in rarely and in connection with atomic weights. In his work after 1836 Dumas continued to use the word atom but it was connected with atomic weights, not ultimate particles. Thus it was the atom (atomic weight) of carbon that he revised in 1840.

In France Dumas received strong support for his position from Thenard in the sixth edition of his Traité de Chimie élémentaire, théorique et pratique, in which there appeared for the first time an "Essai sur la Philosophie chimique" (157). Although he never referred to Dumas' lectures as such, Thenard drew heavily on the ideas that had been expressed in them and Dumas' name appeared frequently (158). In the section on isomers he wrote:

> "Having already adopted and discussed at length the opinion expressed by M. Dumas who accepts the existence of molecular groups and atoms properly so-called (159), we will again adopt what he says, this time on the topic of isomerism." (160)

Thenard's agreement with Dumas' ideas throughout the Essay suggests that the reasons for writing it included the desire to publicly show his support for those ideas. Above all, since Thenard was more inclined towards descriptive and empirical chemistry, he saw that this was a good opportunity to encourage chemists to turn away from theory and return to the search for data. As he noted:

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157. Thenard, op.cit.(4-44), Vol. 5, pp. 409-519.

158. Dumas' lectures were not published until 1837; Thenard's textbook appeared in 1836.

159. Thenard had written earlier: "But these [chemical] atoms would only deserve their name when envisaged in terms of their exposure to chemical forces, and although indivisible by the action of chemical agents, they must be represented as formed of many material particles of a smaller order.
Thus the word atom expresses a relative, not an absolute idea, and it is to be regretted that it has been adopted." Ibid., p.462.

160. Ibid., p.474.

"But since the existence of these atoms is hypothetical after all, and since everyone, these days at least, represents them in his own way, in an arbitrary manner, one must not lose sight of chemical equivalents, which really represent the facts, shorn of every speculative idea. ... These clear and simple principles (161) derived immediately from experiments and free of all hypothesis should cause chemists to limit themselves to equivalents and to leave atoms in the domain of speculation." (162)

In 1837 several chemists attending the summer meeting of the British Association for the Advancement of Science, held in Liverpool, had the opportunity to express their lack of faith in atoms having real physical existence (163). Since Dumas' Leçons had been published, it is possible that they were aware of its contents. News of the content of the lectures may have reached Britain indirectly at the time they were given. Liebig had been at the meeting and visited Dumas on the way back to Giessen. They may have discussed the matter. In the summer of 1838 Liebig, Gmelin, Heinrich Rose, Heinrich Gustave Magnus (1802-1870) and Friedrich Wöhler (1800-1882) met on a holiday and discussed the matter. Liebig wrote to Pelouze:

"We five have agreed to abandon completely the numbers of atoms that express volume relationships; we have decided to adopt equivalent weights in place of atomic weights and numbers of equivalents for numbers of atoms. ... If we follow the law of M. Dulong on specific heats we will have numbers

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161. "The equivalent of an element represents the quantity of that substance that gives a protoxide when it combines with 100 parts of oxygen. The equivalent of a compound is found by adding the equivalents of the elements that comprise it." Ibid., 416.

162. Ibid.

163. Included were Michael Faraday (1791-1867) and Robert John Kane (1809-1890). Some well-known philosophers who were present also raised their voices against real atoms.

> other than those obtained by accepting the theory of volumes or isomorphism; all that is being taught in this regard is based on hypotheses." (164)

While the notion of atoms as real particles was generally abandoned, chemists, including Dumas, continued to use atomic weights for several years. Others, including some of Dumas' students, took up the use of equivalents. In general, French chemists continued using volume formulas in organic chemistry because they found them valuable. Gradually the shift to equivalents was completed by the mid-forties but they were not uniform and the result was a certain amount of confusion. In inorganic chemistry events took a different turn.

Prout's Hypothesis. Dumas' inability to accept indivisible particles raises the question of his attitude towards Prout's hypothesis that the atomic weights of all elements were integral multiples of the atomic weight of hydrogen (165). Dumas' knowledge of the hypothesis seems to have come through Thomson who accepted it (166) and Berzelius who rejected it (167). Since nearly all of Dumas' early memoirs and articles in chemistry contain some criticism of Thomson's work, comparing it unfavourably with that of Berzelius, it would not be surprising to find Dumas criticising Prout. In

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164. Arch. Acad. Sci., Dossier Pelouze, Fonds Dumas, Letter of 14 October 1838. This letter has been quoted in full in the original French by Fox, op.cit.(4-148), pp 319-20. The absence of Mitscherlich from the group is noteworthy though it is not surprising.

165. Ann. Phil., 6 (1815), 321-30 and 7 (1816), 111-13.

166. A new edition of Thomson's Système de Chimie had appeared in 1818 with a supplement in 1822. Thomson had praised Prout's ideas.

167. Berzelius rarely missed an opportunity to disparage Thomson's results. Prout would hardly have benefitted from Thomson's supprt since the fact that he had supported it would have been enough to make the Swedish chemist question the hypothesis.

fact, in his discussion of the atomic weight of phosphorus in 1826 Dumas wrote:

> "Persons who like simple relationships are sure to prefer the number 400. They will settle on M. Dulong's results, for he obtained this number exactly from his analysis of phosphorus perchloride and copper phosphide." (168)

Though he deferred to Berzelius by accepting the value 392.3, there was no clear indication that he had rejected the hypothesis. But his own figures (400.3 and 402.3) were both closer to that of Dulong and it is not surprising that he rounded them off to 200 when he halved the weight in October (169).

In the first volume of his <u>Traité</u> Dumas discussed the hypothesis without naming Prout:

> "Many English chemists, among whom M. Thomson must be singled out, have accepted a simple relationship between the atomic weight of hydrogen and that of other substances. The latter, obtained by experiment, are quite variable multiples of the former. There is no known explanation for this, but that alone would not be a reason for denying it, if its truth can be experimentally demonstrated for all elements. The atomic weights of several elements coincide with this point of view in a striking manner (170). ... The corrections to be made are so small that the need to do so cannot be demonstrated experimentally. ... Moreover, since the multiple is variable, and the weight of hydrogen very small, all experimental results can be represented in an approximate manner, a possibility that gives proof of absolutely nothing concerning the supposed law." (171)

Clearly he was intrigued by the supposed law but his real interest lay in an attempt to find a useful relationship among the weights of the elements

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168. <u>Jan. mem</u>., 151-52.

169. <u>Oct. mem</u>., 354. He may have had the hypothesis in mind when he rounded off, but there is no evidence for this.

170. He gave the experimental values assigned to 10 elements (represented by modern symbols they are: H, O, S, C, Cl, N, Cu, Zn, Hg, Au) in one column and closest whole number figures in another.

171. <u>Traité</u>, Vol. 1, pp. xlviii-xlix.

as a means of classification (172). "Variable multiples" were of no use in this regard. In addition, he was hampered by a sense that the atomic weights were imprecise, so that rounding off seemed quite legitimate but might have given rise to serious errors (173).

In 1831 Dumas' letter to Ampère on isomerism raised the possibility that this phenomenon might exist among elements as well as compounds (174). He listed several groups of 'isomeric' elements with their weights; for example, in one group he placed cobalt (368.99), nickel (369.67) and tin (2 x 367.64) (O = 100) (175) to illustrate his viewpoint. In the Leçons he discussed the same chart, distinguishing two kinds of elemental isomerism: One in which the atoms of the elements involved (e.g., cobalt and nickel) contained the same number of molecules (ultimate particles) arranged differently; the other, polymorphism, in which the atom of an element consisted of atoms of other elements combined in some way (e.g., tin might consist of two atoms of cobalt or nickel, or one of each, linked together) (176). Dumas' ability to think this way arose from his rejection of an indivisible atom. This allowed him to consider that the particles making up an atom of an element could be arranged in different ways just as the atoms of urea and ammonium cyanate were linked differently. Since the question of elemental

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172. In the Traité, Dumas had been able to classify the non-metals quite well by using analogies among their properties, but he was unable to include weight, a very important one.

173. Indeed, in converting from O = 100 to H = 1 he rounded Hg from 202.2 down to 200 and Au from 198.9 up to 200! His other choices were much more valid.

174. Ann. Chim. Phys., 47 (1831), 324-25.

175. Ibid., 335.

176. Leçons, pp. 317-20.

isomerism touched on transmutation, Dumas wrote:

> "The isomerism of two compounds can be proved by analysis and comparison. But elements cannot be analysed. Therefore the only means available is to change one into the other, altering the manner of aggregation of the ultimate particles, and no one has ever done this." (177)

On the other hand, as he pointed out: "No experiment has ever been done to prove that transmutation is impossible." (178)

Although these thoughts drew his attention back to Prout's hypothesis from time to time, it was his preoccupation with the atomic weight of carbon that led him to consider the unity of matter seriously and to undertake the thankless task of verifying it. When Berzelius revised his list of atomic weights in 1818, he assigned a value of 75.33 to carbon. Dumas adopted this value until he moved to Paris, when he halved the value in conformity with French practice. He continued to use 37.66 as late as 1828 (179), despite the fact that Berzelius had increased his figure to 76.438 as early as 1820 (180). By no later than 1833 (and probably much closer to 1828), however, he had bowed to pressure and accepted a value of 38.26. In 1832 he had decided that the formula for naphthalene must be $C^{10}H^{4}$ from vapour density considerations but he had found it necessary to add: "apart from restrictions that must be made because of a slight uncertainty in the atomic weight of carbon" (181). During the ensuing years this uncertainty continued to bother him because he was working with many compounds containing a high

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177. Ibid., p.318.

178. Ibid.

179. Traité, Vol. 1, p.1 (p.50 in the introduction).

180. Ann. Chim. Phys., 15 (1820), 386.

181. Ibid., 50 (1832), 186, but see Note 124.

proportion of carbon. In 1837 one of his students, Philippe Walter (1810-1847), collaborated with Pelletier in research on the resinous oils that were used as a source of illuminating gas (182). Dumas was assigned to the commission appointed to examine the memoir. In his report in 1838 (183) he pointed to discrepancies in the results given by the authors that could not be laid to errors in analysis (184). Suspecting that the error was in the atomic weight of carbon, he had re-examined the composition of naphthalene and found that the sum of weights of the components was higher than the weight of the naphthalene that had produced them, suggesting that the atomic weight of carbon listed by Berzelius should be reduced to 76 or 75.9 (185). Convinced that the Swedish chemist had erred when he changed the weight in 1820, Dumas was left with no alternative but to determine its weight with the greatest rigour. He invited another of his students, a Belgian, Jean Servais Stas (1813-1891), to assist him. To eliminate any necessity for theoretical considerations he chose a simple gravimetric method based on the oxidation of carbon to carbon dioxide (186). Fully aware of the importance of this analysis, they exercised the greatest care possible. Large scale apparatus allowed them to use over a gram of carbon, either in the form of diamond or meticulously purified graphite. Special systems were introduced

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182. "Examen des produits provenant du traitement de la résine dans la fabrication du gaz pour l'éclairage", Comptes Rendus, 4 (1837), 898-99. This was a summary of the memoir read on 12 June.

183. Ibid., 6 (1838), 460-69.

184. Careful use of other methods had only accentuated the discrepancies.

185. Ibid., 464.

186. Dumas' work had led Berzelius to re-examine his value. He analysed lead oxalate and lead carbonate in 1839 and lowered the value to 76.25.

to insure that all of the carbon was converted into carbon dioxide and that all of this gas and no more was absorbed in potash and weighed. Fourteen different samples were reported (187). Throughout their calculations the authors limited themselves to the use of the proper number of significant figures (188). In the end, they were able to conclude that the atomic weight of carbon lay between 74.982 and 75.005 (O = 100) (189). Dumas remarked:

> "Since oxygen manifestly combines with carbon in the ratio of 8 to 3, perhaps this is the place to discuss the reality of the law announced by Dr. Prout. The capable English chemist accepts [as a law, the statement] that the ratios in which elements combine among themselves can be expressed by numbers that are integral multiples of that for hydrogen. Thus 1 part of hydrogen combines with 8 parts of oxygen to form water and with 3 of carbon to form marsh gas. Our experiments fully confirm this statement. We will return to it when more extensive research has revealed the limits within which it must be used." (190)

That this research included nothing less than the recalculation of every atomic weight is evident from a letter that Dumas wrote to Auguste De la Rive just before the new weight for carbon was announced in August:

> "If I announce that a review of the atomic weights leaves much to be said about them, you will think that I am pursuing M. Berzelius with an animosity that would justify his conduct towards me. But M. de Saussure was perfectly right about carbon and like everyone else, he followed the general

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187. They used five samples of diamond, five of natural graphite and four of artificial graphite. The latter was obtained from blast-furnace iron that had absorbed a large quantity of carbon from the charcoal used in the reduction of the iron oxide.

188. Before this time chemists had been rather loose in their respect for figures, sometimes using as many as eight when only two or three were justifiable. The authors normally used four, occasionally estimating a fifth when a weight of about one gram was being weighed on a balance sensitive to one milligram.

189. Between 11.997 and 12.001 (O = 16)

190. "Recherches sur le véritable poids atomique de carbone", Ann. Chim. Phys., 1 (1841), 5-58 (24). A preliminary announcement to the Academy was made on 17 August 1840. Ibid., 11 (1840), 287-89. The complete memoir was read on 21 December. Ibid., 991-1008.

pattern of regarding M. Berzelius as infallible. When you see the singular path that led me to review the whole business of atomic weights, you will be quite convinced that I was not just looking for a quarrel. I think it will be necessary to revise the entire table of atoms; if so, it will be an enormous task, but one must be resigned to it." (191)

He began this task with the three other elements found so frequently in organic compounds; hydrogen, oxygen and nitrogen. Two of these were important constituents of the atmosphere, whose composition Dumas needed to know to verify a hypothesis formed while doing research in agricultural chemistry with Boussingault. Using the same techniques and care, and apparatus large enough to collect and measure several grams of sample, Dumas amd Boussingault obtained vapour density values of 1.1057 for oxygen and 0.972 for nitrogen (192). From these results they were able to say that air from which carbon dioxide and water had been removed was composed of 23.01% oxygen and 76.99% nitrogen by weight (20.80% oxygen and 79.19% nitrogen by volume). The atomic weight for nitrogen was left unmentioned (193).

Revision of the density for oxygen necessitated a new determination for that of hydrogen. Since the value that he had found while working with

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191. This unpublished letter was dated July 1840. Bibl. de Genève, Collection De la Rive, Ms 2315, fol. 293-94.

192. The memoir was read 7 June 1841, Comptes rendus, 12 (1841) 1005-25; Ann. Chim. Phys., 3 (1841), 257-305. Concerning the vapour density of oxygen Dumas noted: "This value agrees almost exactly with the density adopted by M. Th. de Saussure, 1.1056." Ibid., 1013. Berzelius and Dulong had found 1.1026 and for nitrogen 0.976. Because oxygen was the standard for the atomic weights of the other elements, a difference of three parts in a thousand was significant in terms of Prout's hypothesis.

193. Using Dumas' values, its atomic weight = 0.972 x 16/1.1057 = 14.065 (O = 16). No doubt Dumas hoped that improved analytical methods would reduce this to a whole number. The value for atmospheric nitrogen was lowered to 14.04, but it was not until 1894 that the then recognised deviation from that of pure nitrogen led to the discovery of the inert gases.

Boussingault was imprecise (194), Dumas attempted to narrow the range by finding the weight of hydrogen needed to combine with oxygen to form water as exactly as possible. Working alone (195) he completed his initial measurements by April 1841 (196), but with many more to do, it was a full year before he was able to read his memoir "Research on the Composition of Water" to the Academy (197). It was a classic of gravimetric analysis. Again he used large quantities, great care and attention to detail. On the basis of 19 trials, he reported that the ratio of oxygen to hydrogen was 8.000 to 1.003 (or 1.001 applying a correction to account for air dissolved in the sulphuric acid used for drying). Another of his students, Louis Henri Frédéric Melsens (1814-1886), using the same process in Dumas' laboratory showed that a further error caused by absorption of hydrogen by copper during the reduction could permit the value to be lowered to exactly 8 to 1 (198). Even allowing for some uncertainty however, Dumas was able to say:

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194. The limits they assigned were wide (0.0691-0.0695) but did contain the modern value. Berzelius and Dulong had given narrow limits for a value that is unacceptable today (0.0687-0.0688).

195. As Dumas explained: "M. Stas was to have joined me in this research but his nomination to the Chair of Chemistry in the Brussels Ecole Polytechnique only permitted him to assist in experiments that we regarded as preparatory. I must take upon myself all faults commited in the carrying out of this work." Ibid., 8 (1843), 189.

196. An unpublished letter from Dumas to Auguste De la Rive dated 27 April 1841. Bibl. de Genève, Collection De la Rive, Ms 2315 fol. 301-02.

197. Comptes rendus, 14 (1842), 537-47. After allowing some time for criticism, Dumas published it again with further comments. Ann. Chim. Phys., 8 (1843), 189-207.

198. These somewhat questionable corrections were not generally accepted. Partington, The Composition of Water, London (G. Bell & Sons, Ltd), 1928, p.68.

"I can conclude from my own experiments that if the weight of a hydrogen molecule is 1, that of the molecule of carbon is 6, that of the molecule of nitrogen 7 and that of the molecule of oxygen 8. The errors in these ratios are almost insignificant." (199)

As will be shown, Dumas had been involved in theorising long enough to avoid committing himself completely to Prout's hypothesis before sufficient evidence was available. Nonetheless it was difficult for him to suppress his evident interest:

"If molecules of elements are all multiples of the molecule of hydrogen as Dr. Prout supposes, who can foresee the consequences to which a relationship of such a nature will lead chemists when it is well verified and they dare to trust it?" (200)

It was a challenge that he had accepted and encouraged others to accept. It was a programme for his students. His invitation was clear:

"Let us not hesitate to say that up till now the views of Dr. Prout have not been submitted to the sincere and profound discussion that their great importance merits. I do not know whether these views would be true if fully extended; but to find out it is necessary to determine atomic weights all over again on a large scale, using averages based on many experiments, neglecting none of the corrections that physicists have made available." (201)

Dumas was unable to pursue this research further himself until the mid-fifties when he was made director of a research laboratory founded in the Faculty of Sciences for preparing theses for the doctorate (202). In 1857 he read a series of papers to the Academy (203) which were extended and published as

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199. Ann. Chim. Phys., 8 (1843), 202.

200. Ibid., 201. No doubt he envisaged the solving of problems associated with the atomic theory.

201. Ibid., 192.

202. A brief discussion of this work will appear in a later chapter although, in general, my thesis is limited to Dumas' research prior to 1850.

203. Comptes rendus, 45 (1857), 709-12, (731); 46 (1858), 951-53; 47 (1858), 1026-34.

a "Memoir on the Equivalents of Elements" in 1859 (204). These led to lengthy debates with Despretz concerning Prout's hypothesis which were inconclusive. After the Karlsruhe Congress in 1860, it appears that Dumas was virtually alone in continuing the attempt to verify Prout's hypothesis; no doubt he did so because the weights of most elements are not far from whole number multiples of that of hydrogen. Whatever judgment one may wish to make in this matter, it must be said that Dumas initiated two important reforms in 1840, greater precision in the determination of atomic weights and more care in the use of measured values and the calculations in which they were used.

One further contribution must be included in this chapter. Though Dumas was unable to find a consistent method of classification in the atomic volumes of solids, Avogadro's hypothesis or Prout's hypothesis, he did begin to find it in the analogies of properties. In his course at the Athénée and subsequently in the Traité, Dumas organised his discussions of the elements and their compounds by groups. Thus in 1828 he listed five families:

"1st Family. Hydrogen.
2nd Family. Fluorine, chlorine, bromine, iodine.
3rd Family. Selenium, sulphur. Appendix, oxygen.
4th Family. Phosphorus, arsenic. Appendix, nitrogen.
5th Family. Boron, silicon. Appendix, carbon." (205)

Some time before 1836 Dumas arranged these elements so that those having the greatest resemblance to hydrogen (the least attraction for it) were placed closest to it (Table 4-1). Thenard, who reproduced this table in his

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204. Ann. Chim. Phys., 55 (1859), 129-210.

205. Traité, Vol. 1, p. lxxvii.

TABLE 4-1. A Scheme for Classifying Non-Metals.

Fluorine Chlorine Bromine Iodine		Oxygen Sulphur Selenium Tellurium
	Hydrogen	
Zirconium Silicon Boron Carbon		Arsenic Phosphorus Nitrogen

textbook (206) was able to say:

> "Thus we can say with M. Dumas in a definitive way: The basis for the classification of the preceding substances consists in bringing together those that resemble by nature the proportions and method of condensation of their compounds with hydrogen." (207)

This was a chemical method of classification and an important criterion though not the only one. It should be noted that the elements were also listed by weight, with the heaviest element towards hydrogen (208). These were also the most electropositive, which led Thenard to say:

> "Finally M. Dumas concludes that hydrogen is probably nothing more than a gaseous metal, which is in agreement moreover, with considerations of another nature that lead us to classify hydrogen with the most electropositive metals." (209)

In 1830 Dumas wrote in his Traité:

> "Probably similar distinctions should be made among the metals, and it is proper to compare only those that have analogous chemical properties. It is the best way to

206. Thenard, op.cit.(4-44), p.517.

207. Ibid. (Thenard's italics).

208. The weight generally accepted in France for carbon was 38 (O = 100) one-half the modern value; that for boron, 136, was double the modern value. Corrections would put the two in the proper order.

209. Ibid.

> shed light on their history. Although finding exact relationships among all of the metals as a group is difficult, it is easy to compare those having the most similar properties." (210)

Certainly Dumas used the theories that have been discussed in this chapter in his search for a natural method of classifying the elements, but he never lost sight of the importance of similarities in properties as the most natural method, one which must be taken into account no matter what theoretical basis was found. He returned to this idea in a paper read at the annual meeting of the British Association at Ipswich in 1851: "Observations on Atomic Volumes and Atomic Weights, with considerations on the probability that certain bodies now considered as elementary may be decomposed" (211). In it he added several triads to those mentioned by Johann Wolfgang Dobereiner (1780-1849) (212) and went a step beyond the idea that the weight of the middle element of a triad was half that of the extremes by indicating that most of the properties were intermediate. He also showed that a simple numerical relationship existed among the elements in a family, further simplifying his presentation in 1857 in his memoir on equivalents. Indeed, it has been said that "Dumas was quite near the periodic law, but the use of equivalents in many cases obscured his results." (213) Mendeléeff was only 25 when Stanislao Cannizzaro (1826-1910) showed how the anomalies associated with atomic weights could be resolved, and free from any prejudice in

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210. Ibid., Vol. 2, p.32 (my italics). Dumas listed the chemical properties used to group the alkali and alkaline earth metals and tried to group the remaining metals in a similar way.

211. The Athenaeum. Journal of Literature, Science and Fine Arts, 12 July 1851, 750; L'Institut, 19 (17 September 1851), 302 ff.

212. Ann. Phys., 56 (1817), 331-34; Ibid., 15 (1829), 301-07.

213. Partington, op.cit.(2-17), p.886.

favour of equivalents. Thus in 1869 he was able to list the elements rigorously according to their atomic weights and recurring properties in the form of a periodic chart. Though modified somewhat, this chart is still in use today, the prime reference source of chemists, the natural method for classifying the elements that Dumas had sought throughout his scientific career. During his Faraday Lecture on 4 June 1889, Mendeléeff acknowledged his debt to Dumas:

> "Cooke, Cremers, Gladstone, Gmelin, Lenssen, Pettenkofer and especially Dumas had already established many facts bearing on that view. Thus Dumas compared the following groups of analogous elements with organic radicles [sic], ... and pointed out some really striking relationships, such as the following: ..." (214)

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214. J. Chem. Soc., 45 (1889), 634-56 (637) (my italics). The contributions made by these and others whose publications Mendeléeff had not consulted in preparing his chart are discussed by Partington, op.cit. (2-17), Chapter 26.

CHAPTER 5

DUMAS AND THE ECOLE CENTRALE

"The editors of the Annales de l'Industrie ... created the journal to accomplish for all of the arts what the learned editors of the Annales des Mines have succeeded in doing with all of the activities within their sphere, i.e. bringing theory and practice into a close alliance. ...

Until now, men dedicated to the study of science have only considered its application secondarily, because they have rarely found any need to give their opinion in such matters. Thus the arts were only studied by theoreticians who knew nothing about the practical aspects of the arts, or artisans who knew no theory. Trying to clear up the constant confusion and tangled chaos that exists today as a consequence would be useless.

French industry can hope for a better future. His Ex. M. de Vatismenil (sic), Minister of Public Instruction, has authorised the creation of a new institution. Industry has sensed its full importance and foreseen its political consequences. This institution offers France a structured industrial education following a plan broad enough to suffice for all the needs of the country." (1)

Dumas made this statement in 1828 as editor of the journal he had just established, on the eve of founding an industrial school. Only five years earlier he had been immersed in seminal physiological research, when the Industrial Exposition of 1823 drew his attention to the lack of interaction between chemists and industrialists (2). The exhibits showed him that many manufacturers were not conversant with the principles of chemistry. His appointment as professor at the Athénée enabled him to initiate a course in chemistry applied to the arts, a first step towards remedying this situation. Eventually he published his course as a textbook, the Traité de Chimie appliquée aux Arts. He was well aware that these efforts were no more than a beginning. To complement his textbook a journal was necessary devoted to the principle that the observations, experiments and theoretical investigations of chemists were invaluable aids if industrial processes were to undergo rational development. When he became an industrialist himself because of his brother's demise, he invited others who were similarly placed to assist him in reorienting a journal that had just become defunct (3). The new publication was given the name Annales de l'Industrie française et étrangère (4). Fundamentally,

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1. Ann. Ind., 2 (1828), p. 375-76.

2. The French term "industriel" had a much wider meaning in the 19th century than that implied by its English equivalent "industrialist" as used today. The term will be used in the broad sense in my thesis.

3. The Annales de l'Industrie nationale et étrangère, published from 1820 to 1826 had had little scientific orientation, if any. It had experienced difficulties from its inception.

4. The full title of the journal was: Annales de l'Industrie française et étrangère, ou Recueil contenant les mémoires relatifs aux arts industriels, les développemens théoriques utiles à leur intelligence, et toutes les découvertes qui intéressent les manufactures ou l'économie publique (hereafter Ann. Ind.).

however, Dumas was aware that the ultimate answer must be formal education. In great measure his commitment to this ideal made possible the founding in 1829 of the first institution in the world that could properly be called an industrial school, the Ecole Centrale des Arts et Manufactures. The success of this institution in the face of overwhelming difficulties may be gauged from the important part it played in the development of French industry during the latter part of the 19th century. In 1852 Lyon Playfair (1818-1898) wrote:

> "In Paris we find a Central College of Arts and Manufactures, into which students enter at an average age of nineteen years, already well trained in the elements of Science, and going there to be taught how to use these elements for industrial application. Three hundred of the best youth of France are annually receiving at this College the most elaborate education; and the best proof of its practical value is the great demand among manufacturers for its pupils, a diploma from it being equivalent to assured success in life. Can you wonder at the progress making by France in industry, when she pours every year a hundred and fifty of these highly educated manufacturers into her provinces? A similar education to this is going on in almost all parts of Europe; but in England only one such institution exists." (5)

Twenty-five years later C. William Siemens (1823-1883) was able to say that the Ecole Centrale was the most suitable model for English technical education (6). In this chapter the events leading up to its foundation, the more important contributions made by Dumas to its development, especially the chemistry courses which he planned and guided, will be discussed.

At the beginning of the nineteenth century, large centralised

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5. Playfair, L., "On the Chemical Principles Involved in the Manufactures of the Exhibition as Indicating the Necessity of Industrial Instruction", Lectures on the Results of the Great Exhibition, London, 1853, p. 93-94. Most, if not all of the similar institutions throughout Europe followed the pattern of the Ecole Centrale.

6. Siemens pointed this out in a speech given as president of the Iron and Steel Institute at a meeting in Paris on 16 September 1878.

industries were very rare in France. Although the first signs of revolution were beginning to appear before 1815 (7), large increases in production and mechanisation during the Restoration period suggest that it was definitely underway by then (8). The timing of accelerated industrial growth can be attributed to a more liberal attitude towards industry, laissez-faire policies and import barriers on the one hand, but also to improved political relations with England that allowed French visitors to return with long, somewhat detailed reports on the state of industry in that country. Despite British attempts to control exportation of machines and emigration of the skilled workers and consultants needed to operate and maintain these machines as well as to build others, it has been estimated that there may have been as many as 15,000 English workers in France by 1824 (9). Thus, during the early twenties especially, the conversation in circles of the many interested savants in Paris ran to

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7. For example, the process patented by Nicolas Leblanc (1742-1806) in 1791 brought about a large increase in the production of soda in France. In 1828 Dumas was able to say that its manufacture "had exercised a very great influence on our commerce". Traité, Vol. 2, p.475. He also pointed out that the principal manufacturers of soda were located near Marseilles where an abundance of sodium chloride existed as well as the port facilities needed to receive the large amount of sulphur required. Ibid., p.476.

8. Three factors give evidence of such a revolution: Rapid increase in production, increased mechanisation and greater concentration of the labour force. In 1818 only 200 steam engines existed in France to supplement the power supplied for the most part by water wheels or horses. By 1829 this number had nearly tripled to 551, as had the number of patents issued annually. During the same period production in the cotton industry tripled and total industrial production had increased by two-thirds. De Berthier de Sauvigny, op.cit.(3-80), p. 222-23.

9. Derry, T. K. and T. Williams, A Short History of Technology, Oxford (Oxford U. Press), 1960, p.295. A lower figure was given by De Berthier de Sauvigny, loc.cit.(5-8) : "It was necessary to bring workers from England and in 1824 there were 1300 to 1400 English specialists in France". The numbers could be reconciled if the latter were consultants (engineers capable of direction and guidance) and over 90% were skilled workers.

the merits of English industry and what should be done to change the situation.

Efforts to meet the needs of French industry, to encourage its rational growth, came from several quarters. The Société d'Encouragement sponsored a very successful national industrial exhibition in 1819, with the support of the government, in which prizes were awarded (10). In this way attention was drawn both to the achievements of industry and its failings and difficulties. In the same year, a different approach was used by Charles François Dupin (1784-1873) who believed that a higher level of instruction was necessary than that being given in the Ecoles des Arts et Métiers (11). With the support of its Conseil de Perfectionnement, Dupin was able to introduce three courses at the Conservatoire des Arts et Métiers (12): Applied chemistry, taught by Clément, industrial economics, by Jean Baptiste Saye (1767-1832) (13); and applied mechanics, by Dupin himself. The free lectures were attended predominantly by workers, foremen and clerks, as many as 2,000 in 1824 (14). Yet another method, the writing of textbooks and similar works, was used by others.

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10. The first such exhibition was held in 1798. Derry and Williams, op. cit.(5-9), p.290 refer to it as one indication of the "astonishing energy released by the revolutionary era". From 1819 the exhibitions were held about every four or five years.

11. For a good account of the founding and development of these schools see Artz, F. B., The Development of Technical Education in France, 1500-1850, Cambridge, Mass. (The M.I.T. Press), 1966.

12. Most of them belonged to the Société d'Encouragement, but governmental approval was necessary. Fortunately this was made possible by the liberal character of the Decaze government.

13. Each professor gave two lectures during the week, initially from 7.45 to 10.00 p.m., but after a few years, at quite variable hours and even on Sunday.

14. Ibid., 217.

Prior to 1828 Chaptal's applied chemistry, for example, was unexcelled (15). Finally, many journals were founded during the Restoration whose influence cannot be neglected. Some of these, such as Le Globe, were of general interest but focused attention on industry by publishing related articles. Among the several specialised journals whose purpose was to inform, instruct and advise, the Annales de l'Industrie nationale et étrangère was one of the earliest and probably the most important of the period.

By June 1827, when his brother died, Dumas had finished his three-year course in applied chemistry at the Athénée and was completing the first volume of the Traité. As a member of the Comité des Arts chimiques of the Société d'Encouragement he was assisting in preparations for the industrial exhibition of that year. His decision to assume control of his brother's dye factory gave him an additional vantage point from which to consider the exhibits, that of an industrialist. It was apparent that most of the exhibitors had still not been convinced of the need to base industrial processes on scientific principles. This concept had been the central theme of his course, and would be for his textbook as well. He had already spent considerable time and effort in its diffusion. It was hardly surprising, then, that he took another opportunity to do so when it was presented to him.

The Annales de l'Industrie nationale et étrangère was founded in 1820 by Jean Gabriel Victor de Moléon and L. S. Le Normand to inform its readers of industrial advances that were being made in France as well as in foreign countries. It had met with some success, and its popularity would have continued to grow, no doubt, had not the untimely death of de

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15. Chaptal, J. A., Chimie appliquée aux Arts, 4 Vols., Paris, 1807.

Moléon intervened. Because Le Normand was unwilling to continue, the Annales became a journal in search of an editor (16). Within three months the challenge was taken up by an energetic group of scientists who were also educators, industrialists and members of the Société d'Encouragement. It seems very probable that Dumas played a major part in the organisation of this enterprise. Although Béchet no longer published the Annales des Sciences naturelles, he was in frequent contact with Dumas concerning the publication of his Traité which would appear early the following year. The young chemist would have been one of the first to learn of the impending demise of the journal. He was quick to see the possibilities. After consulting relatives and friends and convincing others with similar views to accept the challenge implicit in the task, he entered into a contract with Béchet. Several of its terms are of particular interest to this thesis and are quoted here in their entirety:

> "Contract ... between the undersigned, MM. Jacques Etienne Bérard, professor of chemistry, living in Paris, rue des Francs Bourgeois-St. Michel; Jean Baptiste Dumas, professor of chemistry, living in the King's Garden in Paris; François Emmanuel Molard [1774-1829], assistant director of the Conservatoire and Anselme Payen, manufacturing chemist living in Grenelle, all on the one part, and M. Jean Charles Béchet the younger, living in Paris, place de l'Ecole de Médecine, No. 4, on the other part, have agreed on the following:
> Art. 1. MM. Bérard, Dumas, Molard and Payen have combined to edit a scientific journal under the name of the Annales de l'Industrie etc. to contain
> 1° applications of science to industrial arts and the theoretical developments useful for understanding them;
> 2° extracts of memoirs of this kind read to learned societies and French and foreign journals;
> 3° descriptive announcements of works on manufacturing;
> 4° finally, principal discoveries concerned with the public economy and hygiene. ...

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16. Since Béchet had left his father's bookshop to establish his own in 1820, this was probably the first journal that he had published. Its continuation would have been a matter of pride as much as a source of income.

Art. 3. Issues will appear regularly within the first ten days of each month, bearing the date of the preceding month; each will consist of five printed sheets of the same characters, justification and format as the Annales de l'Industrie presently published, and from one to four engravings in such a manner as to form a volume of four hundred and eighty pages of text and ten figures every six months, format in 8° or in 4°. M. Leblanc will prepare the engravings ...

Art. 5. At the end of every six months, a time will be set aside for settling accounts and dividing profits, to be given to the collaborators by M. Béchet at the rate of ten francs for every subscription sold each year (17). ...

Art. 8. The editors will assemble on a day towards the end of each month to compose the issue to be printed. ...

Art. 13. The present society will publish the journal for ten full, consecutive years, sharing the expenses.

Art. 17. If at the end of three years, M. Béchet is not making three quarters of his expenses and he no longer wishes to pay the costs stipulated in article 2 of the present act, the decision will be his, providing that he gives the society notice three months before the end of the year. ...

Art. 22. So that the annals referred to may appear from the first of January 1828, we agree to destroy the seven issues that have appeared for the year 1827 and to divide all the expenses involved [in the margin: 2,250 francs] five ways. These expenses will be deducted from the funds from the first subscriptions for 1828. Subscribers for 1827 should receive all issues for 1828 free of charge in exchange." (18)

Dumas was the first to sign.

Who were the three others whose signatures indicated goals similar to those of Dumas? Dumas' 'cousin' J. E. Bérard has been mentioned frequently already. He was the only direct link with the Academy of Sciences (19), an extremely important one for the success of the project. A

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17. This would have increased to 15 francs if the number of subscriptions had exceeded 1000 (Art. 10). The annual rate of subscription was 25 francs (28 in the départements and 31 foreign) (Art. 6).

18. Unpublished manuscript, Arch. Acad. Sci., Fonds Dumas, Carton 1, Doss. "Annales de l'Industrie, Annales des Sciences et Annales de Chimie".

19. He was elected Correspondent of the Academy in 1819.

professor of chemistry at the school of pharmacy in Montpellier, he was also director of his father's chemical factory in nearby La Paille (20). Dumas' frequent references to Bérard in the _Traité_ indicate that his 'cousin' had provided him with much valuable information about industrial processes for his course at the _Athénée_. Apparently Bérard was on leave from Montpellier at this time, perhaps hoping to be able to settle in Paris again and engage in serious research (21). He was undoubtedly one of the first that Dumas contacted about taking over the journal.

Molard, a graduate of the _Ecole Polytechnique_, had been director of the _Ecole des Arts et Métiers_ for a long time before he became assistant director of the _Conservatoire_ in 1817 (22). Two years later he was sent to England to study industries there with a view towards preparing a report comparing the state of industry in England with that in France. As an inventor he had earned many prizes and medals. He was a principal editor of the _Dictionnaire technologique_. In addition to these links which were important for the success of the journal, he brought to it a knowledge of the mechanical arts. He was a member of the mechanical arts

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20. Smithson Tennant (1761-1815) wrote in a letter from Lyon in 1814 that Bérard was "one of the best chemists in France", and that he had "succeeded to the chemical works of Chaptal, which are now very extensive and carried on with great intelligence". Quoted by T. Thomson, _Annals of Philosophy_, _6_ (1815), 95.

21. Bérard's Paris address is something of an enigma. Since it was the same as that of Robiquet's pharmacy, it may have been a temporary address, particularly in view of the rule that Correspondents of the Academy could only live in Paris for short periods of time. On the other hand, to keep to the obligations imposed by the contract, he was obliged to be in Paris once each month, a highly impractical arrangement for someone living in Montpellier.

22. F. E. Molard should not be confused with his older brother, Claude Pierre Molard (1758-1837), also an inventor, who was a founder and the first director of the _Conservatoire_. Though he had kept the title when he became a member of the Academy in 1816, he had ceased to perform the director's functions, which he had left to his younger brother.

committee of the Société d'Encouragement, and may have met Dumas at meetings of the society, or at the Conservatoire while Dumas attended Clément's course there, or visited the museum in connection with his course at the Athénée later.

After studying chemistry in the laboratories of Chevreul and Vauquelin for two years, in 1814 Payen began to direct a beet sugar factory owned by his father. Since that time he had dedicated himself to improving the yield of sugar from sugar-beet by studying not only the methods of refining, but also the agricultural aspects, especially fertilising. Of the four, he was the only full-time industrialist. He was the only one who had not been a teacher, but within a few years he accepted a teaching position and spent most of his remaining years as professor of industrial chemistry. Undoubtedly he met Dumas at meetings of the Comité des Arts chimiques of the Société d'Encouragement for he was an assistant member of the committee.

The four editors were able to prepare material for the first issue by the end of the year, and its publication was announced on 26 January 1828 (23). Clearly it was aimed at industrialists and savants, not workers, or even foremen. Dumas began his twelve-page introduction (24) with a few words on the importance of science and industry to the

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23. Bibliographie de la France, 1828, No. 4 (26 January), p.67. It was the last time that it would be ahead of schedule. The February issue appeared 29 March and the remaining four on 5 July, 4 October and 27 December (May and June). Ibid., pp. 243, 506, 731 and 934 respectively. Beginning in 1829 only books were listed in the Bibliographie.

24. Though it was unsigned, the opening sentence is only a sample of the evidence that it was Dumas' approach and style: "The periodical that we offer to the public is based on a simple idea, the desire to be useful to our country and to take part as much as we can in the accomplishment of the great work of civilisation." Ann. Ind., 1 (1828), 5 (my italics).

development of civilisation, but quickly moved on to the four elements that he and his collaborators believed were necessary for the encouragement of industry: Freedom, honour, profit and knowledge. It is evident that they supported the government's laissez-faire policy. Comparing the free-enterprise system with the old Guild system, Dumas wrote:

> "Wherever production and consumption are free, the need to improve constantly animates the entire mass of men involved in industry. ... This continual labour gives birth to great discoveries, each of them permanently effecting the environment (25) and the form of human institutions." (26)

Aware of the importance of honour as an incentive, he emphasised the fact that industrialists and inventors had made lasting contributions by conquering nature rather than men (27). The recognition of their achievements by national awards was both an indication that the importance of industry had been recognised and a source of encouragement because of the advertising value as well as the prizes awarded. He noted: "From the time that industry has been allowed to exhibit its products in the king's palace, its political and social importance has been sanctioned." (28)

The editors, themselves manufacturers, supported the profit motive, not only because of the risk involved, but also because of the benefits that accrued to the whole of society by a thriving industry. To encourage the more pessimistic and those who were wary because others had suffered reverses, Dumas pointed to favourable trends for industry: increased

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25. "bouleverse sans retour la surface du globe".

26. Ibid., 6-7.

27. "Agriculture, navigation and more recently the invention of gunpowder and steam engines have produced modifications in the whole environment that will outlast the human race itself." Ibid., 8. He observed that historians and poets tended to focus on the heroes of war and politics.

28. Ibid., 10.

capital investment, production and consumption, and a desire expressed by the people for cleanliness, order and well-being, all positive indicators for industrialists. He emphasised that it was industry's responsibility to extend the benefits of urban civilisation (29) to other parts of the country that had hardly been touched by them. This would become a profitable enterprise as industry developed. But this development depended on closer links with science. As Dumas was careful to assure his readers:

> "It should not be imagined that this perfection is only a dream. Among the industrial discoveries necessary, there are very few that cannot be found in the form of germinal ideas in purely scientific writings; it is up to those concerned with applications to draw upon them." (30)

But he was forced to continue: "Unfortunately these ideas have not germinated, because, on the one hand, _savants_ do not always see their application, and on the other, industrialists are not aware of them (31)." It was this gap that the editors sought to bridge, Dumas stressed:

> "More than to anything else, the delay in applying new discoveries is due to the paucity of educated men who are involved daily both in the progress of the natural sciences and the search for ideas resulting from it that would be productive for the manufacturing industry. ... To bridge the gap which exists between most industrialists and persons concerned exclusively with science seems to us to be the most attractive and the most important part of the task that we must accomplish. Our close relationship with all of the _savants_, with whom we have worked on occasion, our

29. Dumas compared his own epoch with the middle of the previous century to bring out these benefits: "Porcelain, once reserved for banquet tables, is now found in all households; everywhere wall-paper has replaced the rich tapestries of our fathers, and its low price permits its use even in the most modest room. Our apartments are more comfortable; the air we breathe is no longer polluted with infected vapours; we have good systems of heating and lighting." _Ibid._, 12.

30. _Ibid._

31. _Ibid._ As an example he indicated that crystal tinplate, discovered by Proust, was not introduced into the art of the tinsmith for 20 years.

> extended relations with industrialists, who favour the products of the factories which each of us owns and directs, will render this new kind of research, to which we intend to devote ourselves, less difficult. It could become a productive source of profit and knowledge for industrialists." (32)

The first volume contained six issues dated January to June 1828, although the last issue did not appear until December. It contained a wide variety of articles, most of them several pages only with few exceptions written by industrialists. Some were extracts from other journals and a number of articles on dyes and dyeing as well as on boilers, particularly those used in the dye industry, suggest that Dumas was responsible for obtaining them. His only personal contributions were some brief notes. Indeed apart from several articles in volume 3, he published little of his own research in the <u>Annales de l'Industrie</u>. There were nine articles by Payen, two by Molard and one by Bérard in the first volume. Nothing further was published in the journal by Bérard. Apparently he decided to return to Montpellier and probably took no further part in editorial activities. The second volume contained a report written by Molard just before he died unexpectedly on 12 March 1829. Payen wrote only one more memoir for the journal (33), but seems to have continued as editor. The difficulties of the task were enormous, as may be gathered from the fact that by the end of the first year they were already six months behind the date of publication assigned in the contract, and the following statement written by Dumas:

> "The editors of the <u>Annales de l'Industrie</u> make no

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32. <u>Ibid</u>., 14-15.

33. <u>Ibid</u>., <u>5</u> (1830), 19-26. His report as a member of a commission of the <u>Société d'Encouragement</u>, <u>ibid</u>., <u>6</u> (1830), 190-98, will be discussed later in this chapter.

> attempt to conceal their satisfaction at completing the set of issues for the year 1828. ... Continual pre-occupation with this idea [linking theory and practice] has made them conscious of its importance on the one hand, and the difficulties associated with it on the other. They have seen that they could not attain their goal without considerable and varied assistance. Their courageous struggle throughout the year has made them aware that they have not yet overcome all of the obstacles." (34)

There were other frustrations that arose, as Dumas noted later:

> "We had decided to report on all of the industrial journals published in France and abroad, journal by journal. This work has been done for the month of July. With very few exceptions, however, the French industrial journals, and above all those of England contain so many insignificant articles, absurd recipes, descriptions of known apparatus of no interest, that we could not bring ourselves to use a part of the Annales to aknowledge and discuss them, and we have decided that the best thing to do is to continue to collect the really important articles in all the known journals and to pass over the rest in silence. The delay in publication of this issue is due to the suppression of the report on journals, already partly printed." (35)

Despite these difficulties, there was little indication that the journal would cease publication with the December 1830 issue. Indeed hopes were running particularly high for its prosperity when the editors announced in the second volume the "success of a project destined to favour, from many points of view, the development of French industry" (36). They referred to the Ecole Centrale des Arts et Manufactures, to which they linked the future of the journal.

Even when he began his course at the Athénée Dumas realised that he was only providing an immediate and very limited solution to a vast problem. To prepare a person for the number and variety of situations that

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34. Ibid., 2 (1828), 375.

35. Ibid., 4 (1829), 96.

36. Loc.cit. (5-34).

he would face as the director of a chemical industry was beyond both the scope of Dumas' teaching and the time available. What was needed was a far broader programme that would provide a background in all the relevant sciences and in general industrial activities. The <u>écoles des arts et métiers</u> had been founded primarily to instruct workers, to help them to improve their lot. Though the lectures at the <u>Conservatoire</u> were at a higher level, they were limited and in some respects outdated (37). The <u>Ecole Polytechnique</u> prepared engineers for the various branches of the army and navy and for public service in the building of canals, roads, bridges, etc. As <u>répétiteur</u> at this school for the intellectually élite, Dumas was fully aware that its programme was not intended to prepare industrialists, who were concerned with private enterprise. It could hardly be expected to serve both needs, even though a few of its graduates did take up industrial positions. A growing demand for industrial education at all levels was evident, not only from the large numbers attending courses available, but also from the frequent references to the need, made in the popular and specialised journals of the period (38). The response had been far from adequate. Indeed there was no educational institution designed to give a complete industrial education to those who would be the leaders of industry or consultants available to answer industrial problems. The political ascendance of the 'right' between

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37. Colladon mentioned this in a long letter to Solignac, director of the <u>Ecole Centrale</u>, dated 19 June 1879, to be read at the banquet in celebration of the 50th anniversary of the founding of the school to be held the next day. Bibl. de Genève, <u>Correspondance générale de Daniel Colladon</u>, Ms.fr. 3747, fol. 229 à 233 et v°, p.4. He continued: "The galleries of that institution contained nothing but old models."

38. For extensive and detailed references see Artz, <u>op.cit.(5-11)</u>, p.202.

1822 and 1828 precluded the founding of such a school. When Villèle was replaced by Vicomte Jean Baptiste Silvère Gaye de Martignac (1776-1832) in January 1828, however, more liberal ministers were appointed, including Antoine François Henri Lefebvre de Vatimesnil (1789-1860) who directed the new Ministry of Public Instruction from 6 February (39).

About the same time three young science educators who were also interested in industry, Jean Claude Eugène Péclet (1793-1857), Théodore Olivier (1793-1853) and Dumas, who, as Olivier noted "did not know one another, were brought together by singular circumstances" (40), and began to discuss the problem. Péclet, who had specialised in teaching physics and its applications, had come to Paris from Marseille in 1827 to write textbooks on heating and lighting (41). In 1826 Olivier had returned from Sweden where he had helped in the founding of schools of military engineering and had gained a wide experience in applying descriptive geometry (42). Though they were unknown to each other, they had all been

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39. During the period 1822-28 Church Affairs and Public Instruction were included in a single Ministry, administered by Mgr. Frayssinous. His desire to increase loyalty to the Church and the Throne led him to favour a classical education rather than the instruction in science and technology sought by the liberals.

40. Olivier, T., Mémoires de Géometrie descriptive, théorique et appliquée, Paris, 1851, p. xviii. He did not elaborate, nor is there any indication elsewhere what they might be.

41. Among those entering the Ecole Normale in 1812, Péclet ranked highest and again when he graduated. Appointed professor of physics in the Lycée in Marseille, his liberal views soon cost him his position in the University (the French public education system) and he dedicated himself to giving industrial instruction, particularly in physics. He published his courses in chemistry and physics before leaving the Lycée, and his physics course was developed into a textbook which went through several editions in Paris.

42. A graduate of the Ecole Polytechnique, where he was favoured by Monge and Hachette, Olivier taught at the Ecole d'Application de Metz until invited by the King of Sweden (Bernadotte) in 1821 to teach in the Swedish Artillery School. He published mathematical research in Sweden.

favoured by Ampère and it may well be that he brought them together. Encompassing among themselves the three studies essential to an industrial education, they were in an excellent position to found a school. For some time they discussed the state of industry and the need for industrial education. They were thinking of how they might best fill this need when quite unexpectedly Dumas was approached by a wealthy young lawyer, Alphonse Martin Lavallée (1797-1873) who was interested in industrial investment (43). Colladon described the encounter:

> "It was [Lavallée] who explained to me how the idea of the Ecole Centrale first came into being. He had been attending Dumas' evening lectures at the Athénée, rue de Valois, regularly, and those interesting gatherings, where Dumas drew out the vast consequences of the application of chemistry to certain industries, had given him the desire to dedicate his time and a part of his wealth to an industrial enterprise which would be useful and profitable.
>
> After a lecture one evening he broached the topic and M. Dumas requested several days to think about it. He then suggested that the most desirable undertaking would be the creation of a scientific industrial school. M. Lavallée was pleased with the idea (he had had the same thought), and said that he was disposed to provide the necessary funds and to become the active director of the enterprise. Some provisional calculations showed that these funds would be sufficient, and that no government subvention would be necessary.
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> It was after these preliminaries that M. Dumas, knowing that several persons were concerned with founding an industrial education, conferred once more with MM. Benoît, Olivier and Péclet. All three were happy to find the opportunity to depend on MM. Dumas and Lavallée." (44)

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43. After receiving a degree in law Lavallée was associated for several years with his brother-in-law, Haentjens, a shipbuilder, and in 1827 went to Paris to live. There he bought shares in Le Globe and a subscription for the Athénée. Dumas' opening lecture left him "with the distinct impression that he had heard one of the best professors of his time". Comberousse, Charles de, Histoire de l'Ecole Centrale, Paris, 1879, p.22.

44. Colladon, op.cit.(1-65), p.189. He gave essentially the same details in several letters, emphasising that both Lavallée and Dumas had verified them. Philippe Benoît had graduated from the Ecole Polytechnique in 1812 and had established an office as a consulting mechanical engineer.

Although the project seemed to be well under way, and indeed discussion went on for some time (45), nothing could be done without the approval of the government, since even private schools were subject to the Ministry of Public Instruction, and paid a per capita tax for their privilege. When application was made, it was discovered that a young physicist, Binet Sainte Preuve, had already obtained permission to found such an institution during Mgr. Frayssinous' Ministry, but had been unable to find financial support for it within the government structure. The professors were thus forced to enter into negotiations with the 'director' of the school, who apparently had nothing to offer but his priority and an ambition to found a school. Moreover, he was interested in a government school with numbers limited to a total of 50 to 100, whereas Lavallée, who was now effectively excluded, considered from his calculations that 400 was an optimal number for a private school. Certainly by September there was assurance that there would be a school one way or the other (46). Binet Sainte Preuve applied to Vatimesnil for ratification of his original document of approval. In doing so he provided a general statement of objectives, a curriculum and a list of professors.

On 5 October 1828 the following notice appeared in Le Lycée (the semi-official journal of the educational system):

> "An institution destined to prepare industrial leaders and civil engineers will open in Paris under the name of the Ecole d'Industrie Manufacturière. Among the talented personnel who will teach there are MM. E. Péclet, ex-professor of the physical sciences in Marseille; Dumas,

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45. Lavallée must have contacted Dumas before the conclusion of his lectures in May.

46. "From as early as 11 September 1828 he [Dumas] made known to Brongniart the project of an industrial school in which he would have a position as professor." Launay, op.cit.(2-115), p.148.

professor of chemistry at the Botanical Garden, [sic] répétiteur of chemistry at the Ecole Polytechnique; Ollivier, [sic] ex-professor at the Ecole d'Application de Metz; Gourlier, architect, works inspector of the Mint, etc.; all known by significant works in pure and applied sciences. Naturally, foremost among the difficulties presented by this important enterprise, conceived several years ago, were:
1° obtaining the personnel capable of sustaining it;
2° organising the curriculum.
Whether the former has been resolved may be judged from the names cited. We can assure you that the plan of studies, to be given in the next issue, indicates equal success in overcoming the second obstacle. Already certain of support from many savants and manufacturers, the new school has received strong evidence of special protection from the University. The Royal Council has placed a vast area belonging to the Sorbonne at the disposition of the director, M. Binet Sainte Preuve, in which work will soon begin. The Minister of Public Instruction has shown that he intends to use all his efforts to promote an institution which, to all the immense services that it can render to the manufacturing class, adds the particular advantage that it can provide the University with all the industrial professors it will need. We will refer to this school again, and make known the names of those who have contributed the most to establishing it. The little that we have said indicates that it must be distinguished from the schools of commerce where trading and banking are the principal studies. Inquiries may be directed now to M. Hachette, bookshop, No. 12 rue Pierre Sarrazin." (47)

Whereas the journal Le Lycée was directed towards a limited group of readers, Le Globe was a popular journal founded by a liberal, Paul François Dubois (1793-1874) who had been a close friend of Péclet at the Ecole Normale. It is surprising that despite connections with Péclet and Lavallée, Dubois was obliged to borrow his information from Le Lycée, as he had indicated on 11 October. Only minor changes were made when Dubois

47. Le Lycée, journal général de l'Instruction publique, rédigé par un société de professeurs, d'anciens élèves de l'Ecole Normale, de savants et de gens de lettres, 3 (1828), 336-37. The journal was founded by the bookseller, Louis Christophe François Hachette (1800-1864) in 1827 with the help of several professors from the University. It was intended to serve secondary school professors throughout France.

wrote his account for the issue of Le Globe dated 8 October (48). The plagiarism was even more embarrassing when he learned, evidently from his friends, that Hachette, the editor of Le Lycée had made several errors and important omissions:

1. Binet Sainte Preuve had obtained approval from the previous Minister for a similar project and it had been ratified by Vatimesnil.

2. Péclet, Olivier and Dumas had held conferences with Binet Sainte Preuve but nothing had been finalised.

3. The "vast area" put at their disposal was the amphitheatre of the Sorbonne.

Dubois added that people would profit whether Binet Sainte Preuve was director or "the professors themselves found a new enterprise with the help of some shareholders" (49). Thus, whatever may have been its imperfections, the article in Le Lycée forced an early decision. The 'director' simply could not accept the thinking of Dumas and Lavallée to which the other professors had been led by the persuasive arguments presented by the chemist. Despite the fact that it was technically his project, by October 11 he was still unable to find the financial support necessary, and he knew that he would not be able to rally teachers to his cause. He was unwilling to take the risk inherent in Lavallée's approach so he simply withdrew his claim.

At Dumas' request Colladon was invited to join the five founders and Gourlier in determining the policies of the new school and organising it

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48. Dubois gave a little more of the aim of the school and referred to it as "une sorte d'Ecole Polytechnique civile". Le Globe, 1828 (8 October).

49. Ibid., 11 October.

(50). A meeting was held immediately in which Lavallée was chosen as director. He was advised to contact Vatimesnil as soon as possible for the authorisation necessary to open a private school, a privilege that was given to the director, not the enterprise. It was a tribute to the interest and courage of Vatimesnil (51) in an unstable political environment that was rapidly worsening, as much as to the fact that Dumas had many well-placed friends (52) that the request was approved after only two months (53). Four days later Lavallée signed an agreement to lease the Hôtel de Juigné for 20 years at 14,000 francs per year (54). Further meetings were held regularly at the home of Olivier. Those in which administrative and legal issues were discussed were dominated by Lavallée

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50. "M. Dumas invited me to assist at preparatory meetings of a school of arts and manufacturers; not wishing to change my citizenship, and unable to teach (at that time) in any University institution, the prospect of giving a course in Paris led me to accept." Letter to Pothier dated 29 November 1886, quoted in Pothier, op.cit.(1-66), p.472. Elsewhere Colladon gave his Protestantism as the block.

51. The Minister exempted the new school from the rétribution scolaire, the per capita government tax on all private schools. The tax was assessed by the next Minister and continued until Dumas had the school transferred from the jurisdiction of the Ministry of Public Instruction to that of Agriculture and Commerce in 1835.

52. "All Dumas' renown and his deep friendship with M. Thenard, who was very powerful in the Councils of the University, were necessary to obtain an authorisation which was so unlikely to be given." Loc.cit. (5-37), p.7.

53. Though approval was given on 23 December 1828, promulgation among the Rectors of the various écoles, facultés, lycées and collèges did not take place until 25 April 1829.

54. Guillet, Léon, Cent Ans de la Vie de l'Ecole Centrale des Arts et Manufactures, 1829-1929, Paris, 1929, p.10. The Juigné mansion was constructed in 1657 and needed extensive interior rebuilding to be useful. It was on the rue de Thorigny in the Marais Quarter, a site which Lavallée had chosen so that the students would not be disturbed by those in the Latin Quarter.

who drew up the Founders' Act (55), but in matters concerned directly with the educational programme, Dumas' contribution made him the central figure. Colladon wrote:

> "I assisted at the preparatory meetings of the founders and there I witnessed the indisputable influence of M. Dumas on his colleagues, even though M. Olivier was ten years his senior and M. Péclet nearly as much." (56)

It was Dumas who collated the thoughts put forward at the meetings, including his own fundamental ideas on industrial education formulated during his five years at the Athénée and the Ecole Polytechnique, and prepared the numerous documents used to advertise the school.

Dumas' experiences at the two institutions is reflected in both the name and the aims of the new school. Its name was given in an early policy decision: The Ecole Centrale des Arts et Manufactures, derived from the original name of the Ecole Polytechnique, i.e. the Ecole Centrale des Travaux Publics. In this way the founders indicated their desire to

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55. It included a contract by which Dumas, Olivier, Péclet and Benoît agreed to teach for 20 years at an annual salary of 3000 francs, to which would be added a share of any profits accruing (11/96 to each professor and the rest to Lavallée). Though the profits in the first year amounted to only 1000 francs compared to an expenditure of 150,000 francs, this rose to 50,000 francs by 1880. The owner, Lavallée, directed the school and its finances and enforced its regulations. It was also his duty to preside over meetings of the Founders Council, which admitted students, nominated teaching personnel and regulated internal discipline. A Council of Studies was formed whose membership consisted of all titular professors, including the founders. Dumas presided over its monthly meetings, in which were discussed curriculum problems and schedules, student standing and advancement, the awarding of diplomas, and, in general, any policies involving studies and discipline. A Conseil de Perfectionnement, a phenomenon common to all advanced schools in France during the 19th century, was established at the outset, but was suppressed in 1831 for financial reasons; its chairman, Chaptal, and 16 members including Brongniart, Thenard, Payen and Arago, were all members of the Société d'Encouragement.

56. Colladon, op.cit.(1-65), p.188.

follow the spirit and format impressed on the older school by Monge, but they also wanted to bring out clearly the basic distinction between the two schools: the one to form engineers for public service, the other to form them for private industry. Dumas emphasised the need for such engineers in the school's first prospectus distributed in April 1829 (57). His views, expressed in beautiful prose, can be reduced to three major points:

1. The success of industry in England was due to the existence of many specialised civil engineers (58), consultants who were willing to enter the profession because it was honourable and lucrative.

2. There were not many of these engineers in France, despite the need, because there was no school to prepare men for such an occupation. Special schools do exist for those interested in the army, navy, public works, law medicine, theology, letters, even commerce.

3. Manufacturers were becoming more aware of this need as they learned that progress in their specialty was being made by those with a basic knowledge of science.

This was the theme that Dumas had emphasised constantly, in his teaching, his textbook and the Annales de l'Industrie. His immersion in it made his task of writing the prospectus much easier. The goals were clearer. For example, in one of the founding documents he wrote:

> "The special aim of the school is to form directors of workshops, manufacturers, civil engineers and construction engineers, and also to give to all those who wish to take part in industrial research the instruction necessary

57. "The authorship of Dumas, who was really the 'minister of external relations' for the Ecole Centrale, can be recognised in [the prospectus]." Loc.cit.(5-44), p.24

58. Dumas used this term because it was clearer to his French readers.

either to appreciate its value or to guide its progress." (59) In the prospectus he added more specific goals. The students were to be encouraged to think in terms of integrating theory and practice. Thus, for example, Dumas noted: "In laboratory research no account is taken of the number of operations, nor of the time taken, nor of the quantity of fuel used, though these various elements are very important for artisans, since they have a great influence on the cost." (60) A second objective was the inculcation in students of a deep awareness of the sense of unity that Dumas believed must exist in engineering. His vision was not impossible of attainment at the time; a chemically trained engineer could gain a profound knowledge of mechanical and construction engineering as well as applied physics. Thus his statement that: "Industrial science is one, and every industrialist must know it in its entirety under penalty of being inferior to the competitor who enters the lists better armed" (61) may be taken literally. When a full three year curriculum was introduced in 1831, all courses were required no matter what sort of engineering a student intended to pursue. This was a valuable approach, especially during the early years of the school's existence, as is evident from the ease with which graduates were able to change from one type of engineering to another in order to fulfill the more urgent needs of the district which they wished to serve (62). Finally, Dumas saw a need to infuse into the

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59. Quoted by Guillet, op.cit.(5-55), p.88.

60. Bibl. de l'Ecole Centrale, Prospectus, p.2.

61. Ibid., p.3.

62. In a letter to Dumas, Arch. Acad. Sci., Fonds Dumas, Carton 16, Dossier Ecole Centrale, a former student, Bouscasse, who had earned a certificate of capacity but not a diploma, had been interested in a career in chemical engineering. Rather than leave the district from which he had come, where no opportunities existed, he built roads, bridges, civic buildings, private homes, etc., and even did some engineering research! He mentioned other students who had also done well after taking up engineering of a sort not related to their interest.

students the positive spirit that progress in industry would be the result of hard work, guided by an understanding of the principles and practices necessary in that industry (63). He was himself an indefatigable worker, so that his own example, his own successes were sufficient evidence of the validity of this principle.

While this is not the place to discuss the advantages of a school of higher education over an institution in which lectures were given without any coordination or sequence, nor would it be useful to my purpose to compare the advantages and disadvantages of public and private institutions, it must be said that Dumas' experience in both situations made it possible for him to draw upon the best features of each of them and fuse them into a system which made the Ecole Centrale a success from the start, in spite of the opposition of a government hostile to liberalising influences, and in the face of two major setbacks, the July Revolution which drastically reduced the number of students who had begun the two year programme on 3 November 1829 (64) and the cholera epidemic of 1832 that nearly took the life of Lavallée and left the school in difficult financial straits for several years. Had it not been for Dumas' efforts, its doors would probably have been closed (65). Despite important financial changes introduced after the Revolution, the school was at best a

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63. Dumas was probably not influenced directly by either Saint Simon (1760-1825) or Auguste Comte (1798-1857). He had already absorbed this spirit in Geneva. Promulgation of his own ideas about work and the importance of industry was facilitated by an environment in which such philosophies could appear.

64. 149 young men entered. So great was the attrition due to the reaction to the Revolution that only 19 received diplomas and 9 certificates of aptitude. This represented about half who finished the course so that about two-thirds did not return.

65. The details were given by Colladon: Bibl. de Genève, Extrait d'une lettre de Mr. Colladon à Mr. Loustau, 25 September 1879, Ms.fr. 3745, fol. 132-33; and op.cit.(1-65), p. 209-10.

marginal business. Not only were the students sent home again, but Lavallée needed a long rest. One of the professors convinced Olivier and Péclet that the financial basis should be changed. On hearing this the director resigned. After speaking with Colladon and another of the professors, Dumas called a meeting of the Council of studies to announce that the three men would offer their services without payment until this new crisis had passed. The others were invited to join them (66). All who were there agreed, but Péclet, Olivier and Raucourt (who had provoked the problem) were not present. Dumas called another meeting, inviting the three to appear or resign. Raucourt failed to appear but the others agreed to the plan and it was presented to Lavallée. The director withdrew his resignation on condition that all other employees be paid, and the Founders Act dissolved. New arrangements were to be made that would allow operation on a year to year basis, with the option that he could sell the school or try to convince the government to run it if he could do so. Not until 1857 was he able to accomplish this, but by then the school was well established and showing a handsome profit. It was given to the government to assure that it would continue in existence, for two of the founders had died by then.

In the new administration set up in 1832, Dumas became president of the Council of Studies, the sole governing body of the Ecole Centrale. In this position, which he maintained except for a brief period until his death, his influence on the school was enormous. It assured that the school, particularly its curriculum, would continue to be guided by his

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66. This letter of convocation written by Dumas indicated that the only business to be discussed at the meeting would be the immediate and long term solutions to the problems that were contained in the letter, published by Pothier, op.cit.(1-66), p.458.

original philosophy developing as the needs of industry changed, but maintaining the spirit of the original Ecole Centrale des Travaux Publics. At first a two year course was planned in which the theoretical bases for the other courses was given: chemistry, physics, descriptive geometry and industrial mechanics. Its success led students to demand that an optional third year be made mandatory since there would not be enough time in the second year to absorb all of the industrial topics that were opened to them during the first year courses (67). Thus the prospectus in 1830 indicated a second year of eight courses and a third of eleven. Some of these were only given during one term, so that the number of lecture hours remained approximately the same. Specialisation was introduced only to the extent that students, when they were accepted, chose to attach themselves to one of four sections: mechanical, civil, chemical or mining engineering. The courses were the same at first, the difference being in the type of laboratory work and mechanical drawing that a student undertook. Eventually the course emphasis also changed, though students still attended all courses. The courses in the second and third year continued to be applied counterparts of the theoretical and descriptive courses taken in the first year, to which were added those on construction of buildings and machines, theory of machines, various courses in industrial natural history, steam engines, iron metallurgy and industrial finance. Over the years some change in the nature and number of these courses were

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67. The four courses each involved 60 lectures, each one and one-half hours long, as well as numerous laboratory and drawing sessions. This meant twelve hours of lecture a week, with the rest of the time spent in the laboratory, mechanical drawing room, study, or conferences with professors, assistant professors or laboratory guides.

made, such as the addition of an important one on railway engineering, the first in the world (68).

Dumas' principal influence on deciding what should be taught was certainly in chemistry. He initiated three courses, general, analytical and industrial chemistry, teaching all of them at first, to establish their spirit and content. Thereafter his own teaching varied from year to year as indicated in Table 5-1 (69). Of the 60 lectures given in the

TABLE 5-1. Courses in Chemistry Taught at the Ecole Centrale by Dumas and his Immediate Successors.

General Chemistry		Analytical Chemistry		Industrial Chemistry	
Dumas	1829-32	Dumas, Bussy	1830-31	Dumas, Bussy	1831-32
Pelouze	1833-35	Dumas	1831-40	Dumas	1832-34
Péligot	1835-43	Dumas, Péligot	1840-43	Dumas, Payen	1834-43
Dumas, Péligot	1843-45	Péligot	1843-65	Payen	1843-65
Dumas, Cahours	1845-49				
Cahours	1849-73				

first General Chemistry course, 22 were devoted to the theoretical aspects contained in the Introduction to the Traité (atomic theory, nomenclature and a general discussion of matter and its physical and chemical properties, especially atomic weights, proportions and equivalents, and to the non-metals) (70); in the next 18 he considered the various metals and their

68. From 1832-1838 it was part of the course Exploitation des Mines. From 1838 it was a separate course.

69. This table was compiled from information given in Guillet, op.cit. (5-55), pp 137 and 141. The other professors were: Antoine Alexandre Brutus Bussy (1794-1882), professor at the Paris Ecole de Pharmacie, who succeeded Dumas at the Athénée when he withdrew in 1829; Théophile Jules Pelouze (1807-1867) who had replaced Despretz as the other répétiteur in chemistry at the Ecole Polytechnique; Eugène Melchior Péligot (1811-1890), a student in the first graduating class of the Ecole Centrale whose interest in chemistry, acquired from Dumas, led him to withdraw after one year to work in the laboratories of the school; Auguste André Thomas Cahours (1813-1891).

70. Non-metals were called metalloids at the time.

compounds; the final 20 initiated the students into the rapidly developing study of organic chemistry. In addition there were 24 laboratory periods, probably lasting about two to three hours each (71). In 1830 he offered his analytical chemistry course for the first time. There were 36 lectures and 30 laboratory periods. Qualitative and quantitative analysis in both mineral chemistry and organic chemistry was included, as well as the principles and practice of vapour density measurement. Dumas was very much involved in organic analysis and its implications at the time. He was in the process of preparing the fifth volume of his Traité, which contained a detailed study of theoretical and practical organic chemistry including a special section on organic analysis. In it he described his procedure for the quantitative determination of nitrogen which was used by most chemists of the time.

Some idea of Dumas' course in industrial chemistry can be gathered from the long outline given in the prospectus for 1829-30. An abbreviated version was given in 1830-31 and repeated the following year:

> "This course will present to students a description and discussion of the procedures in use in the most important industries. It will consist of 60 lectures. The many topics included in this course cannot be listed here. It will be enough to mention glass, pottery, chemicals, gunpowder, soap, paper, sugars, spirits, dyes, leathers, etc., as those with which the professor will be particularly concerned. During the course the students will do the

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71. Ibid., p.149. "The founders of the school were well aware that engineers need to come into contact with materials and the methods for measuring them. Thus from 1829 they organised laboratory activities directed above all to chemistry (the preparation and properties of substances; analysis) and physics (the study of some phenomena, and industrial measurement)." Ibid., p.146. Colladon introduced full scale industrial equipment into his laboratory for student use, very probably the first professor ever to do so. An undated manuscript of Dumas' course made by Cahours, probably in the early 1840s, may be found in several libraries in Paris.

> related drawings. They will also do the analyses and chemical research necessary for understanding the work." (72)

The atlas for the <u>Traité</u> indicates the sort of processes that were studied. Undoubtedly there were also visits to the many local industries to acquire direct experience. An industrial project was required of all candidates for graduation. While a student was obliged to achieve a certain minimum average for his three years at the school in order to become a candidate, the final decision whether a diploma would be given rested wholly with the successful completion of this project (73). The minutes of the Council meeting held on 7 September 1831 in which that regulation was established contain the following information:

> "The students from each specialty will be given a project whose elements and foundations must be established by them within 8 hours (74). This work will be stamped and deposited with the administration. Each student will make a tracing and a copy of his work and will then have one month at the most to study his project, make a fair copy of it and prepare a memoir (75). Then, at the beginning of November, the students will submit their projects in the presence of their fellow students and the professors. During this thesis presentation, lasting one and one-half

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72. Bibl. Ecole Centrale, <u>Prospectus</u>, 1830-31. According to the first prospectus there were to be 100 drawings and 70 laboratory periods of six hours. This was reduced considerably.

73. This procedure was followed until 1862, when the value of the project was reduced to 40% of the total score. The remaining 60% was derived from the average of scores obtained in all courses taken during the three year period. These scores were determined from examinations given in the courses periodically, and at their completion.

74. Each student occupied a separate room during the preparation of the basic report. No assistance was allowed.

75. During this time, free consultation with professors and fellow students was allowed, as well as the use of any books available, but no change could be made in the basic contents of the report deposited. The projects themselves had to be done at the school, but the memoir could be written away from the school.

> to two hours, the professors are free to ask the student questions about the various things that he should have learned in his specialty." (76)

The first chemical project presented was the preparation of a "General and Detailed Plan of a Refinery for Gold and Silver" (77). To obtain a diploma of Civil Engineer required the complete satisfaction of the judges in all tests. A student who partially satisfied the examiners was given a certificate of aptitude. Those who failed could try again at a later date without attending further courses. Only those who had obtained a diploma or certificate were regarded as graduates.

Although Dumas retired from his professorial role in 1849, after firmly establishing the content and direction of all three courses in chemistry (78), his activities on behalf of the school never ceased until his death. He had the pleasure of seeing the new quarters for the school, first occupied in 1884, nearly completed before he died and he left his

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76. Quoted by Guillet. Ibid., p.152. Variations in the procedure were made over the years, for example the date of competition was set at 25 June to 1 August.

77. Among the other projects that year (1832) were: A blast furnace using coke, a water wheel capable of transmitting 60 horsepower to an English forge, and "On a given terrain to construct an Ecole Centrale des Arts et Manufactures for 150 externs". One wonders if the founders were already thinking of some future time when they would be able to move into more suitable quarters! Some later chemical projects: "Considering the existing procedures for making nitric acid and sulphuric acid, can an economically feasible factory be set up for the manufacture of nitric acid based on the oxidation of ammonia"; "Complete Details for the Establishment of a Factory for the Manufacture of Super -phosphates (or Refining Sugar; or for the Electrolysis of ?, etc.)." These projects and memoirs became the property of the school.

78. One is struck by the stability which Dumas had imparted to each of these courses, both by reason of the firm foundation which he gave to it and the outstanding men he chose and carefully groomed to be his successors. Each of them held the Chair to which they had been appointed for a period of more than 20 years!

imprint on the chemistry laboratories constructed, so different from those in which he had been forced to carry out his own research. They were described later:

> "With their forced ventilation, distribution of gas, electricity, compressed air and even hydrogen sulphide, their vast tables of Volvic lava, these immense laboratories assuredly constitute a model which has not found its equal in the other *grandes ecoles*. Without doubt their creation was influenced by the final advice of the eminent, learned founder of the school, J. B. Dumas. 230 [students] can do their laboratory work there easily." (79)

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79. *Ibid.*, p.204.

CHAPTER 6

DUMAS AND THE ETHERINE THEORY

"Thus it was quite necessary to adopt the only hypothesis which could reconcile these contradictory phenomena (1). We were aware of that hypothesis from the beginning of these investigations and had been struck by its agreement with our results; but we did not dare to rely on it until we had found that it was supported by all the facts that we have been able to gather. It consists in supposing that the compound ethers we are examining are formed from an oxy-acid and sulphuric ether. If potas~~sium~~h removes alcohol from the compound ether, it is because the nascent sulphuric ether takes up the water required to become alcohol again. ... The most immediate result of our research consists in regarding sulphuric ether as a salt-making base and alcohol as a hydrate of ether. ... But there is another more general way of envisaging the composition of these substances. *It consists in attributing the alkaline character to the bicarboned hydrogen itself*, so that we can include in a single glance the most varied compounds of this type; we attach some importance to this point of view and its simplicity leads us to give it preference over the one we have indicated." (2)

Dumas was a central figure in the accelerated development of organic chemistry during the fourth decade of the nineteenth century, partly on the strength of his efforts in the laboratory, but much more because of the theoretical conclusions that he drew from his own observations combined with reflection on those of others. As a pharmacy student in Geneva he had found an interest in organic chemistry that had been encouraged by de Saussure. For several years other activities permitted a very limited participation in related research, but eventually he was able to resume in Paris the study of ethers that he had begun in Switzerland. Aware of the practical difficulties involved, he invited Polydore Boullay to join him in this endeavour. By the end of 1827 they had gathered enough evidence to enable Dumas to announce his etherine theory to the Academy of Sciences in Paris. In essence his memoir focused attention on bicarboned hydrogen as the principle that was characteristic of all ethers in the same way that ammonia was the principle of salts of the volatile alkali. The simplicity of his theory became evident when he placed rational formulas for corresponding ethers and ammonia salts beside each other in a table (3). The etherine theory soon

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1. The contradiction referred to was between the composition of oxy-ethers, as suggested by their reaction with alkalis, and that found by analysing them. This brief explanation will be discussed at greater length later in this chapter.

2. This quotation was taken from Dumas and Boullay, "Mémoire sur les Ethers Composés", Ann. Chim. Phys., 37 (1828), 15-53 (17-18; 41; 41-42). It was read to the Academy of Sciences on 31 December 1827. In this chapter it will be referred to as the December Memoir. The first part, "Mémoire sur la Formation de l'Ether Sulfurique", Ibid., 36 (1827), 294-310, was read on 27 August 1827 and will be designated as the August Memoir. Terms will be used in my thesis with the sense that they were given at the time, which should be clearly understood. The modern name for sulphuric ether is diethyl ether, $(C_2H_5)_2O$. The term ether or compound ether described then what are now called esters (a word introduced by Gmelin in 1848). A hydracid was a compound of a non-metal with hydrogen. An oxyacid was a compound of a non-metal with oxygen.

3. December Memoir, 49-50.

became the reference point for many experimental investigations undertaken to further verify or to disprove Dumas' claims. Despite strong opposition, especially from Berzelius and Liebig, who derived a theory of hydrocarbon radicals from it, the theory spawned many new compounds as well as several other theories formulated by Dumas. This discussion of the derivation of the etherine theory, Dumas' adherence to it, his rejection of the theory of hydrocarbon radicals, the resulting sometimes acrimonious debates with Liebig and the surprising conclusion to ten years of debate is intended to show the influence of Dumas and his theory on organic chemistry during this period.

In a long and detailed description of ethers in his Traité Dumas included much historical data. As he indicated, several of these compounds had been known for many years (4) before Thenard's important research was published in 1807 and 1809 (5). A careful examination of all the ethers then known led Thenard to classify them into three groups. He found that alcohol would react with:

1. an oxyacid, without combination occurring, forming, for example, sulphuric ether (6);

2. an oxyacid, by simply combining with it to form an oxyether, for example, acetic ether;

3. a hydracid, by combining with it, losing water to form an anhydrous ether, for example, hydrochloric ether.

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4. Acetic ether was discovered by Lauraguais in 1759 and nitric ether by Paracelsus.

5. Mem. Soc. d'Arcueil, Vol. 1, pp. 73-114, 115-34, 135-39, 140-60, 337-58, 359-69; Vol. 2, pp. 5-22, 23-41, 492-95.

6. P.F.G. Boullay, father of Polydore, was well known for his work on ethers. He had shown that ethers formed in this manner from sulphuric, phosphoric and arsenic acids were identical, as Dumas noted, December Memoir, 15. This ether came to be known as sulphuric ether.

Thenard's theory for the constitution of oxyethers was based on his analyses (7) and on the following experimental observation: An aqueous solution of potash reacts with any oxyether to form a salt and release alcohol. For Thenard it was simply a replacement reaction in conformity with the law of Berthollet, and alcohol should be classed with other oxides that neutralise acids by simple combination.

By the time Dumas had begun his experiments on ethers in Geneva (8), analytical procedures had already improved considerably. His own analysis of oxyethers led him to question Thenard's theory. However, the difficulties in the preparation, isolation and purification of the few with which he could work, added to the imperfections that still existed in analytical methods, forced him to delay any serious investigation of the question for a time (9). In the final part of his three year course at the Athénée in 1826-27, Dumas lectured on organic chemistry and its applications (10). During the previous

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7. Both the theory and practice of organic analysis, in its infancy at the time, produced Thenard's values for the percent of carbon that were somewhat low and therefore supported his hypothesis. For the same reasons, the work of P.F.G. Boullay 'confirmed' Thenard's view, and it was generally accepted by chemists.

8. See Chapter 1. In evidence that he was working with ethers in 1821, a sheet of paper dated 2 March 1821 bears calculations used by him to determine the liquid density of nitric ether from laboratory data. Arch. Acad. Sci., Fonds Dumas, Carton 7, Dossier "Ether Nitrique". On the same day he worked out calculations for that of benzoic acid on several sheets of paper. Ibid., Carton 9, Dossier "J.B. Dumas, Notes d'Expériences".

9. Hofmann, op.cit.(1-6), vii, wrote: "He [Dumas] resolved to wait for more favourable circumstances in order to reconstruct this work on a broader foundation, communicating to the Société de Physique for the present only the first results of his experiments in which he had been engaged for the better part of the year 1819 and 1820 and insisting more especially on the probability of these bodies being compounds of ether and not of alcohol with anhydrous acids." There is no indication in the minutes of the Society that it was read.

10. In addition to the isolation and analysis of organic compounds, this course probably included some discussion of organic acids, alcohol, ethers, sugars, oils, fats, soaps, and miscellaneous compounds that were known at the time, as well as foods, drinks, fibres and fabrics, wood, paper, dyes and dyeing, resins, tanning, and other commercial products or processes.

summer he had gathered information for several commercial processes, among them the preparation of sulphuric ether. Some years earlier, P.F.G. Boullay had brought about a revolution in the manufacture of this ether by showing how the procedure could be carried out continuously (11). Doubtless in his conversations with Boullay at meetings of the Société d'Encouragement Dumas learned of the latest developments in the process. Very likely he visited Boullay's pharmacy on several occasions, and may have met Boullay's son, Polydore, there. Dumas was well aware that the mechanism (12) for the reaction between alcohol and sulphuric acid was at best debatable. Its discovery would provide yet another example of how scientific research could be useful to industry. By this time analytical techniques had improved immensely, so Dumas had good reasons for resuming his research on ethers and etherification. Polydore Boullay, his préparateur at the Athénée (13) who had just finished research on double iodides, assisted him in this work. Together they verified what Dumas had found in Geneva. As he observed:

> "The elementary analysis of those ethers already mentioned are not in accord with this [Thenard's] manner of regarding them. Oxalic ether, for example, contains

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11. Since the sulphuric acid remained intact at the end of the process, all that was required was a method for adding alcohol at the same rate as the ether was formed. From this point forward development depended on improving equipment and was rapid. As Dumas indicated in 1835: "Since, to my knowledge, the present improved process has not been put into use on a large scale, I will describe the apparatus used. ..." Traité, Vol. 5, p.499. It was Dumas who described Boullay's idea as a revolutionary one. Ibid., p.509.

12. The term mechanism was not used in Dumas' time. The general term 'theory' was sometimes used, or long discussions were necessary, but the idea was clear: A series of steps describing the over-all reaction. Dumas used the expression "phases de l'éthérification". Ibid., 505.

13. "P. Boullay and [Félix Henri] Boudet [1806-1878], both sons of the foremost pharmacists of Paris, were accepted by him [Dumas] as préparateurs for his course at the Athénée." Gen. Dumas, op. cit. (1-3), p. 70

> almost as much carbon as does alcohol, though oxalic acid contains much less. Acetic ether has more carbon than alcohol has, even though the carbon content of acetic acid is lower than that of alcohol." (14)

To demonstrate the validity of these remarks, a table has been prepared (Table 6-1), comparing the percent of carbon in each of the two oxyacids discussed by Dumas with that in their ethers and in alcohol. Dumas' table of atomic weights and the formulas that he gave or would have given to the compounds at the time were used to determine the values.

TABLE 6-1. The Percentage of Carbon in Two Acids, their Ethers and Alcohol.

	Acid	Ether		Alcohol
		Thenard	Dumas	
Oxalic	33.4	44.0	49.4	52.3
Acetic	47.2	49.6	54.7	52.3

For Thenard's theory to be correct, it was necessary for the percent of carbon in the ether to be between the values for the acid and the alcohol. Since Dumas had shown that this was not true for the acetic ether, Thenard's theory could no longer be accepted. The proximity of the values (54.7 and 52.3) suggests Dumas' uncertainty and his wish to set aside this research until analytical techniques had improved. Although good analyses might have been sufficient evidence if he were established in his career, he wanted the absolute corroboration that was possible. When he returned to the work in Paris there was even more reason for having this proof. He was not just

14. December Memoir, 16 (my italics). His reasoning could not be used with nitric ether because the acid contained no carbon; nor was it useful with benzoic ether because of its high 'atomic' weight. Following the convention used by Kapoor, op.cit.(1-101), 34 (note 102), I have attributed Dumas' memoirs with Boullay to Dumas only, but with the added confidence that most of the ideas did originate with him, including the fundamental one upon which they were based.

rejecting an established theory. It was one that had been formulated by the influential chemist with whom he was serving as répétiteur at the Ecole Polytechnique, one in whom he frequently confided. Moreover he was working with Polydore Boullay, whose father had 'confirmed' Thenard's theory. Although he had found a way of modifying the theory successfully, he could not publish it without making a careful analysis of the various compounds involved and offering a plausible mechanism for the reaction.

Since a knowledge of the correct composition of alcohol and sulphuric ether was essential to any ether theory, his first task was the verification of the values found by de Saussure (15) and Gay Lussac (16). After several analyses, he was able to conclude:

> "We will consider as well proven that alcohol consists of one volume of bicarboned hydrogen, combined with one volume of water vapour, as M. Gay-Lussac has established ... it is no less evident that pure ether is formed from one volume of bicarboned hydrogen combined with one-half volume of water vapour ... Thus we regard as certain that
> alcohol is represented by $H^2C^2 + \frac{1}{2}\,\dot{H}H$;
> sulphuric ether by $2\,H^2C^2 + \frac{1}{2}\,\dot{H}H$." (17)

In the reaction between sulphuric acid and alcohol it was clear that the latter disappeared and sulphuric ether was formed. The relationship between them suggested that water was released in the process. The discovery that other acids having a strong affinity for water formed the same ether when they reacted with alcohol seemed to leave no doubt that the reaction was

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15. De Saussure determined the percentage composition and from it concluded that alcohol and sulphuric ether were "compounds of water and olefiant gas reduced to their elements". Ann. Chim., 89 (1814), 273-305.

16. Ibid., 91 (1814), 5-160. Gay-Lussac used vapour density measurements to confirm the theory suggested by de Saussure.

17. August Memoir, 298; 299; 309. For a discussion of the formulas and their meaning see pp. 156-57 and 159-61. To avoid writing $\frac{1}{2}$ Dumas doubled the second formula, which should have been $2H^2C^2 + \frac{1}{2}\,\dot{H}H$. The dot represented oxygen in Berzelius' notation.

simple dehydration (18). But there were other reactions that occurred. Fourcroy and Vauquelin had observed that sulphurous acid and 'sweet oil of wine' were formed at a higher temperature (19). Dabit had discovered that sulphovinic acid was a product (20). Dumas was satisfied that these reactions were quite distinct from the one in which sulphuric ether was formed and not essential to its formation. Nor did he consider that those reactions had anything to do with a theory of etherification that he had formed. Though most of the August Memoir was devoted to sweet oil of wine and sulphovinic acid, it is significant that it was entitled: "On the Formation of Sulphuric Ether". Some time between the reading of the memoir and its publication, however, he made a discovery that changed everything, and the formation of sulphovinic acid took on much greater importance.

Towards the end of the reaction between sulphuric acid and alcohol a mixture of oils remains. He partially distilled such a mixture, then redistilled it with calcium chloride and potash isolating a substance that he called sweet oil of wine, in the belief that he had obtained the true sweet oil. It was a high-boiling substance with a liquid density of 0.9174 at 10.5°C. Using normal analytical procedures, he found that it was a hydrocarbon composed of four volumes of carbon and three volumes of hydrogen to

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18. As Dumas noted, P.F.G. Boullay had shown that phosphoric and arsenic acids react with alcohol to form the same ether. Later, René DesFosses found that fluoboric acid acted in the same mammer. Traité, Vol. 5, pp. 504-05.

19. Ann. Chim., 23 (1797), 203.

20. Ibid., 34 (1800), 289-305; 43 (1802), 101-12. Dumas remarked on the discovery by Heinrich August Vogel that sulphovinic acid was present to the greatest extent just before sulphurous acid was evolved, that it was formed under the same conditions as was sulphuric ether. August Memoir, 305.

which he assigned the formula C^4H^3 (C = 6) (21). Thus he could say:

> "It will become apparent that this composition is a necessary consequence of the type of reaction in which the sweet oil is produced; the experiments that follow will give the clearest confirmation of the composition indicated while at the same time a theory will be put forward that makes that composition inevitable." (22)

This was a strong statement, but he undoubtedly had the support of Gay-Lussac who had suggested earlier that sulphovinic acid was a compound of hyposulphuric acid with some plant substance. Dumas had every reason to believe that the latter was his sweet oil of wine, for it was to be expected that the acid, $2C^4H^3.S^2O^5$ (23) would decompose when heated (the "type of reaction"

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21. Although a polymer having this formula could have existed, the oxidising conditions in this instance would make it doubtful. Indeed, Partington, op.cit.(2-17), p.349, mentioned that P. Claesson, J. prakt. Chem., 127 (1879), 231, did find a polymer, but it was of ethylene (C_2H_4, C = 12), rather than C^4H^3, C = 6). On the other hand, it is difficult to see how Dumas and Boullay could have made an error of 4 % in a routine determination of the hydrogen in the oil, when they observed in their description of analyses of alcohol and sulphuric ether in the same memoir that 0.2 to 0.4 % was "a little more hydrogen than calculation indicates". August Memoir, 298. Kapoor, op.cit.(1-101), 35, has stated: "Two *assumptions* were made as to its composition: firstly, that it was a hydrocarbon, and secondly, that it contained 3 volumes of hydrogen combined to 4 volumes of carbon. From this *arbitrary hypothesis* [109] the theoretical density of the hydrocarbon, given the accepted values for carbon and hydrogen, was calculated, and shown to agree with the results of the direct experimental determination." (my italics). It should be noted that *analyses*, not *assumptions* were involved. Dumas wrote: "Sweet oil of wine is only a hydrocarbon; but it differs from all others which have been analysed until now by the proportion of its principles. Indeed we have found this substance formed of ..." August Memoir, 300. He gave figures for two analyses and compared them to figures calculated from atomic weights assuming the formula C_4H_3. Moreover, though it may seem strange, there is no indication in the memoir that the vapour density of the sweet oil was determined. Obviously Kapoor's derogatory comment in note 109 that Dumas only paid lip-service to empiricism is based on false premises. Unfortunately his discussion of the August Memoir, loc.cit., 34-38, suffers from several other serious errors and misinterpretations.

22. August Memoir, p.300.

23. Dots will be used in these formulas instead of + signs to indicate that the two parts are bound together and to avoid confusion in writing (cont.)

to which he referred) giving the sweet oil, sulphurous acid and sulphuric acid. To establish this, he prepared and analysed several salts of the acid. These analyses made it possible for him to assign formulas to the sulphovinates like that of the barium salt: $BaO.S^2O^5.2C^4H^3.5H^2O$ (24). Not only did this establish a clear link with sweet oil of wine, but it also assured the validity of his formula for sulphovinic acid, whose formation during the reaction of sulphuric acid with alcohol he could now represent as follows:

sulphuric acid	+	alcohol	=	sulphovinic acid	+	water formed	+	water released	
2 at.		4 vol.		1 at.		2 vol.		4 vol.	
$2\ SO^3$	+	$2\ C^4H^4.H^2O$	=	$S^2O^5.2C^4H^3$	+	H^2O	+	$2\ H^2O$	(25)

While he was still pursuing these studies, research done by Faraday (26) and Henry Hennell (d. 1842) (27) was published. Faraday had found that

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23. (cont.) equations. To avoid another problem raised by this symbolism numbers will be attached when they apply to part of the compound only and detached when they apply to the whole compound. Thus $2C^4H^4.H^2O$ means two atoms of C^4H^4 and one of H^2O; $2\ C^4H^4.H^2O$ means two atoms of $C^4H^4.H^2O$.

24. Water was determined by vacuum drying at 160°C; barium sulphate by heating to red heat; carbon and hydrogen by heating with copper oxide in the usual manner. He did not indicate how the sulphurous acid was determined, but it could not have been by subtraction since separate samples were used for the various determinations.

25. Ibid., p.305. Dumas gave formulas for the sulphuric acid and sulphovinic acid only, using the dot notation of Berzelius and dividing reactants from products by a vertical line rather than an equals sign. The amounts were given in the units indicated.

26. Phil. Trans., 116 (1826), Part II, 140-62. The article also appeared in the Annales de Chimie et de Physique, but Dumas had access to the Philosophical Transactions.

27. Ibid., Part III, 240. Dumas wrote the following description of the work: "In addition to analyses that were evidently inexact, M. Hennell's note contains conclusions that we cannot discuss because we have not understood them, no doubt because information is lacking on procedures or products." August Memoir, 307.

napthalene reacted with sulphuric acid to form a compound in which the latter was only half neutralised (28). He pointed out that Hennell had already discovered a similar reaction between sulphuric acid and olefiant gas, soon to be published. Each author envisaged the reaction as simple combination of the two compounds. Hennell would have given the formula $C_2H_4.SO_3$ to his, using Faraday's "proportional numbers". Using the oxygen theory of acids, then generally accepted, one finds a clear difference in the amount of water present as such in Dumas' formula for barium sulphovinate (note 24) and that of Hennell: $BaO.2SO^3.2C^4H^4.4H^2O$ (written as Dumas would have written it). The former contained 20.4% water, the latter 16.3%. On this basis dehydration should have decided which approach was correct, but only 19% of the water was evolved by heating in a vacuum, so according to Dumas the matter remained unsettled (29). Yet all of the experimental evidence mentioned seemed to favour Gay-Lussac's view that sulphovinic acid contained hyposulphuric acid and a plant substance, apparently Dumas' sweet oil, C^4H^3. Then Dumas added:

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28. He gave "proportions" for the barium salt corresponding to the formula $BaO.2SO^3.C^{20}H^8$ (Ba = 70, O = 8, S = 16, C = 6, H = 1), from which his formula for the acid in modern terms would be $C_{10}H_8.SO_3$, which is correct but not for the right reason. The modern interpretation depends on the hydrogen theory of acids: $C_{10}H_8 + H_2SO_4 = C_{10}H_7.SO_3.H + H_2O$. One of the two acid hydrogen atoms remains, accounting for the acid properties of the new compound, naphthalene sulphonic acid, which Faraday called sulpho-naphthalic acid.

29. The modern formula for anhydrous barium sulphovinate (barium ethyl sulphate) is $Ba(C_2H_5)_2(SO_4)_2$. Its trihydrate would have exactly the same composition as those already given, but only 12.2% of its weight is water. If it were a pentahydrate, however, dehydration would remove 18.9% of the weight! Dumas observed that the dry solid became pasty if heating was continued. Undoubtedly this was caused by the formation of sulphuric acid as the sulphovinic acid decomposed, giving off ethylene (C_2H_4). This same sulphuric acid may explain why Dumas obtained C^4H^3 (C = 6) in his analysis of the sulphovinates. Enough water produced in the copper oxide oxidation of the compound was absorbed by this sulphuric acid to form the monohydrate of the acid, stable at the temperature involved.

> "In the meantime, some new facts, observed since we read this memoir to the Academy, suggest that we leave the choice between the two hypotheses in doubt. These new facts will be presented and discussed in a memoir soon to follow this one." (30)

These "facts" changed the whole thrust of Dumas' thinking. Before they are examined and the change discussed, however, a study of his initial correction of Thenard's theory of oxy-ethers is necessary.

The results of Dumas' preliminary study in Geneva had already given him a possible alternative. To test it, he undertook a careful purification and analysis of four ethers formed by reaction of nitric, acetic, benzoic and oxalic acids, as well as the three organic acids themselves. He also determined the vapour densities and endeavoured to find the acid to base ratio. Finally he studied the reaction of the ethers with potash. The data gathered led him to write:

> "It was necessary for us to adopt the only hypothesis which could reconcile the contradictory phenomena. That hypothesis occurred to us at the beginning of this research, and we have been struck by its agreement with our results (31).

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30. August Memoir, 309.

31. Kapoor, op.cit.(1-101), 38 (note 118), used this statement to question Dumas' devotion to empiricism, but the French chemist was dedicated to neither pure empiricism nor to pure Baconian induction. In most of his work, probably all of it, he used what is now called hypothetico-inductivism. This was particularly apparent in the work to which Kapoor referred. Dumas began experimentation with ethers in Geneva, first by isolating and analysing them, to the best of his ability. This led him to a study of the work done by other chemists, including Thenard, whose hypothesis for the formation of ethers had been generally accepted. His research presented him with data which seemed to be inconsistent with Thenard's hypothesis and he conceived another that seemed more consistent. For reasons already discussed, it was at least six years before he was able to obtain the empirical evidence needed to verify his hypothesis. This said, two points should be noted: The real value of his hypothesis lay precisely in its empirical character, in that it opened the way for new discoveries in the laboratory; his ability to adapt to unexpected results in the laboratory is a clear indication of his regard for experimental evidence, as will be seen later in this discussion.

> ... It consists in supposing that the compound ethers which we have examined are formed from an oxyacid and sulphuric ether. If alcohol is obtained through the action of potash on the ether it is because the nascent sulphuric ether reacts with the water necessary to change it into alcohol again. The alcohol and sulphuric ether are presented here from a new and singular viewpoint ..." (32)

What was "new and singular" was not the view that alcohol was a hydrate of sulphuric ether, but that it was unlike the hydrates of mineral substances. In general, water in hydrates was held loosely; thus it could be removed or restored without great changes in properties and in conditions that were not very severe. Not only was it difficult to deprive alcohol of its water of hydration, but its properties were considerably different from those of sulphuric ether. Furthermore, the ether had never been successfully hydrated. Thus when Thenard had obtained alcohol on reacting ethers with alkalis, he was led to assume that alcohol was present as such in compound ethers. But Dumas' analyses of ethers had shown him that this could not be true, that sulphuric ether, not alcohol, was the base that combined with acids to form the compound ethers. If this were true, however, how was alcohol formed in the reaction with alkalis, since sulphuric ether had never been made to combine with water? Dumas' answer was that the sulphuric ether was in a different condition when it was freshly released by the alkali, that in this "nascent" state it was able to react with water, a property that it did not normally have. This too was "new and singular". As Dumas wrote: "It promises to shed a great light on various phenomena of organic chemistry that are still obscure." (33)

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32. December Memoir, 17-18.

33. Ibid., 18. It is apparent that Dumas not only appreciated the importance of reaction mechanisms, but that he also realised to some extent the existence of intermediate reacting species.

Once he could assume the existence of a reacting species that had temporary properties, he could extend the notion. He was led to do this when an unexpected product was formed in the course of a reaction that had been undertaken to verify his ether hypothesis. Knowing the composition of the reactants, he could have been satisfied that his hypothesis had been proven by analysis and vapour density measurement of the compound ethers. But a persistent doubt would have remained, because he had not established a quantitative relationship between the compounds as parts of the compound ethers. One way to do this was to determine the internal acid-base ratio, a method that was easy when applied to nitric ether, but could not be used for the ethers of the organic acids (34). Another approach, the one he dedided to use, was to decompose the ether into its component acid and base and compare the weights of the products with that of the ether after analysing them. Decomposition of oxalic ether was accomplished by reaction with alkali, as Thenard had done. Then Dumas measured the weight of oxalic acid formed by precipitating the calcium salt, calcining, reacting with sulphuric acid and weighing the sulphate. The liquid obtained in the initial reaction was distilled and the weight of alcohol determined from the weight and density of the distillate (a mixture of water and alcohol). He found that the sum of the weights of the acid and alcohol formed exceeded the weight of the original ether by an amount just equal to the weight of water needed to convert sulphuric ether into alcohol. Though he was unable to extend this procedure to the ethers of acetic and benzoic acids (35), he had enough indirect

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34. Since there was no carbon in the nitric acid or nitrogen in the base, the acid-base ratio could be determined from the original nitrogen-carbon ratio. Since the other acids contained the same elements as the base, no such internal method of comparison was possible.

35. He could not find a completely insoluble salt of these acids.

evidence to be firmly convinced of the validity of his hypothesis. Though direct evidence was not necessary, it would remove the last doubt. Apart from this obvious value, he may have been drawn to seek direct proof because of the difference in opinion that existed over the composition of sulphovinic acid. He may have tried to react solid alkalis with the dry ether without success, but if so he soon turned to ammonia, the 'volatile alkali', which did react easily. For his theory to be correct, when dry ammonia gas, a base, reacted for example with dry oxalic ether, a neutral liquid, the ammonia should have displaced liquid sulphuric ether, also a base, and form solid oxalate of ammonia (36). In fact, a white precipitate was formed. In describing the experiment, Dumas made no attempt to conceal his "great astonishment" that the liquid remaining was not sulphuric ether but alcohol. Furthermore, to his "great surprise", only half as much alcohol was formed as should have been if any were formed at all. The importance of the second observation cannot be overestimated (37), for Dumas wrote:

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36. Dumas could have written the following equation, though he did not:

$$4C^2H^2.H^2O.C^4O^3 + 2\,NH^3 = 2NH^3.C^4O^3 + 4C^2H^2.H^2O$$

oxalic ether + ammonia = oxalate of ammonia + sulphuric ether

37. Kapoor seems to have missed the significance of this second point, for he does not mention it in his narration of the incident. Loc.cit.(6-31), 38-44. He discussed at length from a philosophical point of view why Dumas should have abandoned his hypothesis as soon as he observed the formation of alcohol, since this was the very evidence he would have sought had he been trying to prove Thenard's theory rather than his own. Not only did the formation of half the required amount of alcohol allow another interpretation, however, but it demanded one. Kapoor's confusion may have stemmed from a statement made by Dumas when describing the trial experiment that demonstrated this point: "An undetermined quantity of oxalic ether, through which was passed a current of ammonia gas, was soon changed entirely into a white salt which we could only regard (nous devions regarder) as oxalate of ammonia." December Memoir, 36. Dumas' subsequent discussion left no doubt that this was an expectation that was never fulfilled.

> "In reflecting on these singular facts, convinced as we were of the precision of our preceding experiments, we immediately concluded that the ammonia, in reacting with the oxalic ether, formed a salt composed of all of the oxalic acid, half of the bicarboned hydrogen and ammonia, while the other half of the bicarboned hydrogen, united with water, formed alcohol." (38)

Dumas' bias in favour of his ether theory, which he considered to be well substantiated, may account for the important observation that he made concerning the quantity of alcohol formed. His explanation for the observations led him to a modification of the theory that made it much more general and useful. From the composition that he assigned to the white substance formed, he was able to see that ammonia had replaced half of the bicarboned hydrogen in the original ether (see note 38), instead of replacing the sulphuric ether that he had supposed was present as a unit. Freed from the necessity of concentrating on sulphuric ether, he was now able to focus his attention on bicarboned hydrogen. The consequences were immediately evident, quite striking even at that time, but destined to have a far greater effect on the development of organic chemistry than Dumas himself could possibly have imagined. His announcement is almost understated:

> "But there is another, more general manner of envisaging the composition of these substances. It consists in attributing the alkaline character to the bicarboned hydrogen itself, so that we can include in a single glance the most varied compounds of this type; we attach some importance to this point of view, and its simplicity leads us to give it preference over the one we have indicated." (39)

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38. Ibid., 37. The following equation (not written by Dumas) should be compared with the equation in note 36:

$$4C^2H^2.H^2O.C^4O^3 + NH^3 = 2C^2H^2.NH^3.C^4O^3 + 2C^2H^2.H^2O$$

oxalic ether + ammonia = oxalovinate of ammonia + alcohol

39. Ibid., 41

Immediately before making this statement, he had mentioned almost in passing that the compound ethers studied in the memoir could be considered as compounds of sulphuric ether. Throughout the rest of the memoir he consistently referred to the compound ethers as compounds of bicarboned hydrogen. He drew analogies between the hydrocarbon and ammonia attempting to show that the former would be a strong base if it were soluble in water, though finally he found it necessary to fall back almost completely on its power to neutralise acids:

> "Nevertheless we dare to imagine that the opinion discussed here will be accepted; because isn't the best of all the properties by which bases are identified, the ability to destroy acid characteristics in substances? And could anyone name many salts that are more evidently neutral than the ethers?" (40)

The other most evident indication was the analogy between the composition of its compounds and those of ammonia. Formulas for several ethers are given in Table 6-2, with those of their ammonia analogues. The substances in brackets are included for comparison. Dumas used two-volume formulas for

TABLE 6-2. Dumas' Formulas for some Ethers and their Ammonia Analogues.

Name of Ether	Bicarboned Hydrogen			Ammonia		
	Base	Acid	Water	Base	Acid	Water
(Base)	$2C^2H^2$	-	-	NH^3	-	-
(Sulphuric ether)	$4C^2H^2$	-	H^2O	-	-	-
(Alcohol)	$4C^2H^2$		$2H^2O$	NH^3	-	$2H^2O$
Hydrochlorate	$2C^2H^2$	2HCl	-	NH^3	2HCl	-
Hyponitrite	$4C^2H^2$	N^2O^3	H^2O	$2NH^3$	N^2O^3	H^2O
Bicarbonate	$4C^2H^2$	4CO	H^2O	$2NH^3$	4CO	H^2O
Bisulphate	$4C^2H^2$	$2SO^3$	-	$2NH^3$	$2SO^3$	-

the ethers of they hydracids and four-volume formulas for the others. In this memoir lies the key to the general adoption of four-volume formulas.

40. Ibid., 44.

It has been shown that the one-volume formula for sulphuric ether was $2C^2H^2.\frac{1}{2}H^2O$. (41) The simplest formula that could be written without fractions for the hyponitrite on Dumas' assumption that all oxyethers contained water as such (42) was $4C^2H^2.H^2O.N^2O^3$. As he indicated, this was a four-volume formula. Clearly if a molecular formula showing no arrangement were used ($C^8H^{10}N^2O^4$) it could be reduced to a two-volume formula ($C^4H^5NO^2$). But as long as he insisted on the presence of water as such, the four-volume formula was necessary. Assuming that the formulas used were correct, the number of atoms in a four-volume formula could always be divided by two to give formulas that were in accord with a hydrogen theory of acids, as Charles Frédéric Gerhardt (1816-1856) did much later (43). Such a change could only be made when bicarboned hydrogen ceased to be the cornerstone of the ether theory.

Dumas found confirmation for his work in two other sources, the work of Chevreul on fats (44), and alcoholic fermentation, the first genuine,

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41. See Chapter 4, pp. 159-60. Two volumes of ammonia were produced from one of nitrogen, so NH^3 was a two volume formula.

42. December Memoir, 43. In his chart Dumas gave formulas for bisulphates and binoxalates of ammonia and bicarboned hydrogen without water but this was because the quantities were unknown at the time. All should have had $2\ H^2O$ without considering water of hydration. Bisulphate of bicarboned hydrogen was the new name he gave to sulphovinic acid and the new compound that would have been called oxalovinic acid was christened binoxalate of bicarboned hydrogen.

43. Thus $4C^2H^2.N^2O^3.H^2O$ (C = 6) became $C_2H_5NO_2$ (C = 12). Gerhardt's work will be discussed in Chapter 10.

44. Kapoor, op.cit.(1-10), 33-34, briefly discusses the part played by Chevreul in the development of Dumas' ether theory. Chevreul made many interesting comments about the relationship between fats and ethers in his Recherches Chimiques sur les Corps Gras, Paris, 1823, a summary of his earlier work, some unpublished, and in Considérations Générales sur l'Analyse Organique et sur ses Applications, Paris, 1824. Dumas noted later: "M. Chevreul, in establishing that fats can be regarded as anhydrous ethers, and ordinary ethers as salts of a hydrocarbon, has shown that he has not scorned this kind of theorising." Ann. Chim. Phys., 47 (1831), 326. But Chevreul had worked only on fats, not the lighter ethers and his comparison was speculative.

the second illusory. He was able to point to a strong parallel between ethers and fats: both were composed of an organic base and an acid; both were decomposed by alkalis releasing the base which then combined with water to form a compound. While Chevreul had been aware of other aspects of the relationship between fats and ethers, Dumas' research had shown the exact parallel between the reaction of alkalis with fats and with ethers. This parallel fully satisfied him that fats were ethers (45). Several prominent chemists, including Dumas himself (46) had found that "anhydrous sugar" was composed of 6 volumes of carbon vapour, 5 volumes of hydrogen and 2½ volumes of oxygen (47). This analysis was inconsistent with the composition of a compound formed from simple addition of alcohol and carbonic acid as suggested by Gay-Lussac in his theory of fermentation, but it specified exactly a compound of sulphuric ether and carbonic acid (48). Thus, for Dumas, fermentation became simply analogous to the reactions involved in the decomposition of ethers and fats, for in each case water was required as a reactant.(49)

In 1831 Dumas was led to review the whole question of molecular arrangement (50) by three circumstances: 1) his study of oxamide and

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45. "All the chemical characteristics of fats correspond to those which we have recognised in ethers. ... The resemblance leaves nothing to be desired." December Memoir, 45.

46. Gay-Lussac and Thenard, Berzelius and de Saussure. Ibid., 46.

47. $C_6H_{10}O_5$ (C = 12). The simple sugars actually contain one more molecule of water than this. The correct formula would have represented a real difficulty for Dumas' hypothesis.

48. One volume of ether consisted of 4 volumes of carbon vapour, 5 volumes of hydrogen and ½ volume of oxygen; two volumes of carbonic acid consisted of 2 volumes of carbon vapour and 2 volumes of oxygen.

49. The term hydrolysis is now used for this reaction.

50. "Letter from M. Dumas to M. Ampère on Isomerism", Ann. Chim. Phys., 47 (1831), 324-35. After acknowledging that it was Ampère's whole-hearted encouragement that led him to continue his studies of molecular arrangement, Dumas credited Gay-Lussac, Dulong, Chevreul, Faraday, Robiquet and Georges Simon Serullas (1774-1832), for their part in the development of the Ether Theory. It was from the support of such eminent chemists, according to Dumas, that the theory derived its credibility.

urea (51); 2) some antithetical opinions which had been expressed (52); 3) the discovery of the principle of isomerism (53). The Ether Theory had been one of the earliest attempts at a rational interpretation of the relationship existing between the arrangement of atoms in an organic compound and the manner in which it reacts, using principles that went beyond mere elemental analysis (54). Its usefulness encouraged other chemists to think in terms of grouping atoms within formulas (55). For the most part, such attempts were based on the electrochemical theory. Its application to organic chemistry had recently come into question, at least in some quarters, but there was little doubt about Dumas' attitude towards it at this time:

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51. The precipitate formed when dry ammonia gas was passed into anhydrous oxalic ether had been oxamide, which Dumas had studied in detail, Ibid., 44 (1830), 129-43. Of several possible arrangements for oxamide, Dumas chose $C^4O^2H^4N^2$ (C = 6), which best explained its formation ($C^4O^3 + H^6N^2 = H^2O + C^4O^2H^4N^2$). The modern arrangement is yet another step forward ($NH_2.CO.CO.NH_2$ where C = 12). Early in 1828, Wöhler had succeeded in making urea 'artificially' by rearrangement of ammonium cyanate. Dumas, ibid., 273-78, showed that there was an analogical relationship between urea and oxamide, and chose the formula $C^4O^2.2H^4N^2$ (C = 6), double the modern formula for urea.

52. Robiquet rejected any special arrangement of the atoms. Liebig and Wöhler had drawn quite different conclusions from those enuntiated by Dumas.

53. "Since the discovery of isomerism has introduced a new principle into science, one of my concerns from the moment of its inception has been to relate it to the ideas which I have adopted." Ann. Chim. Phys., 47 (1831), 327. Though the phenomenon had already been recognised, the word 'isomer' was not coined until early in 1831 by Berzelius to describe compounds having the same elemental composition, but different properties. Dumas (Ibid., 332-34) discussed several types of 'isomers' for which other words were eventually coined, including allotropes and polymers.

54. Sensing that he was being accused of pulling arrangements out of the air, Dumas pointed out that elemental analysis was very important, but of little value unless "phenomena resulting from the action of heat, or better yet acids or bases, whose influence is very instructive, can be explained." Ibid., 330.

55. Even Robiquet, who maintained that carbon, hydrogen and oxygen were haphazardly arranged in organic compounds, saw the value of attributing the alkalinity of the salifiable organic bases to the presence of ammonia, existing in the compound as such. Ibid., 326-27.

> "Considered from the [electrochemical] point of view, organic compounds are seen only as binary compounds, capable of more or less numerous doublings, following which they correspond to hydrated salts, double salts, simple salts, etc." (56)

Although the concept of isomerism did not provide a positive proof for this viewpoint, neither could it be used against it (57). Given the complexity of even simple organic compounds, several molecular arrangements should have been possible. Most chemists had come to believe that isomers differed in arrangement as well as in properties. Dumas simply extended his ether and electrochemical theories to include isomerism. Since all compounds could be regarded as combinations of various binary groups, he concluded that isomers must only differ from one another in the constitution of these groups. Thus urea ($C^4O^2.2N^2H^4$) and cyanate of ammonia ($C^4ON^2.N^2H^6.H^2O$) were isomers whose properties differed because of quite different molecular arrangements. Indeed it was precisely because of these differences that the nature of the various binary groups in compounds could be discerned, using heat, acids, bases and other reagents.

During the same year Dumas attempted to establish the Ether Theory on a broader base, by undertaking a study of a new hydrocarbon derived from artificial camphor by Karl Friedrich Oppermann (b.1805) (58) to which Dumas

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56. Ibid., 329. This was obviously an adaptation of Berzelius' theory, ~~the development of an idea first suggested by Georg Ernst Stahl (1660-1734) and extended by Lavoisier.~~ Partington, op.cit.(2-17), p.172 outlined Berzelius' four orders of mineral compounds using alum as an example: "First order: potash = potassium + oxygen; sulphuric acid = sulphur + oxygen; second order: sulphate of potash = potash + sulphuric acid; sulphate of alumina = alumina + sulphuric acid; third order: dry alum = sulphate of alumina + sulphate of potash; fourth order: crystal alum = dry alum + water."

57. Dumas emphasised that the two theories were distinct. The Ether Theory did not stand or fall on the validity of isomerism. He regarded the latter as a "necessary phenomenon" given the complexity of organic compounds. Loc.cit.(6-53), 330-31.

58. Ibid., 225-41.

gave the name camphogen ($C^{10}H^8$, C = 6) (59). It was the first of several hydrocarbons that he intended to examine and compare with one another bearing this idea in mind:

> "These hydrocarbons, in effect, play a role analogous to that of cyanogen; they can combine with many substances without undergoing change, thus forming new organic substances, or at least suggesting a way of forming them." (60)

The thrust of his work was the search for analogues of bicarboned hydrogen, from which ethers could be formed, themselves analogous to the ethers of bicarboned hydrogen. In the many memoirs directed to this search, he returned to the ether theory as his reference point, often reviewing its history (61). It was in this light that he examined camphogen, which he

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59. Ibid., 48 (1831), 430. Oppermann, using Liebig's new analytical method (ibid., 47 (1831), 147-97), had obtained percentages which would have given a formula C^5H^8 (C = 12), exactly the same as that of Dumas. However, by his previous analysis of artificial camphor he had obtained the formula $C^{24}H^{36}$.2HCl (this analysis may have been in error) and he seems to have been satisfied with C:H as 2:3 rather than 5:8. He had succeeded in converting the hydrocarbon to the hydrochloride again, so that there was no doubt about the relationship between the two.

60. Ibid., 50 (1832), 182. Cyanogen came to be regarded as a radical in the sense in which it was first used by Louis Bernard Guyton de Morveau (1737-1816) in Obs.Phys., 19 (1782), 370 (See Partington, op.cit.(2-17), p.234), as a group of elements capable of acting as a unit in combining with other elements or groups of elements. The general belief prior to 1830 was that they were capable of independent existence. Although Dumas did not use the word radical in reference to hydrocarbon groups until he published a memoir on analogues of camphor, Ann. Chim. Phys., 50 (1832), 235, there can be little doubt that his thoughts were running in this line at least from the time that he published the ether theory with Boullay. His conclusions, ibid., 37 (1828), 52, make this abundantly clear.

61. Several examples have already been given. The opening sentence in a note on "Various Compounds of a Hydrocarbon", Ibid., 48 (1831), 430-32 was "Some years ago, together with M. Boullay, I published a work on ethers; the object of the principal results contained therein was to establish that bicarboned hydrogen is a base capable of uniting with water and acids."

later showed to be identical in composition with turpentine (62). Because of the relationship between turpentine and ordinary camphor, Dumas classified the simple oxides of various essences as camphors (63), a decision which he regarded as the first step towards organising these complex organic compounds in some simple fashion. Despite this development, and his discovery of some new hydrocarbons (64), he could claim little further confirmation for his theory.

Meanwhile, his interest in the molecular arrangement of sugar had continued. Originally he had viewed sugar simply as carbonic ether, $C^8H^8.H^2O.C^4O^4$. In a memoir read to the Academy on 16 and 31 December 1833 (65), he indicated that with the advent of isomerism, he was prepared to look upon

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62. "Camphogen, like cyanogen, has the property of being oxidisable, and like bicarboned hydrogen, it has the characteristics of a base, capable of saturating acids". Ibid., 430. Initially Dumas assigned to turpentine the same relationship with camphogen as sulphuric ether had to bicarboned hydrogen, because there was good reason to believe that turpentine contained oxygen. This support for the ether theory had to be rejected when, by careful analysis, he determined that camphogen and turpentine were identical in composition. Ibid., 50 (1832), 230-32. But he did show that artificial camphor was the hydrochloride of the base camphogen, and that ordinary camphor and camphoric acid were analogous to the oxides of nitrogen, N_2O and N_2O_5 respectively.

63. "The genus camphor seems to consist of oxides of various hydrocarbons related among themselves by very simple compositional relationships. Indeed, one has $C^{10}H^{10}O^{\frac{1}{2}}$ solid essence of mint, $C^{10}H^8O^{\frac{1}{2}}$ ordinary camphor, $C^{10}H^6O^{\frac{1}{2}}$ solid essence of anise, $C^{10}H^4$ naphthalene. The compound $C^{10}H^8$ is known in the pure state and constitutes common turpentine. On the contrary, the camphor corresponding to napthalene remains undiscovered." Ibid., 235. It is evident that, at the time, this seemed like a very useful open-ended method of classification.

64. Paranaphthalene (anthracene) and idrialene. He also verified certainly the composition of naphthalene, turpentine and essence of citron. A few months later, after careful analysis, he renamed turpentine, to distinguish it from alkaloids, Ibid., 52 (1833) 409. It would now be called camphene, and artificial camphor, camphene hydrochloride. The substance extracted from camphor of citron he called citrene and essence of citron, citrene hydrochloride.

65. Ibid., 54 (1833), 225-47.

sugar as an isomer of carbonic ether. He approached its arrangement from this point of view without success, however. It was then that he decided to attempt preparation of the ether, "since the ether formed must either have special characteristics, or those of sugar itself" (66). An examination of the arrangement of the ether, suggested that it could be formed by direct union of chloroxicarbonic gas (67) with alcohol, with elimination of hydrochloric acid gas (68). The results were unexpected, and eventually gave rise to the discovery of several new compounds (69). Two of these, urethane and oxamethane (names assigned by Dumas), were necessarily involved in the ether theory, which required the presence of water as such, so Dumas formulated them as combinations of an ether and an amide (70). In so doing, he was able to 'save' the theory by including water and bicarbon hydrogen as such. But this representation also gave support to a theory proposed by

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66. Ibid., 226.

67. Phosgene, $COCl_2$.

68. The resulting ether, $2C^8H^8.2H^2O.C^4O^4$ would contain "only half as much carbonic acid as was contained in sugar, but there should be uncommon relationships in their properties". Ibid., 226.

69. Only half of the chlorine was converted to hydrogen chloride. Thus, oxichlorocarbonic ether $C^8H^8.H^2O.\ C^4O^3Cl^2$ (C = 6), i.e. $C_2H_5O.CO.Cl$ (C = 12) was formed instead of carbonic ether $2C^8H^8.2H^2O.C^4O^4$ (C = 6), i.e. 2 $(C_2H_5)_2CO_3$ (C = 12). Similarly he was able to form urethane, $C_2H_5O.CO.NH_2$, (C = 12) and oxamethane, $C_2H_5O.CO.CO.NH_2$ (C = 12). The latter was formed when dry ammonia was passed into dry oxalic ether:
$$2\ C^8H^8.H^2O.C^4O^3 + N^2H^6 = 2\ C^4H^4.NH^3.C^4O^3 + C^8H^8.2H^2O \quad (C = 6)$$
When a strong ammonia solution was used, oxamide was formed:
$$C^8H^8.H^2O.C^4O^3 + N^2H^6 = N^2H^4.C^4O^2 + C^8H^8.2H^2O \quad (C = 6)$$

70. Thus he considered urethane, $C^8H^8.H^2O.C^2O^2.N^2H^4.C^2O$ (C = 6), to be a simple combination of carbonic ether and urea, oxamethane, $C^8H^8.H^2O.C^4O^3.N^2H^4.C^4O^2$ (C = 6), one ofoxalic ether and oxamide.

Berzelius earlier in 1833 in which sulphuric ether was represented as the oxide of a radical C_4H_{10}(C = 12) rather than a hydrate of C^8H^8 (C = 6) (71). Though Dumas remained firmly convinced of the correctness of the ether theory at this point in time, he admitted that it "was no longer the only one that would fit the known facts" (72).

On 13 January 1834 Dumas announced what he considered to be the proof of his ether theory for which he had been seeking (73). After reviewing briefly the concepts and history of the ether theory again, he made this startling statement:

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71. In a letter written in September 1832 (Annalen, 3 (1832), 282-86), Berzelius had supported the notion of a benzoyl radical put forward by Liebig and Wöhler (Ibid., 249-82), and at the same time proposed the name etherin for the radical C_4H_8(C = 12). For the former he suggested the symbol Bz and for the latter Ae. In his Jahres-Bericht, 13 (1833), 195, 328, quoted in part in Ann. Chim. Phys., 54 (1833), 5-17, he decided for several reasons (See Partington, op.cit.(2-17), p.347) that the radical C_4H_{10} (C = 12) or Ae, rather than the bicarboned hydrogen radical C^8H^8 (C = 6), etherin should be regarded as the simple unit of combination. Thus he represented sulphuric ether ($C_4H_{10}O$) as Æe, and he no longer regarded alcohol, C_2H_6O as a hydrate of ether. Liebig (Ann. Chim. Phys. 55 (1834), 113-56) designated the radical C_4H_{10} = E as the unit and called it the ethyl radical. Ibid., 132. On good evidence (non-metal halides react with water and alcohol but not with sulphuric ether) he decided that this ether was not a hydrate of bicarboned hydrogen, although alcohol was a hydrate of ether. Thus he represented sulphuric ether as EO and alcohol as EO + H_2O. While Dumas was able to say: "After rejecting all interpretations of this kind for a long time, M. Berzelius finally bowed to the evidence of the facts and now he draws up formulas analogous to those we have proposed, under the name of rational formulas" (Ibid., 56 (1834), 114), he was obliged to admit: "Between the two opinions that were offered to our spirit, and that we had compared in our memoir, he [Berzelius] preferred to develop the one we had abandoned [$C_4H_{10}O$] and to reject the one we have accepted [$C^8H^8.H^2O$]." Ibid.

72. Ibid., 54 (1833), 246.

73. Ibid., 56 (1834), 113-54. This memoir was important for other reasons as well. It described the research upon which his substitution theory was based. It also showed his greater facility in working with equations. From this time he could use them not only to represent what was happening during a reaction but to suggest other reactions that might be possible.

> "In our opinion, alcohol contains hydrogen in the state of water and hydrogen in the state of hydrocarbon. The clearest consequence of the facts that I am going to reveal is that these two states of hydrogen can be distinguished to the point of making the difference palpable and manifest, even to the eyes of the most biased of chemists." (74)

Although he had made mention earlier of the existence of carbon in two different electrical states in the ethers of the oxyacids (75), the distinction had been a purely theoretical one, not susceptible to experimental verification. He did not indicate whether he believed that the two different states of hydrogen were electrically different, but it seems very likely that he was thinking in such channels, and simply did not want to cloud the issue. Perhaps because his research involved several compounds with which Liebig had been working just prior to this (some in fact at the same time), Dumas saw a need for offering the evidence which led to this new and important viewpoint in a severely chronological order, rare documentary evidence for such a development of thought (76). He noted that Liebig and Eugène Soubeiran (1797-1858), working independently and at about the same time, had discovered an etherine compound of carbon and chlorine in which Soubeiran had found hydrogen but Liebig had not. Not long afterward, Dumas was led to the investigation of this compound, discovered its correct formula and named

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74. Ibid., 115.

75. Ibid., 47 (1831), 329.

76. This concurrence in research, initiated sometimes by Dumas, sometimes by Liebig, occurred with some frequency. A discussion of this curious fact is beyond the scope of my thesis. Dumas noted "The chain of details which follows is so logical and the natural order of my ideas so well guided, that I think it is necessary to report my experiments precisely in the order in which they were done." Ibid., 56 (1834), 115.

it chloroform, because of its analogy with formic acid (77). But how was the chloroform formed from the reactants - chlorine, alcohol and an alkali (78)? This question led him to a re-examination of the action of chlorine on alcohol, in which chloral is formed. A study of this reaction had been published by Liebig (79). From his own analysis of chloral, Dumas derived its formula, $C^8H^2Cl^6O^2$. The next step, the action of alkali on chloral, was a simple one. The chloral could be represented as a combination of equal volumes of chloroform and oxide of carbon. The latter combined with the alkali and water forming a salt of formic acid, and chloroform was freed:

$$C^4H^2Cl^6.C^4O^2 + H^2O + KO = C^4H^2Cl^6 + C^4H^2O^3.OK$$

But how was the chloral formed? Dumas pointed out: "The alcohol keeps its carbon and oxygen intact, loses 10 out of 12 atoms of hydrogen

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77. The six atoms of chlorine in chloroform ($C^4H^2Cl^6$; C = 6) were equivalent to three atoms of oxygen in formic acid ($C^4H^2O^3$; C = 6). But chloroform had no acid properties so could not be called an acid. Using the same methods, he also prepared and correctly analysed bromoform and iodoform. Several years earlier, when he had tried to analyse iodoform for the presence of hydrogen, he had nearly lost the sight of his right eye as a result of an unexpected explosion. Loc. cit.(6-72), 123.

78. "To grasp the theory which can explain their [chloroform, bromoform, iodoform] formation, one must isolate each of the actions which enter into the process used in their preparation." Ibid., 124. This may have been the first attempt to derive what is now called a 'pathway' in organic chemistry.

79. Annalen der Pharmacie, 1 (1832), 182-230. It is not clear whether Dumas had studied the reaction earlier than Liebig, but he indicates that "he had prepared more than a pound of chloral at a time on various occasions", loc.cit.(6-73), 125, by direct union of dry chlorine and absolute alcohol, a method quite different from that used by Liebig, and much more efficient. He described this method in detail, and compared the rate of formation. He also studied chloral hydrate, $C^8H^6Cl^6O^4$, and dropped a casual but important remark: "There exist incontrovertible relationships between chloral hydrate and the crystallised substance which I have obtained in treating acetic acid with chlorine in the sunlight; at the same time, despite these relationships, the two could be distinct substances". Ibid., 136.

and gains 6 atoms of chlorine." (80) Thus 10 volumes of hydrogen were replaced by only 6 volumes of chlorine. He reasoned:

> "But, I knew, by experiments relating to the action of chlorine on essence of turpentine, that each volume of hydrogen removed was replaced by an equal volume of chlorine, which is also in agreement with the result obtained by Gay-Lussac in treating wax with chlorine. I should have expected that the 10 volumes of hydrogen lost would be replaced by 10 volumes of chlorine, and this did not take place." (81)

From this observation he drew his crucial conclusion:

> "It is easy to grasp the cause of this difference. Alcohol can be represented by water and a hydrocarbon, and the key to the apparent anomaly that has been indicated lies in accepting the fact that chlorine acts on the hydrogen of the water in a completely different manner than on the hydrogen of the hydrocarbon." (82)

The only way he could explain this difference was by considering that reactions such as the one between chlorine and alcohol occur in two steps:

1. The chlorine, reacting with the hydrogen in the water portion simply removed that hydrogen, leaving the oxygen to combine with the hydrocarbon portion (83).

2. "The first residue, $C^8H^8O^2$, in losing H^6, gains precisely Cl^6 to make the 4 vols. of chloral". (84)

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80. Ibid., 140. $C^8H^8.H^4O^2 + Cl^{16} = C^8O^2H^2Cl^6 + H^{10}Cl^{10}$

81. Ibid., Kapoor, op.cit.(1-101), 52, in discussing the origin of the substitution theory, attributes it to Dumas' desire to confirm the ether theory. While it is true that this is a most immediate source, earlier roots will be mentioned in Chapter 8.

82. Loc.cit.(6-73), 140-41 (my italics).

83. $C^8H^8H^4O^2 + Cl^4 = C^8H^8O^2 + H^4Cl^4$. Dumas thought that the $C^8H^8O^2$ was acetic ether, partly because of the formula, partly because by selective chlorination he had been able to obtain a compound which was "perfectly neutral and had the properties of acetic ether to the highest degree." Ibid., 141. It was probably acetaldehyde. Aldehydes had not yet been discovered.

84. Ibid., 142-43. $C^8H^8O^2 + Cl^{12} = C^8H^2Cl^6O^2 + H^6Cl^6$.

For Dumas the results, and their interpretation, were clear. Alcohol, according to Dumas, must have consisted of equal volumes of bicarboned hydrogen and water vapour, as he had been saying since he had first announced the ether theory with Boullay. For Dumas it was a clear confirmation. He gave numerous examples to show that the theory could be extended to any substance that acted as a dehydrogenating agent and generalised the two rules as follows:

1. Any dehydrogenating agent would remove hydrogen from the water portion of an organic compound, but not replace it (85);

2. Any dehydrogenating agent would replace an equivalent amount of the hydrogen present, which is not part of the water portion (86).

These two simple rules clearly emphasised the important role of water in the molecular arrangement of ethers, as well as the difference in character of the hydrogen contained within the water portion from that outside of it (87).

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85. For example, hydrated oxalic acid, $C^4O^3.H^2O$ lost hydrogen without replacement when nitric acid provided the oxygen necessary to remove the hydrogen as water. Carbonic acid, C^4O^4, was formed.

86. For example, alcohol was converted into acetic acid by the replacement of 4 volumes of hydrogen by 2 volumes of oxygen:

$$\underline{C^8H^8}.H^4O^2 + O^4 = \underline{C^8H^4O^2}.H^4O^2 + H^4O^2$$

Replacement of an additional 4 volumes of hydrogen gave rise to the formation of formic acid (actually the anhydride):

$$\underline{C^8H^4O^2}.H^4O^2 + O^4 = \underline{C^8O^4}.H^4O^2 + H^4O^2$$

According to Dumas, "This was the first time that anyone had attempted to express in a rational manner why it is that alcohol is changed so easily into acetic acid." *Ibid.*, 144. He gives several other examples of this rule as well.

87. It would not be overstating the case to emphasise this point. Although modern understanding of the electronic effects involved in molecular activity is very advanced, Dumas observed the fundamental truth, still accepted, that hydrogen attached to oxygen somehow differed electrically from hydrogen attached to carbon. This difference will assume greater importance in Chapter 8.

It is quite possible that certain aspects of this research were undertaken in connection with the preparation of the fifth volume of his Traité, in which he concentrated on organic chemistry from the analytical, theoretical and descriptive viewpoints, leaving the practical applications to the remaining volumes. Because the first three chapters (88) were particularly valuable, they were published separately in the Journal de Pharmacie in issues antedating the appearance of Volume 5 (89). In the third chapter he reviewed the conclusions drawn from his work with Boullay on ethers, his own research on amides and the studies of others derived from these. In listing all of the known ethers, he gave both his own formulas and those of Berzelius. The difference was slight but fundamental. Berzelius based his system on an unknown radical, C_4H_{10} (C = 12). The basis for Dumas' system, on the other hand, was the well known substance, bicarboned hydrogen, C^8H^8, which could also be regarded as a radical (90). Since he regarded the two

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88. Traité, Vol. 5, Paris 1835. Chapter 1: "Elementary Analysis of Organic Compounds", pp. 3-30; Chapter 2: "Determination of the Number of Atoms in Organic Compounds", pp. 30-72; Chapter 3: "General Considerations concerning the Theoretical Composition of Organic Compounds", pp. 72-112. The remaining 16 chapters contained discussions of individual compounds, classified as well as possible. Most discussions were preceded by a bibliography of value to the historian of chemistry.

89. J. Pharm., 20 (1834), 129-56 (March); 185-223 (April); 261-94 (May). The reason for prepublication was given in a footnote on p.129: "In publishing these detached pages of the fifth volume of the work of M. Dumas, which have gone to press, the editors of the Journal de Pharmacie have thought that they would be of service to young chemists who have directed their efforts in this new and fruitful way." This was certainly Dumas' stated purpose for writing the textbook, as has been pointed out in an earlier chapter. It is not clear whether prepublication was with Dumas' permission or at his request. It should be noted that only minor changes were made in the final version. Since material was published first in the journal, it will be given preference in references.

90. Thus oxalic ether for Berzelius was $C^8H^{10}.O + C^4O^3$, for Dumas $C^8H^8.H^2O.C^4O^3$.

systems as simple variants of one another, and emphasised this by comparing representations of ammonia compounds used in each system, he was able, quite honestly, to leave the choice of system open to the young chemists (91). Nevertheless, he discussed some difficulties inherent in Berzelius' system, (92) and concluded:

> "After all, this very unlikely hypothesis solves nothing, since it would leave all of the difficulties in question, not resolving a single one; on the contrary, it would add a supposition which is not well founded, namely the existence of several substances, having complicated formulas, that have never been observed." (93)

Later in 1834, Dumas had cause to exult. On 25 August 1834 he announced that he had identified a new alcohol, the compound that had formerly been known as pyroligneous ether (94). It is quite probable that he was inspired to make the necessary connection after a discussion with Philip Taylor (1786-1870) who had first isolated the compound in 1812 (95).

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91. "One would be able to choose between the two systems at this time. The question is clearer today." Ibid., 280.

92. For example, since $C^8H^{10}Cl^2$ decomposes into C^8H^8 and H^2Cl^2, why not represent it as $C^8H^8.H^2Cl^2$ in the first place?

93. He mentioned N^2H^8, P^2H^8, C^8H^{10}, $C^{40}H^{34}$, $C^{20}H^{18}$, $C^{40}H^{18}$, formulas that Berzelius used for substances that do not exist, where those for actually existing substances containing two atoms of hydrogen less in each case were already in use.

94. J. Pharm., 20 (1834) 548-49. The work which was described fully Ann. Chim. Phys., 58 (1835), 5-74 was done in conjunction with Péligot. There is every reason to believe that the original idea should be ascribed to Dumas although once the work was begun Péligot undoubtedly made important contributions. The "road guide" for the research had, of course, been provided by Dumas' original work on ethers. In any case, for simplicity, references to the memoir will be made in Dumas' name only, in keeping with the original decision (see note 14).

95. Ten years later Taylor had announced his discovery quite casually in a letter to the editors, Phil. Mag., 60 (1822), 315. In his discussion of the history of wood spirit, Ann. Chim. Phys., 58 (1835), 70-74, Dumas shows considerable respect for Taylor ("his long sojourn in France has permitted us to appreciate his rare talents") and his work ("The (cont.)

Certainly Dumas was perfectly justified in saying:

> "No one before this has considered it to be a new alcohol, formed in the same way as common alcohol, but involving a new radical. No one has established that between this substance and alcohol relationships exist similar to those existing between soda and potash, for example, in mineral chemistry, and this base, upon which our work is founded, seems truly new to us." (96)

The work to which he referred was the preparation of all of the analogues of the known compounds of the existing alcohol. Berzelius called it "the most beautiful work in plant chemistry" since Liebig and Wohler's on oil of bitter almonds (97). There is no doubt that the number of new compounds announced by Dumas was greater, but it would be difficult to assess a greater significance to one of the discoveries (98). Dumas' research was a masterful application of the principle of analogy. The importance of the analogue of sulphuric ether led him to attempt its preparation first. Analysis showed that it could be regarded as a hydrate of an unknown

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95. (cont.) observations of M. Philips [sic] Taylor are of the highest exactness, and we have reproduced wood spirit with all the qualities that he has assigned to it.") There had been several erroneous analyses and incorrect compositional interpretations (including Liebig's), but of Taylor he was able to say, "It is quite clear ... that M. Taylor knew all about wood spirit, and that chemists who came after him had added nothing to its history." Unfortunately Taylor was not able to make the crucial ether, analogous to sulphuric ether, that would have given him the necessary clue to the character of the substance that he therefore named pyroligneous ether.

96. Ibid.

97. Berzelius, Jahres-Bericht, 15 (1835), 377 (Quoted in Partington, op.cit. (2-17), p.353).

98. Liebig's benzoyl theory directed thinking towards the sort of radicals used today that do not have independent existence normally, and also towards benzene chemistry, while Dumas' study of wood spirit opened to chemists the series of alcohols, and eventually the whole notion of homologous series.

hydrocarbon, C^4H^4, which he called methylene (99). Pyroligneous ether was renamed bihydrate of methylene. Following the pattern he had used in working with common alcohol, he then studied the sulphovinic analogues and continued with the ethers of hydracids and then the various oxacids. In some cases he was able to prepare substances whose common alcohol analogues had never been prepared. In other cases he was able to discover a way of preparing the latter, thus reversing the analogy. In addition to preparing ethers, he was able to prepare the amide analogues (100).

Dumas did not miss the opportunity to stress the importance of this work to the substantiation of the ether theory:

> "It is now evident that the theory of ethers is one of those which will be applied frequently and with precision in organic chemistry ... in a very complicated series of phenomena, it allows us to predict everything, explain everything, and submit everything to calculation. If there was some doubt on the subject after the first research on ethers, it should have disappeared when a series of compounds of wood

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99. From μέθυ, wine and ὕλη wood, that is spirit of wood. He hoped to isolate it. The hydrate of methylene, $C^4H^4.H^2O$, was analogous to sulphuric ether. He saw its relationship with common alcohol as a most unusual example of isomerism - the same composition and vapour density, hence same number of the same kind of atoms. He saw this as positive verification of the importance of molecular arrangement. Alcohol, $C^8H^8.H^4O^2$, consisted of four volumes of bicarbon hydrogen combined with four of water; methylene hydrate, $2C^4H^4.H^4O^2$, was composed of eight volumes of methylene and four of water. The modern formulas, C_2H_5OH and $CH_3O\ CH_3$ show more clearly the difference in arrangement. He was able to identify a number of such isomeric pairs.

100. He also indicated that an "isomeric" relationship existed between methylene, CH, bicarbon hydrogen, C^2H^2, and carbide of hydrogen, C^4H^4, showing that there are graduations in both chemical and physical properties (stability and boiling points). <u>Ann. Chim. Phys.</u>, <u>58</u> (1835),63-65. There can be little doubt that he was thinking in terms of related series of hydrocarbons as well as alcohols at this time.

spirit were discovered that were exactly parallel to those of common alcohol." (101)

Although he emphasised his view that they were all compounds of methylene, he showed that their formulas and names could be adjusted to fit perfectly into the theory devised by Berzelius (102). It now appeared that he was much less opposed to the latter than he had been.

Dumas continued to consider the Ether Theory in terms of the hydrated bicarboned hydrogen radical for some time, probably until late in 1837 (103). Increasingly, however, it had come under attack from chemists outside France. Henri Victor Regnault (1810-1878) (104), working under Liebig in Giessen, made an important discovery which threatened to undermine Dumas' approach (105). When he distilled Dutch liquid, $C_4H_8Cl_4$ (106) with an alcoholic

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101. Ibid., 63. Dumas and Péligot extended the series in a memoir on the nature of ethal, Ann. Chim. Phys., 62 (1836), 5-23. They showed that ethal was an alcohol, $C^{64}H^{64}.H^4O^2$ (Cetyl alcohol, $C_{16}H_{33}OH$), whose base, cetene $C^{64}H^{64}$ they prepared. They were unable to obtain the analogue of sulphuric ether, $C^{64}H^{64}.H^2O$, but did form sulphocetic acid and the chlorhydrate of cetene. At the same time, using the principles of the ether theory as a guide, they showed that spermaceti could be regarded as consisting of two atoms of margarate of cetene (each of which was composed of one atom of margaric acid, one atom of cetene and one atom of water), and one atom of oleate of cetene (composed of one atom of each of oleic acid, cetene and water). The whole compound had the formula $C^{472}H^{445}O^{14}$! They expected chemists to be astonished, but gave adequate evidence. Once again the 'homologous' relationship was mentioned and further extended by the addition of cetene.

102. C^4H^{64} became the unknown radical, C^4H^6 in the ether of the wood spirit, ~~etc.~~ for example.

103. Leçons, pp.291-320 (Lecture 8, 4 June 1836); Ann. Chim. Phys., 63 (Nov. 1836), 265-72; Comptes Rendus, 4 (April 1837), 496 and 563-65.

104. Regnault, a graduate of the Ecole Polytechnique in 1832 very probably worked under Dumas, who was a répétiteur there at the time. He may have done research in Dumas' laboratory. On graduating, he went to the Ecole des Mines for two years then left for Giessen.

105. Ann. Chim. Phys., 58 (1835), 301-20. (Translated from Liebig's Annalen, 14 (April 1835), 88-100).

106. Regnault verified Dumas' analysis (Ann. Chim. Phys., 48 (1831), 185-98) rejecting that of Liebig.

solution of potash, he found that hydrochloric acid was removed, leaving a new compound, $C_4H_6Cl_2$. He verified this further by preparing the bromine analogue. Using these compounds, their hydrohalides, Liebig's aldehyde (107) and acetic acid, he drew up a series based on the hypothetical radical, aldehydene, C_4H_6 (108). This induced him to reject Dumas' Ether Theory, since clearly it was aldehydene and not bicarbon hydrogen which was the fundamental radical.

Liebig too continued to snipe away (109) though with little effect. Finally, in a long note (110) added to an article on various investigations that he had undertaken with Pelouze who had been visiting in Giessen, he marshalled several statements for and against the theory that olefiant gas was the base of compound ethers, as well as others showing on the one hand that ether was not a hydrate and on the other that it was an oxide. With one exception, almost no discussion was included with these statements, and they varied widely in credibility; some indeed were erroneous. The greatest part of the note was taken up with the strongest argument (111). No doubt

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107. Liebig named this compound aldehyde (modern name acetaldehyde) from "alcool dehydrogenatus". Though Döbereiner had prepared it three years earlier, he had neither studied nor named it. Liebig's detailed study appeared in Annalen, 14 (May 1835), 133-67.

108. Ann. Chim. Phys., 59 (July 1835), 358-75. (Translated from the Annalen, 15 (July 1835), 60-74.

109. For example, Ann. Chim. Phys., 59 (June 1835), 172-87 (176) and 59 (July 1835), 289-327 (326). His arguments were not very cogent. At this time, he even flirted temporarily with the idea of rejecting radicals: "The time is not far hence, I hope, when the idea of permanent organic radicals will be abandoned." Ibid.

110. Ibid., 63 (October 1836), 153-64. (Translated from Annalen, 19 (1836), 270-90.) Liebig said, "In concluding this note I must declare that it has been written after the departure of my friend M. Pelouze, and completely without his knowledge. I do not know whether he shares my opinions, for which I must bear the responsibility."

111. Ibid., 157-63.

Liebig would have expected it to exert the greatest influence on Dumas and perhaps would turn him away from his 'errors'. He stated it simply and clearly: "The Substitution Theory provides a direct proof against the existence of water in ether." (112) The argument is here summarised briefly. When alcohol is oxidised, acetic acid is formed. If alcohol consisted of bicarbon hydrogen and water ($C_4H_8.H_4O_2$), the formation of the acid could be explained in two ways using the substitution theory:

1. The hydrogen of the water was removed without replacement. But in that event, oxygen drew hydrogen away from oxygen, which would be "an extremely curious route" (113) indeed!

2. Oxygen replaced part of the hydrogen from the bicarbon hydrogen portion, forming hydrated acetic acid, $C_4H_4O_2.H_4O_2$.

But all chemists agreed that hydrated acetic acid contained only one atom of water, $C_4H_6O_3.H_2O$, which was not the same thing. Liebig was quick to point out that regarding alcohol as a hydrate of ether, ($C_4H_{10}O.H_2O$), did away with the problem. Oxygen replaced the same four atoms from the ether portion, but the hydrated acid, $C_4H_6O_3.H_2O$ was formed directly. It was an easy matter for him to carry over the application of this principle to the formation and oxidation of aldehyde (114).

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112. Ibid., 155.

113. Ibid., 158. In a note attached to a memoir on the "Law of Substitution", Comptes Rendus, 10 (1840), 149-78 (151), Dumas indicated, "When I had added that oxygen itself could decompose the water fixed in a compound, I was guided by the Theory of Cementation which admits that iron carbide is decomposed by iron." Though it was a weak defence, it was sufficient.

114. Liebig pointed out: "This substance was unknown when M. Dumas drew up his rules." Ann. Chim. Phys., 63 (1836), 160. Since Liebig wrote his formula for aldehyde (acetaldehyde) in the form $C_4H_6O.H_2O$, the parallel was evident.

Undoubtedly this argument had some effect on Dumas. Whereas he had been willing to admit the possibility that a radical theory would explain the facts, he had bent his efforts towards proving that the ether theory did so more effectively and did not have the disadvantages of the radical theory The same was true of Lavoisier's theory of acids compared with Davy's theory that all acids were hydracids. The latter was a special instance of the radical theory. But in 1836 Dumas was bound to admit:

> "It is difficult to find a means of attacking it [Davy's theory]; the more well-established it becomes, the more reasonable it is. Indeed, it seems to simplify chemistry considerably. With it there are only hydracids; with it nothing but similar formulas for all saline compounds; rather, no more salts, nothing but binary compounds, substances regarded as salts becoming analogues of sodium chloride." (115)

The thorn of course was the necessity of assuming the existence of a whole group of substances, not one of them ever isolated. Dumas' inherent distaste for a priori hypotheses, manifested from the beginning of his career, made such a theory inadmissible at this time, despite the greater simplicity that would result. But the tension between these two tendencies was evident in his lectures in 1836:

> "I insist on this reasoning (116), because I have found no other data opposed to the system held by Davy and M. Dulong. Thus the question is not at all irrevocably closed. It is possible that this theory will rise triumphantly at any time, supported by some discovery that will give it new force. For the present I suggest that it be rejected because of the

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115. Leçons, p.341.

116. He raised an additional objection, the obscurity introduced by writing the acids of phosphorus as hydracids:

oxyacid	hydracid	modern formula
$Ph^2O^5.3H^2O$	$Ph^2O^8.H^6$	H_3PO_4
$Ph^2O^5.2H^2O$	$Ph^2O^7.H^4$	$H_4P_2O_7$
$Ph^2O^5.\ H^2O$	$Ph^2O^6.H^2$	HPO_3

> infinity of unknown substances that it supposes. If only I could see a part of them come into being, I would have less repugnance towards believing in the existence of the rest." (117)

Since he planned to give some lectures in the philosophy of organic chemistry the following year (118), he avoided the mention of organic radicals, but the reasoning was exactly the same. Though he continued his search for further support for the ether theory, he was also willing to reconsider if definite proof for the real existence of radicals was forthcoming.

Liebig's attacks on the ether theory had been severe if not effective, but in a letter written to Dumas in May 1837 he tried to explain them away and suggested that they put their differences aside (119). Dumas agreed. In the autumn Liebig attended the annual meeting of the British Association for the Advancement of Science held in Liverpool. At its conclusion he went to Paris with a request from the Association for a paper on the state of organic chemistry at the time, that he and Dumas had been asked to prepare. The timing could hardly have been better for Dumas. During their several meetings, Liebig was able to convince Dumas that the advantages of the

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117. Ibid., 343.

118. "Thus the discussion of the phenomena of this part of chemistry [organic] can be a topic of a more advanced course such as this one. I propose to make it so during the coming year. I am going to gather what is needed to accomplish this project and if nothing stands in the way, a part of the lectures for the coming year will be devoted to the simplest and most general explanation of what goes on in living beings during their life or after their death, relying on the observations that have been made in physiology and organic chemistry." Ibid., 426. The lectures were never given at the Collège de France. See Chapter 3, note 118 and Chapter 9.

119. Arch. Acad. Sci., Dossier Liebig (Fonds Dumas). A recent biographer of Liebig, Holmes, F.L., DSB, Vol. 8 (1973), p.337, has suggested that it was done to assist Liebig's friend Pelouze in his candidacy for membership in the Academy of Sciences in Paris.

radical theory outweighed the disadvantages (120), for the German chemist wrote to Berzelius: "Several discussions were enough to convert Dumas. He has accepted our opinion. We have been reconciled and our old quarrels have come to an end." (121) In a note read to the Academy in his own name and that of Liebig on 23 October, soon after Liebig had left Paris (122), Dumas announced the Association's request, indicating the plans that had been formulated to fulfil it. In the note he said:

> "In forming from three or four elements such a variety of compounds, more varied perhaps than those in the entire mineral kingdom, nature has taken a pathway both simple and unexpected; with these elements she has made compounds that have all the properties of elementary substances. We are convinced that this is the whole secret of organic chemistry. Thus organic chemistry has its own elements, sometimes playing the role belonging to chlorine or oxygen in mineral chemistry, sometimes on the contrary, playing the role of metals. Cyanogen, amide, benzoyl, the radicals of ammonia, fats, alcohols and analogous substances, these are the true elements on which organic chemistry acts, and not at all on the elements defined as such, carbon, hydrogen, oxygen, nitrogen, elements that only appear when all trace of organic origin has disappeared. ... In mineral chemistry the radicals are simple; in organic chemistry the radicals are compound, therein lies the whole difference. ... These radicals combine among themselves or with the elements properly so-called, giving birth, by means of the simplest laws of mineral chemistry to all organic compounds. To find these

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120. In addition, Liebig probably pointed to cyanogen as a radical having real existence.

121. Quoted from the letter, by Blunck, op.cit.(3-44), p.151.

122. In an unpublished letter dated 19 November 1837, Liebig wrote to Dumas: I returned home 15 days ago ... the 17 days that I spent in Paris will never be erased from my memory. I gained a friend who doesn't just talk about science but gives it his body and soul; I become your friend with all my heart." Arch. Acad. Sci., Dossier Liebig (Fonds Dumas). Though he could have been in Paris when the note was read, it is very unlikely.

> radicals, study them, characterise them, such has been our daily effort for ten years." (123)

As early as 1833 Dumas had been able to accept the existence of "oxidisable radicals", but they were groups of elements capable of independent existence as compounds (124). At the time, he was unable to believe that ternary radicals containing oxygen, such as benzoyl, could exist even in that sense (125). The note shows that his attitude had changed considerably by October 1837. It was further evident in a second note written by Dumas in which he presented work that he and Liebig had discussed on the constitution of some organic acids (126). At least part of this work was done as a result

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123. Comptes Rendus, 5 (1837), 569-70. Although much of the note, written by Dumas, had been agreed on, the 'manifesto' made the two scientists directors of a vast research programme in organic chemistry. Liebig wanted no part of this and he made sure that the note was not published in Germany. He wrote to Berzelius: "Dumas has lived to sacrifice everything to his ambition. But this is not my thing. This manifesto that he has given is, of course, quite foolish." Quoted by Blunck, Loc.cit. (6-121), p.158. Dumas' programme was indeed ambitious. For example, he said: "We will analyse every organic substance that has not been analysed. We will check carefully all analyses published by chemists who are engaged in these sorts of questions. ... Since our principal purpose is to characterise each substance, we will dedicate all our efforts to bringing to light reactions proper to every substance that we will study." Comptes Rendus, 5 (1837), 571. Dumas was accustomed to long working hours. He hoped to have the help of equally dedicated students and fellow chemists, as he indicated. This was more than he had a right to expect, as Liebig was well aware.

124. "In my opinion, the various hydrocarbons known, at least many of them, can act sometimes as a base, like ammonia, sometimes as an oxidisable radical, like metals." Ann. Chim. Phys., 54 (1833), 237-38. He gave examples.

125. A positive radical containing oxygen was not in keeping with the electrochemical theory and must be explained by some other hypothesis according to Dumas. However he did use it as a method of classification of these compounds in his Traité, Vol. 5 (1835), pp. 205-15, though he indicated that its existence had not been proven.

126. Dumas and Liebig, "Note sur la constitution de quelques acides", Comptes Rendus, 5 (1837), 863-66. In the note Dumas discussed the constitution of citric and tartaric acids and their salts showing that tartrates could be represented more simply by regarding the acid as a hydracid. This supposed the existence of a tartrate radical lacking independent existence.

of the agreement expressed in Dumas' manifesto. He had reason to recall his own part, in a long letter to Liebig written on 25 March 1838 that began:

> "When you came to Paris, I had completed the analysis of orcine that led me to accept the existence of neutral polybasic organic salts. From this viewpoint and the experiments of M. Berzelius, I had deduced a formula for citric acid and verified it by analyses of the citrates of copper and silver, lime and baryta. We talked about these results. After your return to Giessen, you wrote me in a letter in which you referred to an analysis of tartar emetic, proposing that we work together on a paper concerning the constitution of organic acids. You accepted the existence of acids capable of forming polybasic neutral salts, proposing to apply a theory in which they would be regarded as hydracids. I sought to verify this supposition by some experiments on anhydrous emetic. But from the time of my first attempts I was disturbed by a disagreement in our results which was accounted for later; you accepted the correction that I made in the composition of emetic.
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> You urged me to undertake research with you; that suited me completely and I considered myself free to accept because on my part, I had been led to ideas that you wished to adopt as a basis for work, that is, the necessity of accepting neutral polybasic salts in organic chemistry. A note was read to the Academy on 18 December in our names." (127)

While Dumas saw the simplicity of writing tartaric acid as a hydracid, and its salts as salts of metals rather than metal oxides, he was not convinced that <u>all</u> oxyacids were hydracids. He continued to write most formulas for them as they had been written.

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127. This letter, Arch. Acad. Sci., <u>Dossier Liebig</u> (<u>Fonds Dumas</u>), will be discussed more fully in a later chapter; it seems to be unpublished. There is no indication that Liebig shared with Dumas in Paris the ideas on the constitution of citric acid that he had written to Berzelius in January 1837. <u>Berzelius und Liebig, ihre Briefe von 1831-1845</u>, Ed. J. Carrière, Munich and Leipzig, 1893, p.121 (Referred to by Partington, <u>op.cit.(2-17)</u>, p.278). Support for the opening statement made by Dumas can be found in one of several notebooks of experiments, Arch. Acad. Sci., <u>Fonds Dumas</u>, Carton 9. In folio, undated and unpageinated, it began with research on the "Acide carbazotique de Jacquelain". Several pages later there is one on which analyses of potassium carbomethylate are given, followed by one on lead orcinate, six on orcine, several on other substances; two blank sheets titled orcinate followed by many on citric acid and the four citrates mentioned in the letter to Liebig; then several pages on emetic, presumably after his discussion with Liebig in Paris; several pages on other substances and ten pages on emetic and tartrates. The order of these analyses parallels the events as given by Dumas though there are no dates.

This attitude was still evident in a thesis submitted in March 1838:

> "... in organic chemistry, all the radicals isolated up to now or accepted by hypothesis are compound radicals. ... But it is necessary to know these radicals, to know what rules they follow in compounds with the elements, to have rational formulas for all organic substances ..." (128)

Nevertheless, concerning the reaction in which benzoic acid is changed into benzene by heating with lime ($C^{28}H^{12}O^{4} + 2\ CaO = 2\ C^{2}O^{2}.CaO + C^{24}H^{12}$) he remarked:

> "This is a noteworthy equation in the sense that the water of the benzoic acid reacts as a constituent part of the acid, so that its hydrogen and oxygen are mixed in with that of the acid. All of this is explained better if benzoic acid is considered to be a hydracid rather than as an oxyacid in the usual manner." (129)

And concerning oxalic acid he observed:

> "These facts raise a serious question without resolving it. Is oxalic acid a hydrated acid, $C^{4}O^{3}.H^{2}O$, or a hydracid $C^{4}O^{4}H^{2}$? The first opinion is generally accepted; M. Dulong tried to win acceptance for the second and I am convinced that most chemists float between the two." (130)

Certainly by this time Dumas no longer considered bicarboned hydrogen as the core of the ether theory. For a while he used sulphuric ether, $C^{8}H^{10}O^{2}$, as a 'radical' (131). But when he announced his type theory, even this approach was of limited value. Paradoxically, in his first memoir on types he finally seems to have recognised the ethyl radical as a hypothetical entity, when it had lost much of its usefulness. He wrote:

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128. Dumas, J.B., Thèse sur l'Action du Calorique sur les Corps Organiques, Paris, 1838, p.8 (my italics). This is a clear statement of Dumas' acceptance of radicals in the sense used by Liebig.

129. Ibid., p.78.

130. Ibid., p.98.

131. As late as 1839 he wrote: "The composition of this substance the ether of chloracetic acid , in accord with the general formula for ethers is $C^{8}Cl^{6}O^{3}.C^{8}H^{10}O$." Comptes Rendus, 8 (1839), 617.

> "To say that nitrous vapour replaces hydrogen in nitrobenzene is the same thing as saying that potassium replaces ethyl in ether.
>
> But it must not be concluded that ethyl is a permanent, immutable, unalterable compound, since experience proves the contrary. Only, in losing hydrogen and gaining chlorine, everything leads one to believe that it keeps its character in the same way that the ether does." (132)

Although Dumas eventually abandoned the ether theory as he had first expressed it, there are several reasons for attaching to that theory an importance far greater than its life span: it provided a framework within which many existing substances could be classified and others discovered or produced for the first time; it paved the way for writing formulas and equations extensively in organic chemistry, and these in their turn suggested other avenues for research (133); it gave rise to the radical theory that was devised by Berzelius and defended by Liebig, one that with some modification is in use in modern times; it provided an excellent example of how analogy could be used successfully in classifying organic compounds, understanding their constitution, and extending the boundaries of the science; it showed the need for an explanation of the role played by water in organic chemistry. Much of this was made possible through Dumas' analytical skill, intuition and indefatigable effort. The platform for introducing his ideas to the scientific world was the Academy of Sciences in Paris. Since he was an active member for more than fifty years, his election to the Academy and his life as a member will be described in the next chapter.

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132. Comptes Rendus, 10 (1840), 167.

133. In 1838 Dumas wrote: "If I were asked how I was led to the discovery of oxamide, I would answer very frankly that I was looking for some new compound of cyanogen in the decomposition products of ammonium oxalate, which can be represented by cyanogen and water: $C^4O^3.N^2H^6.H^2O = C^4N^2.H^8O^4$. Instead of a cyanic compound, oxamide was produced, which I represented as a substance formed from carbonic oxide and a particular azide of hydrogen: $C^4O^3.N^2H^6.H^2O = C^4O^2.N^2H^4 + 2H^2O$." Loc.cit. (6-128), p. 98-99.

CHAPTER 7

DUMAS AND THE ACADÉMY OF SCIENCES

"These activities, so well conceived by M. Pelouze opened to him the doors of the Academy in 1837 in replacement of M. Deyeux. It was a great event for him and a great joy; he was barely 30 years old; he had aspired to this honour with a passion and he was chosen in preference to candidates who were very worthy of the votes of the Academy and had spent longer in their careers. ... M. Pelouze did not consider that his entry into the company, where he received Thenard's affection, always assured to the talented, had given him the right to take a rest; he continued his work with a new ardour showing himself to be even more exacting so as to ensure soundness and perfection." (1)

On 20 January 1868 Dumas was elected Permanent Secretary of the Academy of Sciences and two years later, in the public meeting of the Academy he read a long eulogy of Pelouze (2). A change in names and dates would suffice to give some idea of Dumas' reaction to his own election five years earlier. It was virtually the highest honour he could receive as a scientist. Apart from the prestige and power associated with membership, there were options available that were not open to others. In this chapter a brief history of the Academy will serve as a setting for a discussion of the incidents that led up to his election as well as a study of his life as a member.

The Academy of Sciences was formed in Paris in the early part of the 17th century as a small gathering of men interested in the sciences (3). In 1666 it was given official status by Colbert, who appointed a secretary, installed the group in the King's library, but imposed neither ranks nor regulations. In 1699 Louis XIV provided both (4), reserving the confirmation of members who had been nominated by the Academy to himself. In addition, he appointed both the president and vice-president from among its ten honorary members (5). These were not necessarily scientists. Offices and

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1. Dumas, J. ., Discours et Eloges Académiques, Paris, 1885, pp. 155-56. (Hereafter Eloges). He referred to Nicolas Deyeux (1745-1837).

2. Each year one of the permanent secretaries (the other was Jean Baptiste Armand Louis Léonce Elie de Beaumont (1798-1874)) was expected to eulogise a deceased member in the annual public meeting. Dumas chose Faraday (d. 25 August 1867) for his first discourse on 18 May 1868. Ibid., pp. 51-124. His second in 1870 was on Pelouze (d. 31 May 1867). Ibid., pp. 127-98.

3. A history of that period can be found in Gauja, P., L'Académie des Sciences de l'Institut de France, Paris, 1934, pp. 3-12.

4. It was at this time that the number of members was fixed.

5. The Academy was not given the right to name the president and vice-president itself until 1792.

meeting rooms were in the Louvre. All members were required to live in Paris (6). 85 scientists from the provinces and from foreign countries were chosen as corresponding members or correspondents. Each was assigned to one of the members so that the whole Academy could be kept abreast of developments in the sciences that were taking place outside of Paris (7). The secretary, appointed for life to give stability to the administration, became known as the permanent secretary. In 1793 all of the Academies were suppressed, and two years later a new organisation, involving many of the same people, came into being, <u>L'Institut National</u>, composed of three classes. The First Class, the physical and mathematical sciences, consisted of ten sections. In 1803 an eleventh was added and the sections were grouped into two divisions (8):

A. <u>Mathematical Sciences</u>

1. Geometry
2. Mechanics
3. Astronomy
4. Geography and Navigation
5. General Physics

B. <u>Physical Sciences</u>

6. Chemistry
7. Mineralogy
8. Botany
9. Rural Economy
10. Anatomy and Zoology
11. Medicine and Surgery

In each section there were six members (9). From 1816, first from one division, then the other, a vice-president was elected annually who became president the following year. A permanent secretary was elected for each

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6. This restriction was not removed until the decree of 29 June 1964.

7. The number was raised to 100 in 1803, unevenly distributed among the eleven sections (there were 12 in the chemistry section). They were not allowed to live within 10 to 12 leagues of Paris (1 league = 4 kilometres). There were 8 foreign associates and 10 <u>Academiciens Libres</u> were added in 1816. None of these had voting rights.

8. These divisions retained the titles given until 1955, when the present, more suitable titles were adopted: A. Mathematical and Physical Sciences; B. Chemical and Natural Sciences. At the same time, some revision in sectional titles was also made.

9. Section 4 (added in 1803) had only 3 members until the number was raised to 6 in 1866.

division. In 1805 the Institute was moved to its present quarters (10). In 1816 the classes were abolished and became Academies again (11). Although they maintained a certain unity by retaining the title L'Institut de France, the several Academies regained their administrative and legislative independence of one another.

When Dumas arrived in Paris, the prestige of the Academy of Sciences was at a high level. Membership meant more to a young man interested in science than a challenge or a reward for achievement. Since private industry had not yet taken an interest in basic research, unless he was the beneficiary of the patronage of some individual, he was dependent on government positions in which this kind of activity was at least tolerated and even encouraged: the advanced levels of the educational system, the mint, the bureau of longitudes, the bureau of mines, etc. Appointments to such positions came through the Academy, however, and were often given to its members. On the other hand, since membership was in demand, the Academy could afford to be very careful in their choice of a candidate, so that this pre-eminence could be maintained, while scientific research continued to receive guidance and encouragement. Thus elections were an important activity (12). Dumas' candidacy provides an excellent illustration of the manner in which members were chosen. Because it was a goal he had valued highly from the time he was in Geneva and pursued with care, because it was significant to him financially

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10. It was the former home of the Collège des Quatre-Nations on the bank of the Seine River, across from the Louvre. It was to be only a temporary move until their new rooms in the Louvre were ready.

11. Listed in order of their foundation, they were: Académie Francaise, Académie des Inscriptions et Belles Lettres, Académie des Sciences and Académie des Beaux Arts, to which was added in 1832 the Académie des Sciences Morales et Politiques.

12. The statement: "Election is the principal act of the Academy", made by Gauja, op.cit.(7-3), p.39, seems a little strong nevertheless.

and to his career, and finally because it occupied a central place in his life, his election will be discussed at some length.

Among the requirements, demonstrated ability presaging future accomplishment was the most important. Dumas had collaborated with Prevost on a series of important investigations that foreshadowed a promising career in physiology. Though he never lost his interest in that science, circumstances led him to dedicate his time and efforts so completely to the teaching of chemistry and chemical research that he was considered worthy of membership in the chemistry section as early as 1826. After listing those who were vying for a place in the section left vacant by the death of Proust that year (13), the Procès Verbaux of the Academy continued:

> "The reporter Vauquelin observed that many other persons, among whom he cited MM. Robiquet and Dumas, could have been placed very honourably on this list of those who are being presented, but the section did not think that it should present those who have not made known their wish to be included among the candidates." (14)

Certainly Dumas was interested, but he realised that there was little chance of success at this point in his career. He had already developed his vapour density method to a degree that permitted him to draw some important theoretical conclusions, but he had not yet read his memoir on atomic theory nor any other of equivalent significance. Furthermore, Chevreul had already turned down an excellent opportunity in 1823 in favour of Darcet, so that he would almost certainly be elected this time. Thus Dumas had demurred.

When he decided to be a candidate in 1832, however, he was far better prepared. During the interval between 1826 and 1831 he had published no

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13. Those who had asked to be considered had been placed in the following order: 1° Chevreul; 2° Clément; 3° Pelletier and André Laugier (1770-1832); 4° Caventou.

14. PVAS, Vol. 8, p.411 (Meeting of 31 July 1826).

fewer than 20 memoirs or articles in his own name as well as the seminal work with Boullay (15). During this same period, he had completed three volumes of his textbook, Traité de Chimie appliquée aux Arts (16) and had been principal founder of the Ecole Centrale and two journals. There was certainly ample evidence of past ability and future promise.

From the time he had gone to Geneva Dumas had dedicated himself to the principle that hard work was necessary for advancement. It was evident in the sheer quantity of material published. But work alone was not sufficient to attract the attention of the Academy. Even originality, required to some degree in every memoir or article that was published, was no guarantee of a second glance. They were drawn by the impact that a work had on the science of the time. For example, Chevreul was elected because his research had revolutionised the study of fats. It is from this aspect that Dumas' work must be viewed. He had revived interest in the atomic theory; his ether theory gave rise to a flurry of activity in organic chemistry in directions that had never been explored; he had rescued from disuse the formulas that Berzelius had originated and added a new dimension by using them in equations; indeed, he had filled his Traité with quantitative word equations, a form of communication that had been used sparsely, if at all since the time of Lavoisier; by introducing a simple procedure for determining vapour densities up to the temperature at which glass melted he had vastly extended the usefulness of Gay-Lussac's method and had drawn theoretical consequences from the results obtained that were of great value in the interpretation of a wide range of empirical data.

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15. These included work of major significance such as the memoirs of atomic theory (1826) and oxamide (1830).

16. These volumes were published in 1828, 1830 and 1831. The original contract was for four volumes but it was extended to six during this time and finally to eight.

On examining these contributions one finds little that is strikingly original. But to each of them Dumas brought a new approach, identified new directions that could be taken, showed new applications that could be made in the laboratory. In this way he made a tremendous impact on the chemistry of the time. Though he was committed to a sound foundation of observable data, he was well aware that the science of chemistry could only be built on a framework of generalisations. He had an ability, an intuition, indeed a flair for pursuing the kind of investigations whose conclusions could be generalised and extended. It was this that caught the eye of the Parisian chemists and the Academy. These characteristics, along with a sense of timing, judgment and intuition, an ability to organise, to give direction all marked him out not only as a scientist who was worthy to be a member of the Academy, but one who would be a credit to that distinguished body.

Dumas had every right to suppose that such impressive scientific credentials would suffice. However, truism or not, it must be said that elections often depend on personalities as much as on issues (17). While the order in which candidates for the chemistry section were presented was determined by the five members of that section, the five represented less than eight percent of those who would cast the deciding ballots. Having friends in the other sections was a definite asset, both because of their own vote and the opportunity that they would have to encourage others in their section who were less aware of the candidates qualifications to do likewise (18). Through his cousin Bérard and influential friends in Geneva,

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17. Ability could have made membership possible for Auguste Laurent (1808-1853) had he not frequently raised the hackles of the members.

18. Though he was highly regarded by his fellow chemists, Pelletier was not able to gain the support of the Academy as a whole until 1840, two years before his death when he was finally elected Académicien Libre.

Dumas had come to know several members of the Academy who had been in the Society of Arcueil. One of these, Thenard, belonged to the chemistry section and was highly regarded among his confreres. From the time that Dumas had become a _répétiteur_ at the _Ecole Polytechnique_ a friendship had developed and deepened. There too, he came into frequent contact with Gay-Lussac, a member of the physics section, whose ideas he absorbed and in some cases developed and who undoubtedly guided him informally, took an interest in him, and grew to respect his work. Dulong, also in that section, was one of the few scientists in France who had continued research on the atomic theory. In 1823 he had given a favourable report on Dumas' memoir with Pelletier, and Dumas had often referred to Dulong's work on atomic heats. Gay-Lussac was also editor of the important journal the _Annales de Chimie et de Physique_ in which much of the young chemist's work had been published. These were sometimes followed by Academy reports that were quite encouraging, though this was not a common practice. The other editor, Arago, a member of the astronomy section and permanent secretary (19), had been instrumental in obtaining Dumas' appointment to the _Ecole Polytechnique_. Through Ampère, a member of the geometry section, who had also befriended the young man when he had come from Geneva, he had become a professor at the _Athenée_. Geoffroy Saint Hilaire, elected vice-president for 1832, was in the anatomy and zoology section. Dumas had attended his lectures in 1823 and worked in his laboratory at the _Muséum_ with Prevost. From 1826 Dumas lived at the _Muséum_ and came to know other members of the Academy who lived there. Magendie, medicine and surgery section, publisher of a journal, had examined and published some of Dumas' physiological studies, thus indicating his respect

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19. Arago was elected permanent secretary on 7 June 1830, but Félix Savary (1797-1841) was not elected to replace him in the section until 24 December 1832.

for the work. The young chemist had edited the Annales de l'Industrie with Molard, whose brother was in the mechanics section. They shared an interest in industry.

Certainly Dumas' most important contact in the Academy was his father-in-law, Alexander Brongniart (mineralogy section), who was more active than anyone in the effort to draw votes to Jean Baptiste. The young man shared the Brongniarts' close personal friendship with the Cuviers (zoology) and De Jussieus (botany) and could count on their votes. Thus Dumas had powerful friends in nearly every section (20). It should be mentioned that he took it upon himself to maintain and cultivate these friendships. He was a good conversationalist and made a point of attending the various social evenings held by the scientists. Whenever he disagreed with a colleague it was always in a gentlemanly manner, especially in the public forum. There were other characteristics that added to his stature. He wrote and spoke clearly, well, persuasively and with authority. He was a well-organised and influential teacher, full of enthusiasm for chemistry. Because so many of the members were in the teaching profession this could be a valuable asset. In helping to found the Ecole Centrale, he had had to learn a great deal about administration, an acquisition which few could claim at his age. Another was an acquaintance with several different sciences that was far from superficial, and an interest in their application.

All these were only the remote preparation for candidacy. The Academy had devised a procedure for filling the vacancy that resulted when a member died. After a period of mourning lasting about a month, the section of which he had been a member prepared a list, in an agreed order, of those who

20. All but two of the members of the remaining two sections (rural economy, geography and navigation) were absent the day of voting. They were often away during the summer, attending to duties.

sought membership. Each was expected to submit a printed list of his works to all the members. He had the right to read a memoir to the Academy, if he was prepared to do so, before the election (21). The candidate who received an absolute majority of the ballots of those present became a member (22). Dumas' preparation is a good example of what could be done in this regard and will be described in detail.

The death of Serullas from cholera on 25 May left a place vacant in the chemistry section. At the following meeting on 28 May, his death was announced by the president (23). In the same meeting, Dumas read a memoir entitled: "Research on the Composition of Minium" (24). Gay-Lussac and Thenard were assigned to study and give a report on it to the Academy. On 4 June he read another: "Research on Compounds of Hydrogen and Carbon" (25), and the same reporters were assigned. On 11 June Thenard, in his own name and that of Gay-Lussac, read a report on the first of two memoirs read by Dumas on 7 May (26). One week later he read their report on the second

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21. On 17 September 1832 the election to fill a vacancy in the medicine and surgery section was delayed for two weeks because candidates who had been "signed in the registers for a long time to read memoirs" had been prevented from doing so by Academy business. PVAS, 10 (1832-35), p.126.

22. The presence of two-thirds of those who were members at the time was required.

23. Ibid., p.64.

24. Ann. Chim. Phys., 49 (1832), 398-411.

25. Ibid., 50 (1832), 182-97.

26. The report on "The Chlorides of Sulphur" was a little over one column in length (loc.cit.(7-21), p.70). It was quite favourable and Thenard advised that the memoir should be printed in the Mémoires des Savants Etrangers. Implementation of this standard form of approval became unnecessary when the memoir was published elsewhere (loc.cit.(7-24), 204-08).

memoir: "The Vapour Density of some Elements" (27), in which Thenard concluded: "The author intends to continue his research; we can hardly encourage him enough; he is involved in questions of the greatest interest." (28) In the next two meetings the attention of the members was centred on the election of a permanent secretary to replace Cuvier who had died in May (29). On 16 July Thenard gave a verbal report (30) on Dumas' memoir of 28 May. In the meeting of 23 July the Procès Verbaux recorded:

> "M. Deyeux, president of the chemistry section, in the name of this section announced his opinion that it must proceed to the replacement of M. Serullas. The Academy voted on this proposition; 39 members with the right to vote cast 39 ballots into the urn all saying yes; in consequence the Academy invites the chemistry section to present a list of candidates in the following meeting. Notices will be sent to the homes of members, informing them of this before the meeting." (31)

Finally, on 30 July Gay-Lussac reported verbally in his own name and that of Thenard on a memoir whose title was not given (32), and their conclusions

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27. Loc.cit.(7-25), 170-78. This was one of Dumas' doctoral theses. Although it was in the June issue of the journal, this issue did not appear until September. The Academy received a copy on 17 September.

28. Loc.cit.(7-21), p.75. Information on the meetings of the Academy appeared regularly in the Annales de Chimie et de Physique. The author, probably Gay-Lussac, indicated that a "very favourable report" had been given by Thenard. Ibid., 50 (1832), 443.

29. Dulong was elected on the second balloting. Dumas had no other memoirs prepared. Gay-Lussac and Thenard were concentrating on the election of Dulong. Moreover it was advantageous for Dumas that their reports be given in the two meetings following these.

30. No record of verbal reports was kept.

31. Loc.cit.(7-21), p.88.

32. Ibid., p.96. Quite likely it was the research on "Compounds of Hydrogen and Carbon" read on 4 June. Earlier in the meeting Chevreul had reported on a memoir by Pelletier on opium read on 2 July, which he had examined with Gay-Lussac. He concluded: "If the work, done in the way conceived by the author, leaves some points for clarification or completion, we believe at the same time that it contains enough new and important facts so that a place can be reserved for it in the collection of Mémoires des Savants Etrangers." It was the end of any hopes that Pelletier may have entertained concerning membership.

were adopted.

All of these presentations either directly or indirectly kept Dumas' name before the Academy constantly, in a most favourable light, right up to the moment when candidates were nominated. They were made possible by a combination of fortunate circumstances and careful planning. It is difficult to believe that Dumas could have accomplished this on his own. But now the moment he had awaited had arrived. Immediately before Gay-Lussac's report (note 32), the president announced that Chaptal had died (33). The four remaining members of the chemistry section, Deyeux, Thenard, Darcet and Chevreul were all present and at 4.30 p.m. the Academy entered into a secret meeting (34). In the name of the chemistry section, Thenard presented the candidates in the following order: 1° Dumas; 2° Robiquet; 3° Pelletier; 4° Bussy and 5° Caventou (35). In a written report he outlined the credentials of the candidates, and the usual discussion period ensued (36). Undoubtedly it was during this period that someone brought up the problem of Dumas' dye factory and the financial difficulties associated with it. In making the announcement that the election would take place in the next meeting, the president also advised members that they would be notified about the

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33. Chaptal's death from dropsy on the evening of 29 July left a second place vacant in the chemistry section.

34. These secret meetings were open only to Academy members.

35. A minimum of three and a maximum of six names could be presented. Though Deyeux was quite old, it is still surprising that he did not make the announcement.

36. Gauja, op.cit.(7-3), p.42, described the procedure: "A report on the credentials of each of the savants was read; it was followed by a discussion, normally consisting of a series of eulogies centred on two or three of the leading candidates given by a member of the section who supported his candidacy, at times directing pertinent points against his competitors, whose sponsors in their turn took the gauntlet; at times the discussions that resulted were quite cutting."

forthcoming meeting in a letter that would be sent to their homes (37).

Dumas had asked to be listed this time. He would have been confident of a high listing and prepared in advance the printed catalogue of memoirs, articles and other works that was required (38). Despite his friendship with Pelletier and Robiquet, he would have been pleased to be placed first in line (39), but had not expected anyone to raise the problem of his dye factory (40). Quickly he prepared a letter of explanation, had it printed and included it in his catalogue. It began:

> "Before presenting myself as a candidate for the place vacant in the chemistry section, I had only considered my situation from a scientific point of view. Unconcerned about my social position, I had not seen any need for the explanations which have become essential because of false accusations that are spreading about me. I take the liberty of sending you these explanations, and I would have done so earlier had not the zeal of some friends and their solicitude for my peace of mind prevented these rumours from reaching me." (41)

After the explanations necessary had been given, he added:

> "I venture to hope that these positive assertions will again place on a purely scientific ground a question that should never have left it.
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> Sir, I regret infinitely that I have been forced to

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37. This was normal procedure, since rarely, if ever, were all of the members present for a particular meeting.

38. He listed 49 memoirs and articles, describing each with a note, sometimes a line, sometimes a long paragraph.

39. He was placed ahead of men who "had spent longer in their careers" as he had written about Pelouze (see p.270). Dumas had just turned 32. Robiquet (52), Pelletier (44), Bussy (38) and Caventou (37) were all professors at the Ecole de Pharmacie. All but Bussy had pharmacy shops as well. This may account for the fact that Pelletier alone had presented research to the Academy at the time, the work on opium mentioned in note 30, and it suggests another reason for the place Dumas was given by the chemistry section.

40. See pp. 121 ff.

41. Notice sur les Travaux Scientifiques de J. Dumas. (See Chapter 3, note 110).

> tire you with such details, but I am only too well aware of the influence that these rumours can have on the decision of the Academy to hesitate in destroying them by the only means available to me on such short notice." (42)

On 6 August 1832 the Academy met as usual but it was hardly a normal day for Dumas. The members are listed in Table 7-1 with their age at the time and an indication of those who were present that day (43). Since it

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TABLE 7-1. Members of the 11 Sections of the Academy in 1832.

1. Geometry
Le Gendre 79
La Croix (Pres.) 67
Biot 58
Poinsot 55
xAmpère 57
Puissant 62

2. Mechanics
Prony 77
Molard 73
xCauchy 42
Dupin 47
Navier 47
Hachette 63

3. Astronomy
xCassini, J.D. 84
Lalande, Lefrançois de 66
Bouvard 65
xArago 46
Mathieu 48
Damoiseau de Monfort 64

4. Geography & Navigation
xBeautemps-Beaupré 66
Freycinet, L.C. 52
xRoussin 51

5. General Physics
xGay-Lussac 53
Poisson 51
Girard 66
Dulong 47
Savart 41
Becquerel, A.C. 44

6. Chemistry
Deyeux 87
Thenard 55
Darcet 54
Chevreul 45

7. Mineralogy
Lelièvre 80
Brongniart, Alex. 62
xBrochant de Villiers 60
Cordier 55
xBeudant 44
Berthier 50

8. Botany
xJussieu, A.L. de 84
Desfontaines 82
La Billardière 76
Mirbel 56
Saint-Hilaire 52
Jussieu, A. de 34

9. Rural Economy
xTessier 90
xHuzard 76
Silvestre 69
xMorel-Vindé 73
xFlourens 38
xDutrochet 55

10. Anatomy and Zoology
Geoffroy Saint Hilaire, E. (V.P.) 60
Latreille 69
Duméril 58
Savigny 55
Ducrotay de Blainville 54
Cuvier, F. 59

11. Medicine and Surgery
Magendie 48
Boyer 72
Dupuytren 54
Serres 45
Larrey, D.J. 66

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42. Ibid.

43. This list was drawn up from the Annuaire of the Academy of Sciences for 1975. Section numbers precede their titles. Members are listed in order of precedence with their age indicated as of 6 August 1832, and an indication that they were absent (x) that day (had not signed the register). Birth dates were obtained from the Index Biographique des Membres et Correspondants de l'Académie des Sciences du 22 décembre 1666 au 15 décembre 1967. At full strength there were 65 members, at this time 60.

was not a secret meeting the candidates could have been present in the public benches. It began with the reading of the minutes of the last meeting and their approval. Reception of books, journals, etc. was acknowledged and members appointed to review certain of them. A paquet cacheté (44) was deposited. Antoine César Becquerel (1788-1878) presented some notes on the atomic theory in the name of Gaudin. The order approving Dulong as permanent secretary was read and he was invited by the president to assume his new place. The need to form a committee to choose a successor to G. Cuvier at the Collège de France was indicated. There were priority claims, notes on cholera, the usual business. Then "recognising with the chemistry section the superiority of M. Dumas' credentials, Pelletier asked that his name be withdrawn from the list of candidates presented in the last meeting." (45) There were a few more items, and finally, at precisely 3.30, as the Procès Verbaux noted: "The Academy proceeded to the vote for the nomination of a member for the chemistry section in replacement of M. Serullas." (46) The ballots were handed out, filled in, collected quickly in the urn and counted. Since Arago was not present (47), Dulong performed his first function as permanent secretary, announcing the number of voting members present: "The number of voters is 44 (48); that of the ballots cast is also 44." (49)

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44. It was an established practice to hand in sealed packets or letters so that the donor could claim priority for the information contained in it.

45. Loc.cit.(7-21), p.98.

46. Ibid.

47. Arago had written a note to the Academy excusing himself from the meeting of 6 August because of illness.

48. 46 members signed the register (including Gillet de Laumont, an Académicien Libre and the president who had no votes). For the election to take place 44 voting members had to be present (two-thirds of the membership). This may account for the recording of this number. The vote for a successor to Alexandre Henri Gabriel de Cassini (1781-1832) as Associé Libre which was to have taken place on 27 August 1832 was delayed because only 43 voting members were present.

49. Ibid.

The president announced the names inscribed on the ballots for all to hear and for the secretary to record. Soon after the last vote had been tallied, the president announced:

> "The votes are divided thus: M. Dumas 36, M. Robiquet 6, M. Pelletier 1, M. de Bussy 1. M. Dumas, having obtained an absolute majority of the votes, 23, ... is proclaimed elected by the Academy. This election will be submitted for the approval of the king." (50)

On 20 August the president announced that this approval had been given and the young chemist was invited to take his place among the members (51). For the first time he signed the register of members present (52).

An examination of Table 7-1 indicates that most of its members were rather elderly. The average age was just under 70. Only two members were under forty and only ten in their forties (53). This might have been reason enough to expect a vote for one of the older candidates. Robiquet had done good work over a long period and if reward for service had been the greatest consideration he would have had the best claim. Certainly there would have been other opportunities for Dumas to be elected. Chaptal's place was to be filled and Deyeux at 87 was the second oldest member of the Academy. It was both a credit to the Academy and a tribute to Dumas and the friendships he had formed that his ability and character were recognised at so early an age.

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50. Ibid.

51. "The Minister of Commerce and Public Works is sending the Academy a copy of the Royal Order dated 19 August last, confirming the election of M. Dumas to the place vacated in the chemistry section by the death of M. Serullas." Ibid., p.110.

52. This signing gave him the right to a *jeton*, his 'pay' for attending the meeting. Its value at that time was about 6 francs. Once the secretary signed the register it was closed and no further entries could be made. Promptness was more than a virtue!

53. Only one-fifth of the members ~~was~~ were under fifty years of age.

From this time Dumas took an active part in the activities of the Academy, a communications centre for the reception, dissemination and evaluation of scientific information and a forum for the encouragement and evaluation of potential scientists and the reward of those who had made substantial contributions to the development of the sciences through their research.

Reception of Information. Written communications (books, journals, notes, memoirs, letters) and materials (models, samples) directed to the Academy were deposited with the permanent secretary at the Institute. A report on what was received during the week was given at the following meeting. Anyone wishing to give a verbal communication at one of the meetings, held each Monday afternoon, was required to ask in advance to be listed in the agenda. Special Academy business always had priority and could be inserted into any part of this agenda. Members were given priority over non-members, so that normally the latter were obliged to put in their request well in advance of the day on which it might be read. The meetings were opened with a reading of the minutes of the preceding meeting; important letters were read in the order received, followed by memoirs or notes read by members, first their own, then those of non-members. Memoirs by correspondents if any, then followed and finally those read by non-members who sought the judgment of the Academy. Even before becoming a member Dumas made sure that volumes of his Traité and the issues of his journals were given to the Academy, partly to place his name before the members and partly as a sign of respect (54). He had sent written memoirs for entry into the Montyon competition and had read many to the Academy. As a member he was now able to read those of others.

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54. The French Revolution brought an end to the law that every book required royal authorisation to be printed. For ~~most~~ many scientific works it had been administered by the Academy of Sciences.

This he did for the first time on 24 September (55). He was also given the right to make comments on the work of others, as he did when Biot read a memoir on the rotatory power of the essences of turpentine and lemon in 1836 (56). From this time he used this mode of communication more frequently.

Dissemination of Information. Until 1835 the proceedings of the Academy were not published. Information given to the Academy had limited direct circulation. Memoirs of members were sometimes published in the Mémoires de l'Institut and those of non-members read at meetings that did not appear elsewhere would be printed in the Mémoires des Savants Etrangers if permission were given (57). But these journals were published infrequently and irregularly (58), so that the memoirs had often lost their timeliness. Regular scientific journals such as the Annales de Chimie et de Physique and the Journal de Pharmacie, in which Dumas' work appeared most often, were the normal outlets for memoirs read in the Academy. Though several of Dumas' memoirs were published in the Mémoires de l'Institut (59), it was always

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55. Dumas read a memoir by Pelouze, a répétiteur at the Ecole Polytechnique on "The Influence of Water on a Great Number of Chemical Reactions", Ann. Chim. Phys., 50 (1832) 314-19 and 434-38.

56. For Dumas' remarks see Comptes Rendus, 2 (1836), 547.

57. Dumas' work always appeared elsewhere.

58. Volume 14 of the Mémoires de l'Institut contained memoirs read from 1829 to 1834. Its publication was "well underway" in May 1835. Loc. cit.(7-21), p.699.

59. For example his "Mémoire sur la Loi de Substitution, ou Métalepsie" appeared in Mémoires de l'Institut, Série II, 14 (1838), p. 495-556. He made a few minor changes.

several years after they had been published elsewhere (60). To solve the problem of publication delay and misinterpretation by the popular press, Arago proposed on 23 March 1835 that "a detailed and faithful account of the weekly meetings" be published every Saturday, that he and Flourens were willing to see to it; the Academy agreed (61). Regulations were drawn up and adopted by the Academy on 13 July 1835 for the Comptes-Rendus Hebdomadaire des Séances de l'Académie des Sciences (62). The first issue was dated 8 August (63). From this time Dumas' work tended to appear more in the Comptes Rendus than in the Annales de Chimie et de Physique despite the fact that he became one of the editors of the latter in 1841 with the beginning of the third series (64).

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60. The memoir on metalepsy was originally published in Ann. Chim. Phys., 56 (1834), 113-50. It was the last of three articles, "Recherches de Chimie organique", the others: Ibid., 53 (1833), 164-81 and 54 (1833), 225-47. Liebig had published the first two parts in 1834, Annalen 9 (1834), 65-85 and 10 (1834), 277-98, but not the third. When the whole appeared in loc.cit.(7-59), he took the opportunity to publish the third part, which, by that time, he was willing to accept. Annalen, 27 (1838), 135-55.

61. PVAS, 10 (1832-35), 679. Several proposals presented by Arago 30 March were left in the Academy for examination by members; discussion began 18 May and was concluded in a closed session on 13 July.

62. Ibid., 731. The regulations are given Ibid., 756. They include the following which are of interest: Weekly issues are a minimum of 40 pages in length and form two volumes per year. They consist of extracts of the work of members as well as reports on work presented by non-members before the Academy. Members are allowed 50 pages per year (not more than 6-8 pages in any issue). This is in addition to reports which members are required to make, which are not to exceed four pages in length in any issue. These numbers were not strictly adhered to after 1836. It seems probable that the amount of material coming in was not as great as was anticipated.

63. The Procès Verbaux (Printed version, Paris, 1922) ended with the meeting of 27 July 1835. Vol. I of the Comptes-Rendus covered August to December 1835. Thus odd number volumes end the years instead of beginning them as might be expected.

64. The others were Gay-Lussac and Arago who had stayed on, Chevreul, Savary, Pelouze, Boussingault and Regnault.

Evaluation of Information. Apart from communications by members, much of the plethora of information coming into the Academy required evaluation, some sort of judgment concerning its merit (65). This was done by individual members or commissions of two or three who were assigned officially by the president to examine the work (66). For the one submitting the work, there was hope for approval, perhaps eventually prestige. For the Academy, there was always the possibility of discovering another talented young man to complete its own ranks or at least to take up one of the teaching positions that fell vacant from time to time in the various advanced schools in Paris, a young man who may have opened another path towards a better understanding of science, who could carry on the French tradition of excellence in scientific achievement. Dumas had been the beneficiary of good reports by members since his arrival in Paris. He was now given the opportunity to make similar judgments. His first assignment, a verbal report of a work sent to the Academy was not demanding (67). In the same session, he was invited to join Chevreul in the examination of samples of the two iodides of platinum prepared by Jean Louis Lassaigne, (1800-1859) which the latter claimed were analogous to the chlorides of the metal (68). In his report, Dumas reviewed clearly and

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65. Although this judgment was reserved to verification of data, it is easy to see that the opinions or prejudices of the examiners could slip in quite subtly or even openly. Thus for example, Dumas showed approval of work that verified his substitution theory.

66. Assignment was probably made in advance by the section (or the ~~perpetual~~ permanent secretary?) since they would be more aware of the particular slant of the work as well as the current work-load of the various members of the section.

67. In the meeting of 10 September 1832 he was asked to report on "Recherches sur le Mauvais Cuir [sic] et ses Effets" by Rigaud, Lille, 2 vol., 1832. Loc.cit.(7-61), 117. The report on "Mauvais Air" was given 12 November. Ibid., 152.

68. They were included with a letter of explanation. Ibid., 118.

concisely what had been done, put it into its proper historical and theoretical perspective, suggested its predictive value, offered a direction in which the work could be extended and finally encouraged the author in the usual fashion by urging publication of the work in the _Mémoires des Savants Etrangers_ (69). This was the general pattern which he followed whenever his reports were presented. Normally he repeated the work of the author (70), and later in his career he sometimes announced discoveries of his own made while he investigated the claims of the author (71). Even more frequently he used the reports to reinforce his own ideas, approaches or theoretical considerations (72). Dumas became heavily involved with commissions, perhaps because the demands on the chemistry section were greater (73).

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69. Dumas read this 2½ column report on 12 November. _Ibid._, 152-154.

70. "It is easy to obtain the pure platinum iodides with the help of the precautions indicated by the author." _Ibid._, 153. Where he had directed the work in some way this would not have been necessary (e.g., his report on Péligot's memoir "The Distillation of Calcium Benzoate", _ibid._, 551-52.

71. It was Dumas' report on the work of Pelletier and Walter that led to his reexamination of the atomic weight of carbon (see page 186).

72. Dumas used half of a lengthy report on a memoir by Pelletier (_ibid._, 173-75) to extol the work as an example of the proper method of doing research in organic chemistry. Pelletier had discovered an organic compound, isolated it, analysed it and using theoretical considerations had related it to other known substances. Dumas noted that prior to the development of easy analytical methods analyses and the determination of relationships were left to others but that his was no longer necessary. Certainly Dumas had been using this procedure for some time.

73. A count of references in the _Procès Verbaux_ for 1832-35 shows that of the ten members who had the heaviest working load during that period there were three chemists: Thenard, Chevreul and Dumas, and this despite the fact that Dumas had not been a member until September 1832. There were three from the anatomy and zoology section, Geoffroy St. Hilaire, Duméril and Henri Marie Ducrotay de Blainville (1777-1850); two from medicine and surgery, Magendie and Serres, Siméon Denis Poisson (1781-1840) from physics and Arago from astronomy.

Evaluation and Encouragement of Scientists. The Academy had to fill its own ranks, and also positions in certain schools. To ensure the choice of capable men meant evaluating them in the terms outlined in the discussion of Dumas' election. Members of the Academy were always looking for talented young men. As professors on the staff of the various schools, they were in a particularly good position to find those who were outstanding. A research laboratory, founded by Dumas in 1832 (which will be discussed later), was especially fruitful in this regard. There were two sorts of elections involved: Election of its own members, associates and correspondents, and activity considered of the utmost importance by its members as has been pointed out; election of candidates for Chairs at the Ecole Polytechnique, Muséum, Collège de France and Ecole de Pharmacie (74). Shortly after his own election, Dumas took part in what was for him the first election of an Academician, an Associé Libre (75). On the same day, he participated in the election whereby Flourens succeeded Cuvier in the Chair of Human Anatomy at the Muséum (76). On 31 December the chemistry section indicated that it was time to fill Chaptal's place which had been vacant since 30 July. During that time Robiquet had been busy, so that he was able to present a memoir on 10 December and two others in the meeting in which the announcement was made (77). Pelletier too had read a memoir, "Researches on the Elementary

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74. The staff of these schools also named a candidate, so that theoretically they had a voice. In practice the choice of the Academy almost always held sway. The decision for Balard over Laurent at the Collège de France, rightly or wrongly, has become infamous.

75. The delayed election of René Nicolas Dufriche Desgenettes (1762-1837) (Cassini's successor) on 3 September (Note 7-48).

76. Before the end of the year, several more elections of both types took place.

77. Ibid., 165, 172, 173.

Composition of Several Fundamental Constituents of Plants", on 22 October, which Gay-Lussac and Dumas were asked to examine. On 31 December Dumas gave the report (see note 72), immediately before Chevreul read his report, prepared with Thenard, on Robiquet's first memoir. On 17 December one of the members (probably Dumas) had asked that a letter from Pelletier announcing the discovery of a new substance in opium be read (78). On 7 January in his own name and Dumas', Chevreul reported, not unfavourably, on another of Robiquet's memoirs (79). At this point Dumas most likely favoured Pelletier's candidacy, though it must have been difficult for him to face the choice. How much more difficult it must have been, when it became evident that the other members of his section showed a preference for Clément and he was obliged to agree on the following list, announced in a closed meeting the same day: Clément on the first line, then Robiquet, Pelletier, Bussy and Caventou in that order. Both the length of the waiting period and the nomination of Clément seem to indicate that there was a prejudice against the pharmacists despite the research they had done (80). Certainly Dumas could have accepted Clément under other circumstances (81), but his friendship with the pharmacists, indeed his debt to them, made it quite impossible in this

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78. Ibid., 167.

79. Ibid., 184-85.

80. Clément, professor at the Conservatoire, had collaborated with his father-in-law, Charles Bernard Désormes (1777-1862), a Correspondent of the Academy (chemistry), on several memoirs on specific heats. Like the pharmacists he had failed as a candidate but had published nothing for several years, whereas his opponents had continued active research. It may well be that the prejudice was in the Academy rather than the section and the section hesitated to present only pharmacists.

81. Dumas had been a student of Clément.

instance. Fortunately Robiquet was elected on the second round of ballots (82).

Dumas was involved as a candidate in a very important election. On 15 July 1833 Arago, in a closed session, announced the resignation of Dulong as permanent secretary, due to ill health (83). Commissioners to name a replacement were elected on 22 July: Duméril, Thenard, Adr. de Jussieu, Brongniart, Chevreul and De Blainville (84). Immediately before the candidates were announced on 5 August, Dumas read a memoir "Researches in Organic Chemistry" (85). In alphabetical order the names of those who had "manifested the wish to be listed as candidates for the position of permanent secretary" were presented: François Sulpice Beudant (1787-1850), 45 years old, elected 1824; Dumas, 33, recently elected; Flourens, 39, elected 1828; and Augustin François César Prouvansal (called Auguste) de Saint-Hilaire, (1779-1853), 53, elected 1819. The election was held at the next meeting. There were 46 voting members present. 44 voted. On the first ballot: Flourens 20; Saint-Hilaire 12; Dumas 9; Beudant 3. On the second: Flourens 23; Saint-Hilaire 15; Dumas 6. Flourens had received the absolute majority and hence was elected (86). Brongniart declared, "He is the <u>savant</u> who appears to me to be the least right for this position, and neither a prince

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82. On the first round 50 voted. The results: Robiquet 23, Clément 18 and Pelletier 9. One more voted the second time: Robiquet 31, Clément 18, Pelletier 2. This was one time when the Academy overrode the decision of the section, and the section may well have been happy that it had.

83. <u>Ibid</u>., 324.

84. <u>Ibid</u>., 331.

85. <u>Ibid</u>., 334.

86. <u>Ibid</u>., 336.

nor a minister has named him" (87). It was over 34 years before Dumas succeeded Flourens (88).

The Academy offered several incentives whereby scientists might be encouraged to pursue research: Prizes, grants and assurance of priority (hence a place in history). Probably the greatest encouragement was the awarding of prizes. Among the most well-known were the various Montyon prizes, which are the oldest administered by the Academy and certainly the most numerous. They are still awarded for work in improving health conditions in industry; mechanics; medicine and surgery; physiology; and statistics. The principal value of these awards lay in the prestige associated with them. As a recipient of the Montyon prize in physiology in 1824 (89), Dumas was well aware of this and was often called upon to serve on or preside over commissions that decided the topics for competitions or judged the memoirs that were entered. Apparently the Jecker prize was founded in 1851 at Dumas' suggestion (90). In 1943 a decennial prize in chemistry was founded in honour of Dumas. Its value when it is given in 1980 will be 3,000 francs (91).

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87. Launay, op.cit.(1-42), p.149. Launay says that Dumas "began making enemies and malevolent journal articles in which father-in-law and son-in-law were both attacked at the same time distressed poor Brongniart. Dumas, already hardened, imperturbably continued his ascent." Ibid., p.148.

88. 20 January 1868.

89. See Chapter 2.

90. When Jecker heard that Dumas was closing his private laboratory in 1849, he offered to contribute financially towards keeping it open. Dumas refused, but suggested that if Jecker wished to help young men interested in chemistry he could donate a prize for this purpose. This prize, still awarded biennially, is given to "the author of the most useful written work on organic chemistry, or failing this, the work most proper for hastening its progress." It is currently valued at 6,500 francs. Annuaire, (1975), p.170.

91. Ibid., p.172.

CHAPTER 8

THE LAW OF SUBSTITUTION AND THE TYPE THEORY

"In examining with care the action of chlorine on various substances, I have been led to suggest the following rules:

1°. When a substance containing hydrogen is submitted to the dehydrogenating action of chlorine, bromine, iodine, oxygen, etc., for every atom of hydrogen that it loses it gains one atom of chlorine, bromine or iodine and a half-atom of oxygen.

2°. When the substance containing hydrogen also contains oxygen, the same rule applies without modification.

3°. When the substance containing hydrogen also contains water, the latter loses its hydrogen without anything replacing it, and if a new quantity of hydrogen is removed after this, it is replaced in the way previously indicated." (1)

In these words Dumas gathered together the basic tenets of his substitution theory, first announced to the Academy of Sciences on 13 January 1834 (2). His approach radically changed the direction of research in organic chemistry. Using the dualistic theory, which had served as such a valuable tool in the hands of Berzelius for developing mineral chemistry, Dumas had introduced his ether theory, providing the first rational attempt at the classification of organic compounds. From that time, many chemists focused on what Berzelius later called rational formulas, and on groups of elements that acted as units in chemical reactions. With the introduction of the substitution theory, many investigations centred on the reaction of organic compounds with oxidising agents (the halogens, oxygen, nitric acid, etc.) and were interpreted in terms of the theory. In the course of these studies the dualistic theory began to come under fire. As a working hypothesis it was rejected publicly by Dumas in 1839, although he had had doubts about it much earlier. Having set aside other theories by that time (see Chapter 4), he was able to see the value in a unitary hypothesis, which could be used in combination with the properties deduced from chemical reactions to classify compounds into types. While Dumas' type theory was an important step forward in the more general classification of organic compounds, it did have inherent faults which soon became evident, and Dumas was able to initiate the next classificatory phase by introducing the concept of homologues. In this chapter these ideas will be expanded in an attempt to bring out the central role that Dumas played in the development of theoretical

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1. J. Pharm., 20 (1834), 285-86. See also note 6-88.

2. Ann. Chim. Phys., 56 (1834), 113-50. This memoir was reprinted with minor revisions in 1838. Mem. Acad. Sci., 15 (1838), 519-56. It was then that Dumas attempted to introduce the term metalepsy (μετάληψις, exchange) for the process of substitution, but it never came into general use. Ibid., 554.

organic chemistry with particular emphasis on the law of substitution and the type theory.

It would appear that Dumas first became interested in the chlorination of organic compounds some time before 1828, for in the first volume of the Traité he discussed the experimental details of the reaction of several hydrocarbons with gaseous chlorine (3). Moreover, he was interested in bleaching as a chemical industry in which organic substances reacted with chlorine (4). Thus it would not be surprising if he were "asked by a merchant to suggest a method of bleaching certain kinds of wax which resisted the ordinary processes and thus remained unsaleable" (5). Nor should ones credulity be strained in any way by Hofmann's claim that Dumas gave a royal 'incident' as the origin of his substitution theory (6). Guests at a reception given by Charles X at the palace of the Tuileries were, as Hofmann noted:

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3. After listing eleven different hydrocarbons known at the time with their composition in numbers of atoms (Traité, Vol. 1, p.464), he discussed the chemistry of each, including the reaction of chlorine with four of them: hydrogène demi-carboné (methane); hydrogène carboné (ethylene); carbure d'hydrogène (probably propylene); and bicarbure d'hydrogène (benzene). He used worded equations to describe the first of these quantitatively: "Atoms used. 4 at. chlorine. 1 at. hydrog.demi-carb. 2 at. water. Atoms produced. 8 at. hydrochloric acid. 1 at. carbonic acid." Ibid., p.465. In modern chemical notation these would be $CH_4 + 4Cl_2 + 2H_2O = 8HCl + CO_2$ and $CH_4 + 3Cl_2 + H_2O = 6HCl + CO$. He also discussed the reaction of hydrocyanic acid with chlorine in which hydrochloric acid and cyanogen chloride were formed. Ibid., 533.

4. In his discussion of chlorine bleaching he described the reaction as simple removal of hydrogen from the organic dye, the hydrogen combining with the chlorine to form hydrochloric acid. Ibid., p.60. Other compounds were formed, some no doubt combined with chlorine. He acknowledged the complexity of these reactions and his interest in them when he said: "It is highly desirable that these various reactions be examined in all their details." Ibid.

5. Hofmann, op.cit.(1-6), xiv.

6. "This account of the peculiar origin of the substitution theory the author of this sketch owes to Dumas himself." Ibid.

> "greatly incommoded by irritating vapours ... obviously arising from the wax candles burning with a smoky flame. Alexandre Brongniart, in his capacity of director of the porcelain factory at Sevres, was looked upon as a chemist to the king's household, and it appeared but natural that he should be consulted respecting this unpleasant incident. Brongniart intrusted his son-in-law with the task of investigating the suspicious candles ... Nor had Dumas any difficulty in supplying the explanation. The irritating vapours were chlorhydric acid ... the chlorine bleached wax had retained chlorine, which during combustion of the wax was evolved in the form of chlorhydric acid." (7)

Recently this incident has been used to denigrate "anecdotal history", but, in fact, there is no reason to question Hofmann's claim concerning its significance (8). In a lecture given during the first semester in which Gay-Lussac replaced Dulong as chemistry professor in the Faculty of Science, he said:

> "When gaseous chlorine comes into contact with oils, it removes part of their hydrogen, combining with it to form hydrochloric acid gas that can be collected; at the same time, part of the chlorine combines with the oil and takes the place of the hydrogen removed. ...
>
> Wax is bleached by chlorine but it combines with the wax and when it burns, irritating vapours of hydrochloric acid are released in rooms. This method of bleaching must be discontinued." (9)

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7. Ibid.

8. Kapoor, op.cit.(1-101), 52-54, considers such "anecdotal history" as "an attempt at the trivialization of science, which is in fact a highly sophisticated and abstract kind of activity, necessarily involving a complicated background of theory and experiment for its growth." On the other hand, it should be remembered that science is also a human activity, influenced by such factors as intuition, serendipity and other human events. No one, least of all the chemist Hofmann, would claim that this event provided a full-fledged theory of substitution. Indeed, he had said earlier: "A strange incident *directed the attention of Dumas to a perfectly different order of phenomena*, the study of which occupied him for many years of his life, and ultimately led him to one of his finest conceptions, the theory of substitution." Ibid. (my italics).

9. *Cours de Chimie*, Paris, 1828 (version not authorised by Gay-Lussac). Lecture of 16 July 1828. Quoted by Partington, op.cit.(2-17), p.360. Dulong's health had failed because of overwork. Crosland, op.cit.(1-28), p.227.

There is no indication when he did the original research on this topic, but it may have been well before July 1828. Quite probably he studied the action of chlorine on wax, as well as on oils, in connection with his course at the Ecole Polytechnique and mentioned it in a lecture there. Thus when he added the remark about wax in the above quotation, he could have been referring to the incident in the palace. Otherwise it is difficult to explain the use of the candles in such circumstances if the effects were already known. Hofmann pointed out that Dumas was working on his ether theory at the time. Thus the reception was probably in 1827. Dumas may have attended the lecture in which Gay-Lussac had mentioned his research on chlorination, or he may have heard him speaking about it privately. Thus when Brongniart approached him, he felt obliged to repeat the experiment because of the importance of the occasion. More than ten years later he wrote:

> "But in publishing [experiments involving the action of chlorine on alcohol] I did not fail to recall that M. Gay-Lussac had already made a comment about the action of chlorine on wax analogous to the one to which I was led. Even though M. Gay-Lussac had never published this fact, had only mentioned it in his course, I felt compelled to reproduce his observations as soon as I found that I was in agreement with my illustrious confrère, and I took care to do so." (10)

At that time he became sufficiently interested to undertake a deeper investigation of the matter, particularly with a view to including chlorination studies in his Traité. He soon discovered the difficulties involved and it was 1833 before he completed research on chlorinated oil of turpentine, from which he could say:

> "I knew from experiments relating to the action of chlorine on oil of turpentine that each volume of

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10. Comptes-Rendus, 6 (1838), 695. Dumas' words were chosen with care because of the priority disputes in which he had been involved.

> hydrogen removed was replaced by an equal volume of chlorine, which, moreover, agrees with the result obtained by M. Gay-Lussac when he treated wax with chlorine." (11)

~~By that time Dumas was aware that reactions with chlorine could occur in two different ways: At times it simply removed hydrogen (for example, in the reaction with marsh gas hydrochloric acid gas and carbonic acid were formed), at times it became a part of the compound while also releasing hydrochloric acid gas (for example, wax and turpentine). But the rule governing the choice of the one or the other was not at all evident, and is now known to be quite complex.~~ Usually chlorination reactions gave rise to several compounds. In Dumas' time they were almost always difficult, if not impossible, to separate. He continued to work on the problem, sometimes alone, sometimes assisting students in his laboratory. Laurent, a graduate of the Ecole des Mines, chose a career in organic chemistry as a result of the work with Dumas on naphthalene and continued to work under Dumas' guidance on the chlorination of naphthalene. Victor Auguste Jacquelain (1804-1885), Félix D'Arcet (1807?-1846) and many others were also guided by Dumas in the study of organic reactions involving chlorine. Dumas continued to search for rules governing the reactions involved.

At the same time, of course, he was intent upon finding evidence for the validity of his rational formulas for alcohol and the ethers. Thus when a chloroether was obtained by the chlorination of alcohol in two different ways late in 1831, he was particularly interested. Liebig, by passing chlorine gas through alcohol, had obtained a new compound that he called chloral (12). When he treated it carefully with aqueous alkali, the ether

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11. Loc.cit.(8-2), 140. He touched on his research on the action of chlorine on turpentine in a memoir "Sur les camphres artificiels des essences de térébenthine et de citron", Ann. Chim. Phys., 52 (1833), 400-10.

12. Ann. Phys., 23 (1831), 444. Liebig first gave the formula in a longer article that he had written for the journal that he had just acquired. Annalen, 1 (1832), 182-230 (189).

was formed along with a formate. He gave it the formula C_4Cl_{10} (C = 12). Soubeiran (13) obtained a chloroether by reacting bleaching powder (14) with alcohol and found its formula to be $C^4H^4Cl^4$ (C = 6). Dumas prepared both and found they were the same liquid which he later called chloroform. As usual he measured the vapour density, finding that it was 4.2, which he could reconcile with neither formula. From Soubeiran's formula the value should have been 2.9, so he dismissed it saying that the chloroform was not perfectly pure. The value from Liebig's formula was 3.5. He was not as quick to reject it, for as he noted:"The particular care with which M. Liebig had purified the substance analysed made me think that the composition of that substance was known exactly"(15). After satisfying himself that his vapour density value was correct he began to search for another formula. As in the past, he found the answer in a chemical reaction, this time one in which chloroform inter-acting with aqueous potash formed potassium formate and potassium chloride. The comparison left no doubt and undoubtedly it was then that he decided that chloroform must have the formula $C^4H^2Cl^6$, the "equivalent of anhydrous formic acid" ($C^4H^2O^3$) (16). He calculated its theoretical vapour density, 4.113, very close to the value he had obtained by measurement. Several new analyses carried out even more carefully

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13. Ann. Chim. Phys., 48 (1831), 113-57.

14. Chloride of lime. For the composition of the dry substance, Dumas gave 2 atoms of lime, 4 atoms of water and 1 atom of chlorine. Traité, Vol. 2 (1830), p.808. The modern formula is $CaOCl_2$.

15. Loc.cit.(8-2), 116.

16. Ibid., 120. The equation for the reaction, had Dumas written it, would have been:

$$C^4H^2Cl^6 + 4\ KO = C^6H^2O^3.KO + 3\ KCl^2$$

Though Dumas used the symbol Ch for chlorine until after 1840, the modern symbol Cl will be used throughout for clarity.

confirmed the formula (17). He then turned to chloral and by comparing its formula ($C^8H^2O^2Cl^6$) with that of alcohol ($C^8H^8.H^4O^2$ or $C^8H^{12}O^2$) was able to say:

> "From a careful study of these results it is evident that ten volumes of hydrogen taken from the alcohol have been replaced by only six volumes of chlorine. ... Though ten volumes of hydrogen lost by the alcohol should have been replaced by ten volumes of chlorine, this did not occur.
> The cause of this difference is easy to see. Alcohol must be represented by water and bicarboned hydrogen, and when it is accepted that chlorine acts on the hydrogen of the water in a completely different manner than on the hydrogen of the hydrocarbon, one has the key to the apparent anomaly that has been pointed out." (18)

Thus he seemed to have found not only a truly formidable support for his ether theory, as has been indicated earlier, but he had also found the rules governing the two ways in which chlorine would act in contact with organic compounds, the basis for a new theory, the substitution theory (19). When chlorine reacted with aqueous hydrogen forming hydrochloric acid, the hydrogen was simply removed. When it reacted with the hydrogen in the bicarbon hydrogen portion forming hydrochloric acid, the hydrogen was not simple removed, but was replaced by the chlorine, atom for atom. However, rules drawn from a single compound would have been of little value. Dumas set about establishing the generality of an hypothesis which could prove to be so useful. He examined a number of reactions, some new, some already known and concluded:

> "The rule governing the action of chlorine [on alcohol] that flows from the preceding experiments applies certainly to all substances capable of reacting as dehydrogenating agents. In

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17. The amount of hydrogen in the compound was less than 1 % by weight.

18. Loc.cit.(8-2), 140-41. For the missing portion see note 11.

19. Because this memoir was so important for both theories, some duplication of material from Chapter 6 is unavoidable.

> testing it, I have been able to account for some of the most well-defined reactions of organic chemistry." (20)

What were these reactions?

1 and 2. The oxidation of alcohol to acetic acid and finally formic acid. In each case 4 volumes of hydrogen in the hydrocarbon portion are replaced by 2 volumes of oxygen (21).

3. Chlorination of Dutch liquid to a chloride of carbon containing 2 volumes of carbon and 3 volumes of chlorine, i.e. $C^8H^8.Cl^4 + Cl^{16} = C^8Cl^{12} + H^8Cl^8$ (22).

4. Chlorination of hydrocyanic acid to chlorocyanic acid, $Cy^2H^2 + Cl^4 = Cy^2Cl^2 + H^2Cl^2$.

5. Oxidation of oil of bitter almonds to anhydrous benzoic acid, $C^{28}H^{12}O^2 + O^2 = C^{28}H^{10}O^3 + H^2O$ (23).

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20. Loc.cit.(8-2), 143. Of the several examples that he gives involving substitution, only two illustrate simple removal of hydrogen.

21. See Chapter 6, note 8~~5~~6. Elsewhere Dumas discussed oxidation of alcohol to acetic acid by air, and alcohol to formic acid by the action of manganese peroxide and sulphuric acid, rather than the two-step reaction suggested. Loc.cit.(8-1), 286-87.

22. Apart from the oxidation of alcohol to acetic acid, Dumas uses no equations in this set of examples. Those used by the present author are drawn from verbal data and some formulas supplied by Dumas. They are used for greater compactness and clarity.

23. Dumas did not give the formula for the oil in this article. Elsewhere he gave it as $C^{28}H^{10}O^2 + H^2$ as Liebig wrote it. Loc.cit.(8-1), 292. In his discussion of the benzoic acid theory, Dumas suggested that $C^{28}H^{10}$ be called benzogen, so that Liebig's benzoyl radical $C^{28}H^{10}O^2$ became benzogen oxide, analogous to oxide of carbon C^4O^2. In a footnote (ibid.) which was omitted from the Traité, he said that he had sent word of this to Wöhler and Magnus in August 1833 and that Liebig had used it in December. Partington, op.cit.(1-14), p.362, suggested that Liebig regarded this as an addition reaction, but this depended on whether the water formed was regarded as an integral part of the atom of benzoic acid or not and Dumas specified anhydrous benzoic acid, the condition in which most chemists at this time considered that acids existed.

6. Oxidation of grape sugar to oxalic acid,

$$C^4O^4.C^8H^8.H^2O + O^9 = C^{12}O^9 + H^{10}O^5$$ (24).

7. Oxidation of anyhdrous formic acid to carbonic acid,

$$C^4H^2O^3 + O^2 = C^4O^4 + H^2O$$

8. Oxidation of oxalic acid to carbonic acid,

$$C^4O^3.H^2O + O = C^4O^4 + H^2O$$ (25).

In his memoir, it is well to note, Dumas admitted the provisional character of the substitution theory, due to the limited number of examples that he had studied.

By this time Dumas had proposed three theories that were of some importance in the development of organic chemistry: a controversial one linking ethers by means of a common molecular arrangement, a second introducing amides and a third involving the substitution of one element for another in organic compounds. He had weathered unjust criticism of his theories (26).

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24. The hydrogen from the water portion was simply removed. The hydrogen in the hydrocarbon portion was replaced by oxygen. Dumas used it more to establish that Berzelius' formula $C_{12}H_{21}O_{10}$ was in error than to establish definitely the formula for sugar. That it could not be used to accomplish the latter is evident from the following equations using possible formulas (Dumas' notation) offered by the present author to 'explain' the phenomenon:

grape sugar: $C^{12}H^6O^3.H^6O^3 + O^9 = C^{12}O^9 + H^{12}O^6$ $(C^{12}O^9 = 3C^4O^3)$

cane sugar : $C^{24}H^{14}O^7.H^8O^4 + O^{18} = C^{24}O^{18} + H^{22}O^{11}$ $(C^{24}O^{18} = 6C^4O^3)$

25. Here again hydrogen is removed, not replaced.

26. Apparently using some source that was full of errors, Liebig (Ann. Chim. Phys., 55 (1834), 113-56) had included the following statement among his many criticisms: "Certainly these theories lack the perfection which should be expected from such distinguished chemists, because of the excessive haste with which new theories are established and published in France since M. Dumas arrived." Ibid., 137. In a note following his memoir on substitution, Dumas called attention in detail to the errors that Liebig had made, then observed with some feeling: "What more is there to say when the errors laid to me rest completely on such documents? [He had concluded that Liebig had not referred to the original memoir but a bad extract.] ... If a certain amount of zeal and a sincere desire to arrive at the truth are evident in my response to the objections that (cont.)

For some years he had been gathering data for the section of his Traité in which he would organise organic chemistry and examine its applications. This included both general and specific information: methods for the isolation and elemental analysis of organic compounds; densities (especially vapour densities); melting and boiling temperatures; crystalline form; derivatives (particularly salts and ethers). But before he could draw together the rapidly expanding body of information (27), it was necessary to decide not only what substances were compounds, but also which were organic. Only then could he arrive at a method of classification, and so be able to use the essential tool of all natural scientists. His attempts in this regard will be discussed in terms of the nature and methods of organic chemistry.

The Nature of Organic Chemistry. Initially, all substances had been classified according to their origin as plant, animal and mineral. By 1833 great strides had been made in the purification and analysis of the first two classes, but exposing them to strong chemical agents and drastic temperature conditions had yielded new compounds, not found in nature. These had to be included in any classificatory system. Dumas' definition of an organic compound did so:

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26. (cont.) have been levelled at me, it is because I have every right to reject with disgust anything that would tend to reduce the questions I am studying to the mosquito-like proportions of a struggle involving self-love. I will not bow out of any truly scientific discussion, but in the future I will remain deaf and dumb towards this kind of wholly personal criticism, which I have not provoked, have no wish to feed and to which the progress of human reason will do severe justice some day." Ibid., 56 (1834), 150-54.

27. "Tracing the history of these substances is a very difficult task to fulfill in an era when discoveries and serious modifications in this branch of our knowledge are occurring daily." Traité, Vol. 5 (1835), p.1.

> "By organic substances are to be understood definite chemical materials that are found completely formed in living things, or obtained from the latter by modifications that are becoming easier to make every day. These materials may be considered definite when they have the property of crystallising in a regular manner, or of forming compounds that will crystallise and have a fixed boiling temperature." (28)

He regarded all other organic substances as mixtures, to be studied by physiologists, not chemists. Clearly Dumas' definition depended on the origin of the compound, not on its nature. He used it as a practical guide simply because he had no other, although he suggested that carbon did have a central role:

> "I have searched in vain for another definition, and it is precisely because I have been incapable of finding one that I am attracted to the belief that organic chemistry and mineral chemistry are indistinguishable. ... In my opinion, organic substances do not exist; that is to say, I see in living beings only slow-working instruments (29) acting on nascent materials, thereby producing very diverse <u>inorganic compounds</u> from a small number of elements. Living beings do for compounds of carbon with the elements of air and water what great global revolutions have done for compounds of silicic acid with bases which come in contact with it." (30)

<u>The Methods of Organic Chemistry</u>. Dumas rejected the use of purely <u>a priori</u> hypotheses convinced that they led to no practical consequences. But he also rejected pure empiricism, even though he was probably the best analyst of his day and constantly insisted on the need for collecting data. But the science of organic chemistry involved much more than this: classifying all knownorganic compounds, finding their molecular arrangement, understanding their interaction, so that predictions could be made and new

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28. <u>Loc.cit.(8-1)</u>, 262. This was an early use of derivatives as a means of identifying organic substances as compounds.

29. "appareils".

30. <u>Ibid</u>., 267-68 (Dumas' italics).

directions for research opened to chemists. As he pointed out:

> "Sciences are based on facts, but they only become sciences when these facts, grouped together by sure concepts, take their place in the system, leaving unfilled spaces to be filled in by discovering other facts, and revealing the generalisations and predictions that arise from such a methodical arrangement." (31)

He emphasised the importance of following a plan that took into account not only data, but also relationships between substances, found by hypotheses:

> "Until now, a coherent pathway in chemistry has consisted simply in gathering facts, grouping them by analogies, drawing consequences from their relationship, and verifying them by experiments that are becoming more and more sensitive and certain." (32)

But he introduced a new note that would be characteristic of all hypotheses that he framed. Because relatively few organic compounds were known he believed that any hypothesis could only be tentative and was valid as long as it was in conformity with the content of the science at that time, as long as it tended to facilitate prediction and classification. Its primary importance lay in its ability to open new avenues of research leading to the development of a given part of the science or to the growth of the science as a whole:

> "The theories that we are about to discuss are doubtless not absolute truths at all, and everyone can regard them in a way that seems personally suitable. At the same time, it should be evident that those who were the first to devise them, or support them with the weight of their assent, basically are far from seeing in them the necessary expression of the truth. These theories must be judged from the viewpoint of their pure and current usefulness, because their immediate consequence is the classification of many substances into groups for ease in their study and the simple representation of a mass of complex phenomena. Moreover, they permit the prediction of many new reactions, or presume the existence of unknown substances susceptible of

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31. Ibid., 262.

32. Ibid., 265.

> being created by methods that the theory itself indicates to us. Seen in this way, perhaps the transitory theories that we adopt in organic chemistry suffice when they give us a clear explanation of the known facts. When two theories explain them equally well, it is always necessary to prefer the more general, the simpler, and above all the one richer in consequences and susceptible to immediate translation into new experiments." (33)

A second method that he emphasised at this time was the use of molecular arrangement as a particularly useful tool for the classification of organic compounds:

> "From all of this a single consequence may be drawn, that the elements can be grouped under many forms. ... What chemist would become involved in this kind of study for the sole purpose of knowing the proportion of the elements of any organic material whatever, if he were not animated with the hope of discovering some unexpected relationship, or some new and fruitful law? But these laws cannot be established without accepting some molecular arrangement which simplifies formulas ordinarily too complicated to enable relationships to be understood." (34)

To determine the nature of these groups required a study of the chemical reactions of the compounds (35). To do this properly involved the writing of chemical equations for the reactions, following the principle that matter is conserved during the course of these reactions. There were other theories, that had been derived from and applied to mineral chemistry, that he applied to organic chemistry. The determination of a uniform system of formulas for organic compounds from their vapour densities depended on Avogadro's hypothesis (36) for example. He also made constant use of

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33. Ibid., 271.

34. Ibid., 270, 272.

35. "Multiply analyses, follow with care the study of reactions in all their details, and relate the two classes of facts with a view of the whole. From this route many partial theories will arise, which, themselves interrelated, will soon result in a body of knowledge." Ibid., 290.

36. The atomic weights of compounds derived from their vapour densities represented one-volume formulas. With few exceptions Dumas wrote four volume formulas, thus providing an internally consistent system of formulas.

electrochemical theory in arriving at molecular arrangements (37). With his new theories, the ether, amide and substitution theories, and Liebig's benzoyl theory, he saw the beginning of a trend in the other direction:

> "I have the deep inner conviction that the future progress of general chemistry will be due to the application of laws observed in organic chemistry. ... Far from being surprised that organic chemistry offers us new types, I am astonished that these are not more different from corresponding mineral types than they are; and far from limiting myself to the application of the rules of mineral chemistry to organic chemistry, I think that one day, and soon perhaps, organic chemistry will provide the rules for mineral chemistry." (38)

Dumas was not a mechanist, but he did believe that living things were composed of particles of the same elements that could be found in inorganic compounds (39). He was already finding the distinction between organic and mineral compounds a difficult one to make and saw that as rules were discovered in the one or the other type of chemistry they ought to be applicable to both eventually. This philosophical principle which was both a derivative of the destructive methods that chemists were beginning to apply to organic compounds and a harbinger of an even more wide-spread use of such methods, profoundly affected Dumas' attitude, not only towards organic chemistry, but also to that grey area which was called either physiology or chemical biology depending on the direction from which it was approached.

These were the ideas and attitudes that Dumas brought to his substitution theory. In writing this section in his textbook, he had crystallised

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37. Dumas was probably the first to call attention to what is now recognised as the amphoteric character of carbon: "Oxalic ether, for example, considered as a compound of oxalic acid, bicarboned hydrogen and water, contains a positive carbon in the acid and a negative one in the base." Ibid., 270.

38. Ibid.

39. Until Dumas used the term inorganic (see reference, note 30), compounds not originating in, or derived from plants or animals were called mineral compounds. The change in attitude involved was subtle but definite.

his rules for substitution in the form quoted at the beginning of this chapter, a form both clear and useful for students. Moreover, he had discovered two new reactions that had given further support for the theory (40). During the ensuing years, research based on the theory was carried out by a number of young chemists, including Regnault, Faustino Malaguti (1802-1878) and Laurent. Since Laurent is generally given credit for the theory along with Dumas, it is particularly important to examine their relationship and the contributions made by Laurent before accepting or rejecting this claim (41).

After several years as an external student at the Ecole des Mines, Laurent was accepted by Dumas as répétiteur at the Ecole Centrale in 1830. He had served in this capacity for only two years when Dumas suggested to Brongniart that he be made chief chemist in the laboratory of the Sèvres porcelain works. Though this meant that Laurent would have a place in which to do research, he accepted the offer reluctantly because it meant doing research on topics related to porcelain manufacture (42). While he was qualified because of his mineralogical training, he had acquired a deep and abiding interest in organic chemistry while working with Dumas. Unable to continue his research in that branch of chemistry, he finally decided to

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40. In cinnamon oil, $C^{36}H^{16}O^{2}$, oxygen replaced hydrogen to form cinnamic acid, $C^{36}H^{14}O^{3}$. In pyroacetic spirit (acetone), three atoms of chlorine replaced three of hydrogen to form $C^{6}H^{3}OCl^{3}$ (not $C^{6}H^{4}OCl^{2}$ as Partington indicated, op.cit.(2-17), p.362). Dumas made the interesting comment that even if the substitution theory was a "game of chance ... at least the facts upon which it was established had become a part of the science." Loc. cit.(8-1), 288.

41. A long discussion of Laurent's relationship with Dumas will be found in Kapoor, S., "The Origins of Laurent's Organic Classification", Isis, 60, (1969), 477-527.

42. Laurent did not want to leave the school but did so because Dumas had offered the position, and in the circumstances he was in no position to refuse. While he was at Sèvres he completed work on one of the two theses required for the degree Doctor of Sciences: "Sur la densité des argiles cuites à diverses températures", Ann. Chim. Phys., 66 (1837), 96-99. This was his physics thesis.

resign in 1835. Although personal misunderstandings may have begun even before he went to Sèvres, it seems that the roots of later disputes with his mentor can be traced to the years he spent at the porcelain factory and the manner of his departure.

While Laurent worked at the Ecole Centrale, he undertook extensive research on naphthalene and the compounds formed when it reacted with several chemical reagents. His first memoir in 1832 described a new method for preparing naphthalene (43). One year later it was followed by a memoir on some chlorides of naphthalene (44). In 1834 Dumas announced his substitution theory and obtained further confirmation for it in his work with Péligot on cinnamon oil (45). Their chlorination experiments had yielded mixtures whose components were impossible to isolate for the most part, but they had obtained one pure substance, $C^{36}H^{8}Cl^{8}O^{2}$, which they had decided: "... we will

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43. Ann. Chim. Phys., 49 (1832), 214-21.

44. Ibid., 52 (1833), 275-85. Laurent referred to Dumas' discovery that chlorine acted on Dutch liquid and the hydrocarbon of turpentine in two different ways: at first equal volumes of chlorine and the hydrogen combined; then, as excess chlorine reacted, the hydrogen decomposed, as part of the hydrogen combined with chlorine; this made possible further combination with chlorine. Laurent observed that he could explain on this basis the formation of two chlorides of naphthalene, a liquid, $C^{10}H^{4} + Cl$ and a solid $C^{10}H^{3} + Cl^{2}$. Partington, op.cit.(2-17), p. 378-79, says "The work was conceived in terms of the Radical Theory" (his capitals). Laurent's concept of a radical was that of Dumas (e.g., $C^{8}H^{8}$) rather than that of Berzelius and Liebig (e.g., C_4H_{10}). Laurent seems to have been looking for a compound analogous to Dutch liquid. What he (or Dumas) found was another compound which was analogous to the $CHCl_2$ later announced by Regnault (see Chapter 6, p.260) and about which he had published nothing at that time, and a similar chloride of turpentine which Dumas had not yet mentioned in any of his published work. Laurent concluded, "I believe, meanwhile, that I have rendered *probable* the existence of a compound of equal volumes of chlorine and naphthalene which was indicated by the analogy. Some chemist more fortunate than I will perhaps obtain it in the pure state." Ann. Chim. Phys., 52 (1833), 285 (my italics). He was able to obtain the solid in a fairly pure state and identify it. What he had discovered unexpectedly then became the focus for his further work.

45. Ibid., 57 (November 1834), 305-34.

call chlorocinnose provisionally, not knowing with what to compare it among known organic substances " (46). They also reserved the suffixes -ase, -ese and -ise for those compounds in which 2, 4 and 6 atoms of hydrogen had been replaced by equivalent amounts of chlorine. Laurent applied these suffixes to names for his chlorides of naphthalene (47) and gradually developed a system of nomenclature which eventually became a foreign language to most chemists. In his memoir on nitronaphthalase, nitronaphthalese and naphthalase (48), Laurent introduced his first 'modification' to the substitution theory, the notion of fundamental and derived radicals (49). Two months later, after describing the oxidation of paranaphthalene (anthracene), and using it "to confirm perfectly the substitution theory discovered by M. Dumas and the theory of derived radicals of which I have already given a brief

46. Ibid., 317-18.

47. Ibid., 59 (June 1835), 196-220. Much of this work was read to the Academy a year earlier, according to Laurent.

48. Ibid., 59 (August 1835), 376-97.

49. "Naphthalene forms a radical of 56 atoms or 28 equivalents analogous to bicarboned hydrogen. This radical placed in contact with various substances, chlorine, bromine, nitric acid, loses hydrogen; but it always gains in exchange an equivalent of chlorine or bromine or oxygen; in such a way that there is constantly a radical containing like naphthalene 28 equivalents, of which 20 of carbon and 8 of hydrogen and chlorine, or of hydrogen and bromine or of hydrogen and oxygen. These new radicals can all exist free or combined. The hydrogen which has been removed is released or remains combined with the new radical in the state of hydrochloric acid, hydrobromic acid or water. I will call the naphthalene a fundamental radical and those to which it gives birth by these transformations derived radicals. The naphthalene put in contact with bromine releases hydrobromic acid, and conforming to the theory of substitutions, the hydrogen removed was replaced by an equivalent of bromine." Ibid., 388-89. At first sight this might seem to be an important step forward, but such an attitude will not survive close scrutiny. What Laurent said was clear enough, but what did it add to the content of existing knowledge? Organic radicals, free and combined, had been posited as early as Gay-Lussac's work on alcohol; the substitution theory accounted for replacement in exactly the manner described; Dumas had already accepted the relationship of the chlorinated products of a compound with one another and to their parent in his naming of chlorocinnose and the possible related chlorinated products of cinnamon oil.

summary" (50), he added another rule: When dehydrogenating agents react with hydrocarbons according to these theories, "at the same time, hydrochloric, hydrobromic or nitric acids, or water are formed, which sometimes is released, sometimes remains combined with the new radical" (51). In May 1836 he made what seemed to be the first move towards an addition theory (52), but here again he was anticipated by Dumas (53). In the same article Laurent predicted the existence of chloracetic acid (54) as he was later to claim. Dumas, however, had been chlorinating acetic acid at various times without conclusive success at least since 1831 (55). In September 1836 Laurent developed a rule which does seem to be original, "Given a derived radical, the fundamental radical which has given rise to it will be found

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50. Ibid., 60 (October 1835), 220-23 (222).

51. Ibid., 223. He supported this with twelve examples. Again there seems to be nothing new. Dumas and Péligot had said this in 1834 in their memoir on cinnamon oil, Ann. Chim. Phys., 57 (1834), 305-34.

52. Ibid., 62 (1836), 23-31 (29). "But according to my proposition, substances which are outside the radical can be removed by oxygen, for example, without being replaced, or in replacing them with any quantity of oxygen whatever, not necessarily only by its equivalent."

53. "When a hydrogenated organic substance is submitted to the action of a dehydrogenating agent it takes on a portion of the agent equivalent to the quantity of hydrogen removed. It is taken for granted that if the product thus formed can afterward unite with the reagent, this can happen, and it will mask the true character of the reaction." Ibid., 56 (1834), 148.

54. "I hope to make known in a short time a new chloracid, and to prove that all the chlorine it contains is in the radical, while all its oxygen is outside. These acids will assist my hypothesis that chloral is a compound of an unknown acid, which I have named chloracetic; I am at the same time very disposed to believe that this acid will be obtained by treating the aldehydrate of silver with chlorine." Loc.cit.(8-52), 30. While his method is somewhat questionable, theoretically it could form the acid he suggests. In fact, however, Laurent never seems to have been able to do so by this or any other method.

55. Ibid., 47 (1831), 203. In preparing his list of works for membership in the Academy, Dumas had included a memoir "Recherches sur deux corps nouveaux résultant de l'action du chlore sur l'acid acétique" which was (cont.)

by replacing the substituting substances by the hydrogen which was removed, or supposed so, in the first place" (56).

In the summer of 1836 Dumas gave his course on chemical philosophy at the Collège de France. During the ninth lecture, he mentioned that Laurent and Jean François Persoz (1805-1868) had "greatly extended" his ideas on the carbonic oxide radical (57). Laurent had tried to explain the neutrality of such substances as sugar and carbonic oxide that had a high proportion of oxygen, the principle of acidity, by putting the oxygen inside the radical and making it inaccessible. Thus stearic acid, which contained a small proportion of oxygen was an acid because part of the oxygen was outside the radical, and it should be written $C^{140}H^{134}O^3 + O^2$ (58). Rather than attack Laurent's representation, he mentioned the simpler representations given by Persoz for nitrous acid $N^2O^2 + O$, and nitric acid, $N^2O^4 + O$, and advised his students:

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55. (cont.) never published. He observed: "This work was finished and was about to be printed when M. Liebig made known the result of his observations on the action of chlorine on alcohol. The analogy of the products and the difference in results made it necessary for the author to re-examine the question." (See Chapter 7, note 41). In 1834 he said: "Undeniable relationships exist between chloral hydrate and the crystallised product that I obtained by treating acetic acid with chlorine in sunlight; nevertheless these two substances could well be different despite those relationships." Ibid., 56 (1834), 136.

56. Ibid., 63 (1836), 27-45 (27). In the article, what are now called chlorophenols were studied. Laurent says, "It has been 4 years since I prepared these acids, but then I had the laboratory and the courtyard of the Ecole Centrale at my disposal and had no neighbours to bother with the odours." Ibid., 41. Also, "I give the name phene, from φαίνω (I light up), to the fundamental radical of the preceding acids, since benzene is found in lighting gas." Ibid. This radical was $C^{24}H^{12}$ or any combination equivalent to H^{12}. The name was given to avoid confusion with benzoyl.

57. Leçons, p.351.

58. Ann. Chim. Phys., 61 (1836), 137-38.

"Should these hypotheses be accepted? I dont think so. There are too few reasons in their favour. Avoid gratuitous suppositions carefully. Always remember that it is most dangerous to create hypothetical radicals unnecessarily." (59)

He recommended caution in generalisation:

"I owe it to myself, I owe it to my young colleagues and students to speak my thoughts plainly. It is with regret that I view young chemists, so capable of making good use of their time, dedicating even a small part of it to combining formulas vaguely in a way that is no more than possible or probable." (60)

Laurent reacted strongly to Dumas' remarks in his memoir on camphoric acid, read on 26 December:

"While I will pay homage to his undeniable superiority, nevertheless I cannot submit to the advice that he has thought he must address to me in a public course, attended by a large and knowledgeable audience, inviting me to limit myself to gathering data." (61)

He pointed out what Dumas himself had said in this regard (62), that no one would choose a career in chemistry "just to find some new compounds", gathering further support from "Berthollet's Statics, a work that the professor of whom I speak had studied profoundly" (63). Though Dumas had not been kind to hypothesising throughout his lectures, he constantly made it

59. Loc.cit.(8-57).

60. Ibid., 351-52.

61. Ann. Chim. Phys., 63 (1836), 207-19 (215). By this time Laurent was announcing new theories in nearly every memoir, and this was no exception. One in this memoir was particularly gratuitous and rather poor, for he had generalised broadly on the basis of a single example, camphoric acid, but it shows how completely he had absorbed Dumas' approach: "From all of this must I conclude that my theory is infallible? No, I know very well what is meant by a theory; but as long as mine provides means for making discoveries, I will not abandon it." Ibid., 214-15.

62. See page 308.

63. Loc.cit.(8-61).

clear that he was attacking hypotheses that were a priori or founded on insufficient evidence, suggesting in this lecture that the views of Laurent and Persoz fit into the latter category. Amand Bineau (1812-1861), who was responsible for the publication of Dumas' Leçons, had been a student at the Ecole Centrale while Laurent was there. He remarked in one of the three footnotes that he wrote:

> "Among the many students who have always thronged to these lectures, there were none who misunderstood what the professor had in mind. He spoke freely, in kindness, in a friendly manner, believing that his words would not be taken out of context. But M. Laurent has reproached M. Dumas for this phrase, as though in opening his laboratory to all young chemists, to the unfortunate Boullay, to M. Péligot, M. Pelouze, M. Laurent, and many others, in initiating them into the secrets of his own experiments, in firing them up with the warmth of his own personality, M. Dumas had renounced the right to counsel them." (64)

Laurent defended his second thesis for the degree Doctor of Sciences in the Faculty of Sciences on 20 December 1837 before an examining board composed of François Sulpice Beudant (1787-1850), Despretz, Dulong and Dumas (65). After presenting his research, Laurent summarised various theories that had been formulated by organic chemists including his own. In attempting to differentiate his own ideas from those of Dumas he put himself in the awkward position of attacking the man who had given him his start, and who was one of his examiners (66). By this time Laurent's ideas

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64. Leçons, p.352.

65. "Recherches diverses de chimie organique". The manuscript is extant. Kapoor, op.cit.(8-41), 511, indicates that extracts from it were published in Ann. Chim. Phys., 66 (1837), 136-213, 314-35.

66. He defended Dumas' ether theory, regretting that "it was on the point of being abandoned in favour of another that has no more certitude". Ibid., 320. Dumas had just issued his manifesto with Liebig so this was a mild rebuke. He also considered the benzoyl theory, more to show the complexity introduced by Dumas' modifications, which, he noted, required no less than four hypotheses.

with respect to the substitution theory had developed in a quite different manner because of his crystallographic approach, and though the two chemists used the same word, they did not mean the same thing by it. Thus in his thesis he voiced some indignation against chemists who had first ridiculed his theories, then when their usefulness had become evident, attributed them to Dumas. He rejected the opinion that they were nothing more than modifications of Dumas' theory:

> "It is well-known that certain substances are removed by others that replace them. M. Dumas has tried to provide us with a law governing substitutions, a law that I used initially; because it no longer agreed with the facts, I proposed another. But in any case, the law that I suggested is only part of a general theory to which I have tried to attach all the known data. ... All my work has been for a long time directed towards the same goal and under the influence of one dominant idea, the theory of derived radicals." (67)

He listed the discoveries that had resulted from adopting this viewpoint, pointing out that it could be a powerful instrument for bringing order into organic chemistry. Again he concluded: "I will accept the possibility that my theory may be incorrect, but no one has shown that it is erroneous." (68)

Dumas could hardly have been happy about the thesis, but he was somewhat mollified by a letter from Laurent written shortly after the thesis was defended (69). In any case, he was concerned about other events. Liebig's

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67. Ibid., 330. (Laurent's italics).

68. Ibid., 334-35.

69. Arch. Acad. Sci., Dossier Laurent (Fonds Dumas). In this undated letter, published by Jean Jacques, "Auguste Laurent et J.B. Dumas, d'après une correspondance inédite", Revue d'Histoire des Sciences, 6, (1953), 329-49, Laurent indicated that he could not afford to have his thesis published. Its publication in the Annales de Chimie et de Physique fulfilled the requirement. Jacques suggests that the letter was written in the summer of 1837, but a later date probably 22 December or shortly afterward seems much more plausible in view of the contents. The first four parts of the thesis were published in the October 1837 issue, but that issue was not given to the Academy until sometime between 19 and 26 March (Comptes-Rendus, 6 (1838), 387). Thus it was quite possible that a memoir read in December could appear in the October issue. Kapoor, loc. (cont.)

objections to the theory, raised earlier that year (70) had been suppressed in favour of their cooperation in the development of organic chemistry, but reaction was beginning to set in to Dumas' manifesto. A place had become vacant in the Faculté de Médecine that particularly attracted him. He was in the midst of research on acids begun at Liebig's suggestion as part of common enterprise. Problems with Pelouze involving priority in the discovery of the polybasic character of some organic acids had arisen. These came to a head when a letter from Berzelius to Pelouze was read in the 7 May 1838 meeting of the Academy of Sciences. But Berzelius was less concerned with that problem than he was with the substitution theory and Dumas knew this. Berzelius aired his opposition to the theory strongly (71). He made it clear that he could no longer remain silent in view of Dumas' increasing influence among French chemists, particularly on Laurent and Malaguti, to say nothing of the many other young chemists directly or indirectly under his guidance. The basis for this opposition was equally clear:

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69. (cont.) cit.(8-65), indicated that a correction made on the manuscript of the thesis notes that the degree was given on 28 December. Dumas may have held up his approval initially, then relented after receiving the letter. Clara De Milt, "Auguste Laurent, Founder of Modern Organic Chemistry", Chymia, 4 (1953), 85-114 (95, note 49), must have made the same assumption as Jacques when she wrote: "His thesis was a summary of papers already published", quoting Grimaux, "Aug. Laurent", Rev. Sci., 6 (1896), 164.

70. Ann. Phys., 40 (1837), 292-304. It is noteworthy that Liebig did not publish it in his own journal.

71. Comptes-Rendus, 6 (1838), 633-36. He had already done so in his reports to the Academy of Sciences of Stockholm, but this was the first time that his views were officially proclaimed in France. Ibid., 636. "The Substitution Theory ... appears to me to exercise a bad influence on the progress of chemistry; it throws a wrong light on objects, and hinders one from distinguishing their true forms." Ibid., 633. He purported to show how Malaguti and Laurent were both led astray by this influence, but was more sympathetic towards Malaguti, who had been an assistant to his good friend Pelouze.

> "An element as eminently electronegative as chlorine could never enter an organic radical; this idea is contrary to the first principles of chemistry; its electronegative nature and its powerful affinities only permit it to be part of a special group." (72)

The letter was provocative, and Dumas reacted immediately. He reminded the Academy that he had consistently rejected the views which Berzelius accused him of holding and spreading. He restated his theory briefly and continued, "But I have never said that the new substances formed by substitution had the same radical, the same rational formula as the first. I have said completely the contrary on a hundred occasions." (73) A closer examination of the letter permitted him to respond more fully on 21 May (74). The tenor of his reply made it clear that he was concerned about the empirical character of the theory. He referred to the "phenomenon of substitution" (75), and described it as "an empirical rule, to which one paid attention so long as it was in accord with experimental evidence" (76). It expressed "a simple relation between the hydrogen leaving and the chlorine entering" (77). Dumas was sensitive to the attacks on his theory and was keenly aware of what he

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72. Ibid. Among examples of special groups Berzelius gave $COCl_2$, $COCl_2$. Because of this Berzelius eventually fell into the trap of making up radicals, which Dumas had studiously avoided by accepting only existing substances such as bicarboned hydrogen (ethylene) as radicals. According to Laurent, Chemical Method, transl. W. Odling, London, 1855, p.197, "The labours of Malaguti [Comptes-Rendus, 5 (1837), 334-35 and 798-800] excited Berzelius to undertake the defence of dualism." Malaguti had chlorinated ordinary ether, a simple replacement of 4 atoms of chlorine for 4 atoms of hydrogen in complete conformity with Dumas' theory. But Laurent had taken the opportunity to emphasise that "ethers, in becoming chlorinated, still continued to be ethers". Laurent, loc.cit., p.197.

73. Comptes-Rendus, 6 (1838), 647.

74. Ibid., 689-702.

75. Ibid., 695.

76. Ibid., 702.

77. Ibid., 699.

believed were the unwarranted excesses of Laurent. He emphasised the extension of empirical data and growth in analytical precision that had resulted from the application of this theory to the chemistry of chlorinated organic compounds. He asked chemists to study the limits within which it should be applied, but not to reject it. Dumas had dissociated himself from Laurent for some time because of the latter's volatility and his tendency towards hasty conclusions from very limited data. It is not surprising that he was reluctant to accept rules and theoretical considerations founded so tenuously. It was just as logical that he should be quite emphatic in limiting his own theory to its empirical ramifications until strong enough evidence was available to permit a well founded development in the theoretical aspects. It is in this context that we must interpret the remarks made by Dumas and quoted by Laurent that have so often been used by historians of chemistry to fault Dumas, sometimes quite seriously:

> "On this subject M. Berzelius attributes to me an opinion precisely contrary to that which I have always expressed, namely that on these occasions, chlorine takes the place of hydrogen without changing the nature of the substance; I have never said anything of the kind, and certainly it could not be deduced from opinions which I have put forward concerning this class of facts. ... To represent me as saying that hydrogen is replaced by chlorine <u>which fulfils the same functions</u> (78) is to attribute to me an opinion against which I protest most strongly as it is opposed to all I have written upon these matters. ... [The Substitution Theory] is an empirical rule. ... it expresses a simple relationship between the hydrogen expelled and the chlorine which enters." (79)

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78. "joue le même rôle que lui" (Dumas' italics).

79. <u>Comptes-Rendus</u>, <u>6</u> (1838), 695-96, 699, 702, 699. The quotation is taken in the order in which it was given by Laurent, <u>op.cit.</u>(10-72), p.199. However Laurent's 'quotation' (translated by Odling, <u>loc.cit.</u>(8-22) ends as follows, "The law of substitutions is an empiric law and nothing more; it expresses a relation between the hydrogen expelled and the chlorine retained. I am not responsible for the gross exaggeration with which Laurent has invested my theory; his analyses moreover do not merit any confidence." <u>Ibid</u>. Dumas did not add "and nothing more", although he (cont.)

Apart from the unfortunate relationship with Laurent, there were two strong reasons for Dumas' attitude:

1. Accepting the hypothesis that chlorine and hydrogen could fulfil the same function in a compound meant rejecting Berzelius' theory of Electro-chemical Dualism. This kind of substitution theory demanded the replacement of highly electronegative chlorine for highly electropositive hydrogen. Dumas later indicated that he was aware of this long before he had announced the theory (80). From the moment he had accepted the substitution theory

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79. (cont.) did say "Do not reject an empirical rule, *and this is nothing more*, which far from obstructing the advance of science has obtained for it, over several years, a great many exact analyses of which no one could have dreamed." *Comptes-Rendus*, *6* (1838), 700 (my italics). It is obvious that Laurent's 'quotation' is cut and paste. But nowhere in his answer to Berzelius' letter does Dumas make the last statement. Laurent once again over-reacted to Dumas' statement about a single experiment done by Laurent whose authenticity was in question at the time because Malaguti had performed nearly the same experiment and had said in a letter to Dumas: "Without wishing to contest M. Laurent's results, it must be acknowledged that in my experiments I have obtained no results which resemble his" (quoted by Dumas, *ibid.*, 696), to which Dumas had replied, "M. Berzelius has distorted my ideas; something more is needed to show the harm my theory has done to M. Malaguti or to M. Laurent than formulas based on the unfinished experiments of M. Malaguti or the inexact experiments of M. Laurent." *Ibid.*, 697. It may be that Dumas lacked confidence in Laurent's theorising because the younger chemist filled in a lot of spaces, without sufficient experimental evidence, in order to establish or strengthen his theories, and he was forced on occasion to correct errors that he had made as a result. But Dumas had made no such accusation in this article. It serves as a further indication of the sense of persecution which dogged Laurent throughout his lifetime. This matter has been dealt with at some length because of the misuse of the quotation. Partington, *op.cit.(2-17)*, p.388, is only one among several who have used Laurent's version, and he is also guilty of referencing it erroneously as *Comptes-Rendus*, *6* (1838), 645-48. Kapoor, *op.cit.(1-101)*, 64-65, indicating that he was unable to locate Laurent's quotation in Dumas' response, rightly rejected attempts by historians to use it, since they do so on the basis of Laurent's word rather than on what Dumas actually said. Once again it is worth noting Dumas' emphasis on the proper integration of theory and experimentation.

80. Unfortunately he had no published proof for this. "The objection is so natural that I would like to think that you would accept, on my simple assertion, that it occurred to me long before it was announced, from the very time when I observed the first evidence of substitution." *Comptes-Rendus*, *8* (1839), 611.

as a guiding principle he had tried to save electrochemical dualism. Evidence for the existence of this attitude appeared as early as 1831 when he pointed out that carbon could be regarded as positive or negative depending on the electronegativity of the element to which it was linked (81). Although he had not gone as far with hydrogen, he did believe that hydrogen in a hydrocarbon radical differed from that in the water portion of organic compounds. When a dehydrogenating agent reacted, it substituted in the former case, and simply removed hydrogen in the latter. When substitution occurred, the hydrogen was first removed, then chlorine entered into the vacated place. This side-stepped the problem, since it merely stated that for every atom of hydrogen removed, an atom of chlorine entered.

2. The evidence for accepting equivalence of function was neither sufficient, clear, nor unequivocal. From the beginning, one observation was abundantly clear: When chlorine that was present in organic compounds through substitution came in contact with certain reagents it did not react in the same way as chlorine in mineral chlorides; for example the former would not react with silver nitrate solution. Nor did substituted chlorine act like free chlorine (a decolorising agent) or acid chlorine (which reacted with alkali to form neutral salts). Laurent could easily explain this by saying

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81. In an attempt to explain the difference between organic and mineral compounds in both their physiogonomy and their reactions, Dumas had said, "Almost all compounds of an organic nature contain carbon in two states. To take the simplest case, that of a compound analogous to an ordinary salt, an oxyacid of carbon is united to a carbide of hydrogen. Thus the carbon is at the same time positive in the acid and negative in the base." Ann. Chim. Phys., 47 (1831), 329. Ammonium nitrate was the only mineral analogue listed by Dumas that was known to exist, and it was often regarded as 'organic'. It is difficult to know whether Dumas ascribed an absolute or a relative character to the charge on the carbon atoms. A relative charge differential is recognised currently. One should be slow to believe that Dumas accepted a simple relationship between the reactivity of organic compounds and the presence of carbon atoms of both types. Clearly he must have seen that other factors were at work.

that the function of the substituted chlorine had changed, that it now played the same role as that of the hydrogen that it had replaced. Yet could it be said that a chlorinated hydrocarbon acted like a hydrocarbon? The number of hydrocarbons known was not large, and certainly those known varied sufficiently in their characteristics to make this question unanswerable. Indeed Dumas had seen that chlorination of naphthalene gave compounds varying in their degree of saturation, thus a change in properties which presumably indicated a change in type (82). Few alcohols were known. When ordinary alcohol was chlorinated, it no longer had the properties of alcohol (83). One aldehyde was known (acetaldehyde) and Dumas himself had chlorinated it without recognising it as an aldehyde (84). Chlorinated pyroacetic spirit (chloracetone) had been mentioned in Dumas' first memoir on substitution, but it too was one of a kind. A great deal of confusion still surrounded the constitution of organic nitrogen compounds. The two largest and most important classes of organic compounds known were the acids and their ethers. Not until these were successfully chlorinated would it be possible to determine whether substituted chlorine played the same role, fulfilled

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82. Comptes-Rendus, 10 (1840), 521-22.

83. Apparently before chloral was formed, the alcohol was converted into acetaldehyde. However, Cahours, who had just succeeded in identifying the oil of potatoes as amyl alcohol, had now been able to prepare chlorinated amyl alcohol. Dumas commented, "Let us not hasten to conclude too much on this point; furthermore, the thought of finding anything conclusive in it for the ether theory at the present time is far from my mind." Ibid., 6 (1838), 699. The chlorination products of wood spirit (methyl alcohol) had not yet been successfully studied.

84. Liebig had identified the intermediate between alcohol and chloral as what he had called aldehyde, $C_4H_8O_2$ (C = 12). Dumas had taken it to be acetic ether (ethyl acetate) which is isomeric with aldehyde. Fortunately Dumas named chloral from chlorine and alcohol so that the name retained significance when it was recognised that it was the substitution product of aldehyde (alcool dehydrogenatus).

the same function as hydrogen. This was the crucial experiment for this aspect of the substitution theory, and conclusive results had yet to be achieved. Therefore Dumas could not abandon the theory of electrochemical dualism at this time. It would have been inconsistent with his whole philosophy of chemistry to do so. Despite any claims by Laurent, sufficient experimental evidence was simply not available.

It would be difficult to hold that Dumas realised fully the theoretical importance of chloracetic acid as early as 1829 when he first began his efforts to chlorinate acetic acid (85). The reaction was light sensitive. Among the many substances formed (86) was a crystallisable chlorinated acid which he was able to recognise as such but could not purify. For many years he was unable to devise a reproducible process giving sufficiently

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85. The first published indication that he had been working on this reaction appeared in June 1831, Ann. Chim. Phys., 47 (1831), 203. Depending on the precision of a statement made in 1840: "Ten years have now passed since I first submitted pure acetic acid to the action of dry chlorine" (Ibid., 73 (January 1840),75), it can be presumed that this event occurred late in 1829, certainly no later than the early part of 1830. This would fit well into the progression of his studies on chlorination of organic compounds suggested by what had appeared in volume one of the Traité. Furthermore, he had studied the ether of acetic acid with Polydore Boullay (see Chapter 6 and Arch. Acad. Sci., Fonds Dumas, Carton 7, Dossier "Ethers") and was completing research for another with Boullay: "Mémoire sur l'acide acétique, les acétates, l'esprit pyroacétique, la liqueur fumante de Cadet et la fermentation acétique" Arch. Acad. Sci., Fonds Dumas, Carton 4, Dossier "Mémoires de Dumas sur les Atomes; Mémoire sur l'acide acétique". Unfortunately it remained incomplete because of a serious injury to Boullay at that time.

86. In addition to the gases formed, hydrochloric acid, carbonic acid, chlorocarbonic acid, "a solid or liquid product contains the new chlorinated acid, oxalic acid and other substances which I have not studied sufficiently". Ibid., 76.

large yields of the new acid (87). After isolating chloral in 1834, he indicated that in chlorinating acetic acid he had obtained a substance which seemed to be like chloral but could have been distinctive (88). He was still attempting the purification of the acid when Berzelius' objections were read in May 1838, compelling his reply. It was unfortunate that the letter arrived at this time. Left unanswered it could have led to the erosion of confidence in the substitution theory. For the reasons indicated, he could not yet have accepted the true role of chlorine in substitution. This was the first serious attack on his theory, and it had to be dealt with decisively. Thus we find Dumas forced to disclaim strongly the excesses of Laurent, to severely limit the extension of the theory beyond the limits he had already set down in 1834, and to which he had carefully adhered ever since. But Malaguti had successfully chlorinated ordinary ether (89), and in May 1838 was still working on the chlorination of methyl acetate (90).

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87. "Among the considerable number of trials to which I submitted acetic acid in order that I might study the modifications which chlorine could make on it, the only ones until now which have had complete success are those which have consisted in submitting pure acetic acid to the action of dry gaseous chlorine in direct sunlight." Ibid., 77; also Comptes-Rendus, 8 (1839), 612. Dumas made a number of changes when he rewrote the article for the Annales de Chimie et de Physique (e.g. he realised the importance of showing that he had been working for ten years on this project and why).

88. Ibid., 56 (1834), 125. See also Chapter 7, note 78. Both chloracetic acid and chloral reacted with alkalis to form chloroform.

89. "Note on the Action of Chlorine on Compound Ethers of Oxyacids and on Sulphuric Ether", Comptes-Rendus, 5 (1837), 334-35. It was expanded into a long article appearing in Ann. Chim. Phys., 70 (1839), 337-406. Dumas said later that he owed the first conviction of his type theory to this discovery by Malaguti that ether, when chlorinated, retained the characteristics of ether including its combining power. Malaguti was led to this work by the surprising discovery, without parallel at the time, that chlorine simply added to pyromucic ether to form $C^{20}H^{6}O^{5}Cl^{8} + C^{8}H^{10}O$. Comptes-Rendus, 4 (1837), 702 (expanded in Ann. Chim. Phys., 64 (1837), 275-86.

90. Acétate de méthylène.

Though his results were incomplete, he was able to give the formula for the compound he had obtained (91). Dumas' work now took on a sense of urgency. No chloroacid had ever been prepared in the pure state. It seemed that the chlorinated acetic acid that he had obtained retained its acid properties, but what was the degree of saturation? This was not an idle question. According to Dumas, if the degree of saturation changed, then there was more involved than simple substitution (92) in which chlorine takes the place of and plays the same role as hydrogen. The answer was not long in coming:

> "I have determined, a long time ago, that in submitting crystallisable acetic acid to dry chlorine under solar influence, a volatile, crystallisable chlorinated acid forms at the same time as various other substances which are only separated with difficulty.
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> In dissolving this acid in water, evaporating the liquor in vacuo and distilling the dry residue on anhydrous phosphoric acid, I have finally succeeded in obtaining the new acid in a state of purity. Its analysis has given me the

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91. Comptes-Rendus, 6 (1838), 696-97. Malaguti had obtained the formula $C^{12}H^{8}Cl^{4}O^{4}$ and had adopted the arrangement $C^{8}H^{6}O^{3} + C^{4}H^{2}Cl^{4}O$ which is nearly correct for dichloromethyl acetate ($CH_3COOCHCl_2$; C = 12). Laurent, who had chlorinated the same ether two years earlier, Ann. Chim. Phys., 63 (1836), 382-86, obtained $C^{12}H^{6}Cl^{6}O^{4}$ which would be correct for trichloromethyl acetate, but he chose to arrange it as $C^{8}H^{2}Cl^{4}O^{3}$ + $C^{4}H^{2}Cl^{2} + H^{2}O$, which divided the chlorine between the acetate and the methyl group. Probably both were correct in their analyses despite Dumas' comment "the inexact experiments of Laurent", Comptes-Rendus, 6 (1838), 697, but it is difficult to say whether either of them was correct in his arrangement. Malaguti had not finished his work. Laurent based his decision on the formation of $C^{4}H^{2}Cl^{2}$ as a product of the reaction of the chloroether with potash, along with potassium formate "if I have not been led into error". Ann. Chim. Phys., 63 (1836), 383.

92. As he pointed out later, Comptes-Rendus, 10 (1840), 522-23, one equivalent of acetic acid on chlorination could have given rise to two equivalents of a chloroacid analogous to formic acid, which would have been a change in saturation, and hence not just substitution:

$$\underset{\text{acetic acid}}{C^{8}H^{8}O^{4}} \xrightarrow{4\ O} \underset{\text{formic acid}}{2\ C^{4}H^{2}O^{3}} \xrightarrow{4\ O} \underset{\text{carbonic acid}}{4\ C^{2}O^{2}}$$

$$\underset{\text{acetic acid}}{C^{8}H^{8}O^{4}} \xrightarrow{8\ Cl} \underset{?}{2\ C^{4}H^{2}O^{2}Cl^{2}} \xrightarrow{8\ Cl} \underset{\text{chlorocarbonic acid}}{4\ C^{2}Cl^{2}O}$$

following formula:

$$C^8H^2Cl^6O^4$$

I have verified this analysis by the alcoholic ether and the methylic ether of this acid and also by the analysis of its calcium salt." (93)

This brief notice was not amplified until the following April when Dumas read a memoir to the Academy on the new acid and announced what seemed to be a radical change in his thinking (94). Again he emphasised the importance of the concept of substitution, but he restricted its application to the first rule that he had given. So long as this rule had been regarded as a special case of the theory of equivalents, even one which allowed the replacement of hydrogen, equivalent for equivalent, Berzelius could find no objection. What he would in no way accept was the "ability of hydrogen with its electropositive properties to be replaced by the most electronegative

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93. Comptes-Rendus, 7 (27 August 1838), 474. The complete notice given at the time has been quoted.

94. "On the Constitution of some Organic Substances and on the Theory of Substitution (An Extract)", Ibid., 8 (1839), 609-22. Several suggestions for the long delay may be offered, but none are very convincing: 1) His research was not yet complete; several reactions are mentioned in the memoir that do not appear in the notice. 2) He had been chosen in March 1838 to occupy a new chair in pharmacy and organic chemistry in the Faculty of Medicine and it was necessary to prepare a course of studies. 3) The most likely reason is that during this time he had conceived his type theory. In a non-pageinated, undated notebook, Arch. Acad. Sci., Fonds Dumas, Carton 9, containing analyses of compounds paralleling studies published at this time, a chart listing what was undoubtedly his first very primitive attempt at gathering compounds into types was drawn up on a page among many on chloracetic acid and salts, ethers and other compounds derived from it. Doubtless he saw considerable importance in announcing it in connection with the work on chloracetic acid, but this disclosure demanded that the theory be on firm footing. This would have required time. In his conclusion to the memoir, he was able to say, "In organic chemistry certain types are conserved even though equal volumes of chlorine, bromine or iodine are introduced in place of the hydrogen which they contain." Comptes-Rendus, 8 (1839), 621-22. Earlier he had indicated that he would deal with the constitution of organic acids and the substitution theory in a series of memoirs. Ibid., 609.

substances known" (95). Dumas' answer could now be based on incontrovertable evidence:

> "Here then is a new organic acid in which there enters a very considerable quantity of chlorine, and which offers no reactions of chlorine, in which the hydrogen has disappeared, replaced by chlorine and which as a result of this very peculiar substitution has undergone only a slight change in physical properties. All of the essential characteristics of the substance remain intact; those which are altered have undergone such clear modifications that all the properties of the new acid and those of the compounds which they produce can be predicted and calculated in some way." (96)

This was exactly what he had been looking for, a clear, unequivocal case of substitution without a change in the fundamental properties of the original compound. Throughout the article he emphasised that the word metalepsy (exchange) was even more fitting than substitution (97). Dumas believed that such an exchange necessitated the existence of certain types of compounds, e.g. acetic acid, aldehyde, ether, olefiant gas, "in which hydrogen can be replaced by chlorine without the type undergoing a change in its essential qualities." (98) Although there were still many limitations he was free to reject the theory of electrochemical dualism (99). His thought had developed to the point where he had accepted isomorphism as the best guide for mineral chemistry, now the substitution theory was playing the same role in organic chemistry. There was no further need for Berzelius' electrochemical theory.

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95. Ibid., 610.

96. Ibid., 611.

97. See note 8-2. He believed that the word exchange gave a clearer understanding of the reaction 'mechanism'.

98. Ibid., 619.

99. "Do electrochemical ideas rest on facts so evident that they must become articles of faith? ... Nothing of the kind, it must be agreed." Ibid., 621.

On 3 February 1840, Dumas read a long memoir, "Sur la loi des substitution et la théorie des types" (100), in which he discussed these approaches by answering a question he raised on each of six topics:

1. Substitution. He began by limiting the law to the first statement given at the beginning of this chapter because chemists who had accepted the law had rejected the existence of water as such in compounds like alcohol. Observing that the law would not be so important if it were just a particular example of the law of equivalents, he showed that the latter had little predictive value whereas this was the real strength of the new law, when it was combined with his theory that most organic compounds could be classified into a limited number of interrelated types. It was in this light that he made clear the restriction that gave his law its value:

> "If white indigo loses hydrogen without gaining anything, it passes to a new molecular type ; ... olefiant gas can produce a chloride of carbon of its same type and by a new addition of chlorine, a new chloride of a different type. The law of substitutions is observed when substances conserve their initial types; it is no longer applicable when they do not. ... Among the numerous reactions possible and almost equally predictable by the theory of equivalents, the law of substitutions sorts out with certitude those which are going to occur." (101)

He indicated that substitution was not limited to replacement of hydrogen although it was the most easily replaced because of its great affinity; oxygen, nitrogen, even carbon (102) could also be replaced, as well as groups

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100. Comptes-Rendus, 10 (1840), 149-78.

101. Ibid., 153-55.

102. He had added carbon to show the artificiality of a system based on the permanence of the number of equivalents of carbon. It was an addition that seemed unnecessary, especially in view of his belief that it was very difficult to accomplish this because of carbon's affinity, and he retracted it within a short time. This 'excess' earned the satirical letter written by Wöhler but signed S.C.H. Windler in which all of the atoms of manganous acetate, $MnO.C_4H_6O_3$ were replaced by means of standard reactions by chlorine to give $Cl_2Cl_2.Cl_8Cl_6Cl_6$, faithful to type and having all the properties of the original compound, though entirely chlorine. Partington, op.cit.(2-17), 367, refers to the original letter written to Berzelius. It appeared in French, Annalen, 33 (1840), 308, slightly altered by Liebig.

of elements acting as a unit (e.g., cyanogen, sulphurous acid). The vistas were very broad indeed (103).

2. Chemical Types. Dumas defined compounds belonging to the same chemical type as those composed of the same number of equivalents united in the same way and having the same fundamental chemical properties. What he meant by the latter characteristic was the ability to react in an analogous manner. Acetic acid and chloracetic acid could be classed as members of the same chemical type according to the first two criteria but did they have the same fundamental properties? While studying chloracetic acid he had found that reaction with potash produced chloroform and potassium carbonate:

$$C^8H^2Cl^6O^4 + KO = C^4H^2Cl^6 + KO.C^4O^4$$

If it was of the same chemical type, acetic acid should react with potash to form marsh gas, a compound which had been found in nature but never prepared in the laboratory: $C^8H^8O^4 + KO = C^4H^8 + KO.C^4O^4$ His efforts were crowned with success and the first test of his theory assured him that its validity was very probable (104). Obtaining chloroform by chlorination of marsh gas added to his assurance, since the above equations indicated that it must be possible since the two substances were of the same chemical type. As he indicated:

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103. When the distinction between his law and the law of equivalents was finally impressed on Ampère, "a very dear friend, so kind-hearted, so rich intellectually and full of discernment in his insights", he said: "Ah, my friend, you have enough work for a lifetime." Loc.cit.(8-100), 156.

104. The objection raised by Persoz and mentioned by Fisher, N., "Organic Classification before Kekulé", Ambix, 20 (1973), 106-31 (129), is unrelated to the question. The theory required that marsh gas be formed. It was. Whether it was produced by the reaction of alkali with another compound was beside the point. In fact an examination of its reaction with alkali shows that acetone forms twice as much marsh gas as its equivalent of acetic acid does.

"When these necessary facts have been recognised as true by experiment, it has been proved that they were possible, that they were not contrary to the general laws of chemistry. I claim that one has not come to grips with the difficulty at all. In such a case it would be necessary to show how the general theory allows us to predict that acetic acid must give marsh gas and that marsh gas must give chloroform." (105)

Once he was able to identify chemical types, Dumas' next step was clear:

"I tried to apply the type theory in a general manner to all known series produced by substitution, and I made this system of ideas the basis of my course at the Ecole de Médecine last year." (106)

But there were difficulties:

"But always faithful to the experimental route, and never wishing to discard it, I asked myself if it was a good thing to classify side by side substances having the same formula, produced by substitution, but differing essentially from one another in their most striking chemical properties." (107)

3. Mechanical Types. He found the answer in Regnault's work on ethers, where Regnault had suggested, but not yet proved, that compounds could be related to one another in a useful manner in a completely mechanical way (108). Aware of the power that this viewpoint had for classification, Dumas now believed that he could build a general theory of substitution around his law, involving three tenets:

"1°. Experiments prove that a substance can lose one of its elements and take another in its place, equivalent for equivalent; that is the general fact of substitution.
2°. When a substance is modified in this way, it can be accepted that its molecule always remained intact, forming a group, a system in which one element has purely and simply ~~taken~~ taken the place of another.

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105. Loc.cit.(8-100), 160.

106. Ibid., 162.

107. Ibid. By "same formula" he meant having the same number of equivalents (e.g., alcohol, $C^8H^{12}O^2$ and acetic acid, $C^8H^8O^4$).

108. Ann. Chim. Phys., 71 (1839), 353-430. Regnault had intended to pursue this topic but became involved in physics research and teaching and abandoned it. Dumas listed 13 substances among many belonging to the same mechanical class as marsh gas (C^4H^8), including methyl ether (C^4OH^6), formic acid ($C^4H^2O^3$), chloroform ($C^4H^2Cl^6$).

> From this point of view, completely mechanical, that M. Regnault is pursuing, all substances produced by substitution will present the same grouping and will be classified in the same molecular type. In my eyes, they constitute a natural family.
>
> 3°. Among substances produced by substitution, there are many that conserve in an evident manner the same chemical characteristics, playing the role of an acid or base in the same manner and to the same degree as before undergoing modification.
>
> These are the substances that I consider as belonging to the same chemical type, as being part of the same genus, to use the language of the naturalists." (109)

4. Organic radicals. Before he could gain acceptance for his type theory, it was necessary to show how other accepted theories fit into it. For over ten years he had advocated a radical theory. He did not suddenly reject the idea of groups of elements that could act as a unit. But he could not accept their permanence, for he believed in the free substitution of elements within these groups:

> "Nothing stands in the way of retaining the name organic radical for certain molecular groups capable of replacing elements and being replaced by them; but these groups can be modified in their turn by substitution, as are other substances that do not play this role." (110).

For Dumas the value of radicals lay in considering them as substitutive units.

5. Nomenclature. New organic compounds were being discovered so rapidly that the need for a system of naming them was imperative, and Dumas believed, as De Candolle had in devising a system for botany, that a natural method was necessary. He now believed that he had the rudiments of such a system. Because so few elements formed so many compounds, Lavoisier's system was not a useful one. Thus Dumas observed:

> "It is necessary that each type have a name, that this name be found in the numerous modifications that it can

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109. Loc.cit.(8-100), 163-64.

110. Ibid., 168.

> undergo, and that it never disappears so long as the type itself is not destroyed." (111)

He had used this method in naming chloroacetic acid, chloroether and chlorolefiant gas. He saw the need for a complete reform of organic nomenclature based on such principles. The modern system, developed gradually along these lines, is a tribute to Dumas' astuteness and in a large measure to his type theory (112).

6. The Electrochemical Theory. In articles that he wrote about Dumas' discoveries, Berzelius had been led by his theory of electrochemical dualism to rewrite Dumas' formulas in accordance with his own views. Noting Liebig's support for the substitution theory (113), Dumas now expressed his opposition to Berzelius' theory, despite the fact that he had been one of its most ardent advocates:

> "All the difficulties we have experiences for many years in searching for the fundamental formulas of substances, the discussions, the misunderstandings, the errors, derive from the prejudices created in our minds by this view." (114)

He rejected the inflexible demand that all compounds must consist of two antagonistic groups, chosen without regard for their fundamental properties

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111. Ibid., 169.

112. Led by the conviction that he had to pursue a different pathway to distinguish his chemical method from that of Dumas, Laurent devised a system of nomenclature that tended to obscure relationships rather than reveal them, and it was never accepted by other chemists.

113. In a letter read by Dumas, ibid., 161-62, Liebig said, "In the interest of science, I must declare that I do not share the opinions of M. Berzelius, because they rest on a mass of suppositions that one would not know how to verify." Recognising the very close analogy existing between $KMnO_4$ and $KClO_4$ despite the evident lack of similarity between Mn and Cl, Liebig could no longer fail to see that chlorine could replace hydrogen. He continued, "The interpretation of these phenomena which has been given by M. Dumas seems to me to provide the key to most phenomena of organic chemistry. ... a reciprocal substitution of elements or compounds acting in the manner of isomorphs must be regarded as a veritable law of nature."

114. Ibid., 172.

(115). He admitted that electricity was involved in chemical reactions, but not in the fashion suggested by Berzelius:

> "At the moment when compounds are formed, at the moment when they are destroyed, the role of electricity can be observed. But when elementary molecules have reached equilibrium, we no longer know how to define the influence that their electrical properties can exercise, and no one has offered views which agree with the experimental evidence." (116)

By ignoring these electrochemical considerations, Dumas could concentrate on the <u>position</u> of the elements in the compound, the molecular arrangement, rather than the electrical <u>nature</u> of the elements:

> "From an electrochemical viewpoint, the <u>nature</u> of elementary particles must determine the fundamental properties of a substance, while in the substitution theory, these properties are derived above all from the <u>position</u> of the particles." (117)

To illustrate his point, he gave a striking example: $C^8H^6Cl^4O$ reacts with potash, forming potassium chloride and acetic acid. It would appear that this compound was chlorinated acetic acid (chlorine having replaced some of the oxygen). In fact it was chloroether. This could only mean that there was a difference in the position of the atoms. Thus Dumas could say about his type theory:

> "It attributes to the number and arrangement of particles an influence of the highest order which is given to their nature, above all, in the generally accepted concepts of chemistry. The law of substitution is the experimental demonstration of this new system, and has led some of its partisans to adopt this system." (118)

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115. Berzelius' formula for chloroether gives no clue to its properties.

116. <u>Ibid</u>., 174.

117. <u>Ibid</u>., 171 (Dumas' italics).

118. <u>Ibid</u>., 177. Dumas commented that it would be absurd to reject either position totally: "Ruled by experimentation, and kept by it within wise limits, each of them must play a large role in the explanation of chemical phenomena." <u>Ibid</u>., 178.

He concluded by summarising the role of scientists who contributed very significantly to the understanding of the relationship between molecules and their properties:

> "Lavoisier defined so well the influence of the nature of the molecules; that of their weight has been characterised by the immortal work of Berzelius. It can be said that the discoveries of M. Mitscherlich are related to the influence of their form, and the future will decide whether the present work of French chemists is destined to give us the key to the role which belongs to their position." (119)

In the first of five memoirs on his type theory (120) he concentrated on the theory, reorganising the ideas he had read to the Academy and adding some new ones that were quite thought provoking. He devised a new particle model for organic chemistry, analogous to a planetary system, thus freeing the system from the rigidity and the limitations imposed on it by the crystalline model used from the time of Haüy and the focus of studies by Laurent and Alexandre Edouard Baudrimont (1806-1880). According to Dumas:

> "If, on the contrary, various chemical compounds are seen as constituting so many planetary systems formed from particles held in position by various molecular forces whose resultant constitutes affinity, no further need would be seen for this universal application of the dualistic law accepted by Lavoisier. These particles could be more or less numerous; they could be simple or compound; they would play the same role in the constitution of substances that the simple planets such as Mars or Venus, or the compound planets like the Earth, with its moon, and Jupiter with its satellites play in our planetary system." (121)

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119. Ibid.

120. Ann. Chim. Phys., 73 (1840), 73-100. This was the first issue in which Dumas was a co-editor. He had contributed only three articles to the journal (one a report) since the founding of Comptes-Rendus in 1835, where most of his work was published.

121. Ibid., 73. By replacing the single force of electrical dualism by several forces associated with each particle, Dumas could account for the indifference that most organic compounds exhibited towards electricity.

If the analogy limped slightly, it did have the advantage of providing a much more fluid system allowing for the exit and entry of atoms and groups.

The discovery of a natural means of classifying organic compounds made possible the development of a "comparative chemistry" (122). Two unique features arose from his new approach: two-line formulas and two dimensional charts. He first used the former in a memoir in 1839, in which he wrote one formula (chlorinated ether) in the form $\genfrac{}{}{0pt}{}{C^8H^6O}{Cl^4}$ (123). In 1840 he began to use them frequently (124). Although they were in two parts, they were not divided electrically but substitutionally and to call them dualistic would be misleading. On the other hand, since he was prepared to introduce groups (e.g. NO^2), they were not strictly speaking unitary (125). In the first memoir on types he drew up a chart (TABLE 8-1) showing relationships among a few organic compounds. The very limited value of the chart is not

TABLE 8-1. Dumas' Two-line Formulas Arranged in a Two-dimensional Classification.

Modern names	Hydrocarbon	Chloro-compound	Acid
Ethane	$\genfrac{}{}{0pt}{}{C^8H^6}{H^6}$	$\genfrac{}{}{0pt}{}{C^8H^6}{Cl^6}$	$\genfrac{}{}{0pt}{}{C^8H^6}{O^3}$
Methane	$\genfrac{}{}{0pt}{}{C^4H^2}{H^6}$	etc.	
Toluene	$\genfrac{}{}{0pt}{}{C^{28}H^{10}}{H^6}$		
Benzene	$\genfrac{}{}{0pt}{}{C^{24}H^6}{H^6}$		

122. Ibid., 100.

123. Comptes-Rendus, 8 (1839), 620.

124. Loc.cit.(8-1[illegible]), (8-120).

125. For a discussion of the problems involved in using this term, see Fisher, loc.cit.(8-104), note 46.

surprising when it is considered that this was his first tentative venture into classification on a much broader scale than anyone had yet attempted. Understandably it was based on $C^8H^6O^3$, the supposed anhydride of acetic acid, the compound that had been so influential in redirecting his thoughts.

Dumas was able to extend his theory considerably in a second memoir on types (125). He had invited Stas, one of his students at the time, to join him in a study of the oxidative action of hydrated potash on several alcohols (126), aldehyde (127) acetone (128) and some ethers (129). From their experiments the authors concluded that all true alcohols are capable of forming an acid that contained the same number of equivalents. They predicted that an alcohol would be discovered that would be equivalent to each

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125. Ann. Chim. Phys., 73 (1840), 113-66.

126. Those used were: ordinary (ethyl) alcohol, wood spirit (methyl alcohol), ethal (cetyl alcohol) and potato oil (amyl alcohol). They showed the relation of amyl alcohol with valeric acid.

127. The only aldehyde known was acetaldehyde. They showed its relationship to oil of bitter almonds (benzaldehyde).

128. It has been pointed out (note 104) that Persoz had obtained marsh gas and potassium carbonate by alkali oxidation of acetone and the error in his conclusion has been indicated. In the second memoir on types, Dumas noted, without comment, that bichromate oxidation of acetone produces carbonic acid and acetic acid (not formic acid). Ibid., 150. Thus his type was conserved. This reaction served another purpose: "Since the manner in which potash acts on this substance [acetone] is completely particular, it seems quite likely that the constitution of pyroacetic spirit [acetone] is radically distinct from that of ordinary alcohols." Ibid., 151.

129. Oxyethers formed two acids in the presence of an alkali, since the alcohol normally formed was oxidised to an acid. Thus methyl acetate formed formic and acetic acids. Ethers of the hydracids underwent a variety of reactions: $C^{40}H^{32}.H^2Cl^2$ reacted with alkali to form $C^{40}H^{32}$, and the original compound could be formed again by reaction with hydrochloric acid; $C^8H^8.H^2Cl^2$ released C^8H^8 but bicarboned hydrogen would not react with the acid; with $C^4H^4.H^2Cl^2$ neither reaction occurred. Thus the first reaction supported the original ether theory, the third, the ethyl theory and the second neither. Similar difficulties were raised by other ethers. Apparently he was still thinking along these lines.

of the known organic acids. The memoir was concluded with a chart (TABLE 8-2). Dumas' only comment was: "Chemists will understand the table at a glance, and the relationships that it establishes between certain elements and compounds." (130) While the chart has provided great difficulties for historians of science (131), what Dumas said was quite true at the time. Chemists were involved in the study of controlled pyrogenic reactions. Under the influence of heat many compounds released either water (not present as such), carbonic acid or both (132). To understand Dumas' chart, one must think that way. The alcohol and acetic (133) types were the same mechanical type because they consisted of the same number of equivalents. Since the elements were not arranged in the same way and the fundamental properties differed, they were not the same chemical type. The change from alcohol to acid resulted from substitution, equivalent for equivalent of hydrogen by oxygen and was consistent in all of the cases studied. But removal of an atom of water, (two volumes) forming ether, produced a new type, the second mechanical type, which, when modified by oxidation produced aldehydes and anhydrous acids. Removal of two atoms (four volumes) of water produced a third mechanical type, the olefiant type. No derivatives of this type by oxygen substitution were known. But assuming that the formulas given for alcohols and acids were equivalent, Dumas must have reasoned that removal of the same number of equivalents should leave formulas that were mechanically equivalent.

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130. Ibid., 165.

131. The most recent was Fisher, loc.cit.(8-104), 130.

132. In his preliminary discussion of essential oils in the Traite, Vol. 7 (1844), Chapter 1, Dumas described laboratory methods for doing this.

133. Dumas gave the name "acetic" type to the hydrated form of the acid, i.e., the modern form, because the term acid was used universally for the anhydrous form.

TABLE 8-2. Dumas' 1840 Classification of Organic Compounds.

	I^er TYPE MÉCANIQUE.		II^e TYPE MÉCANIQUE.			III^e TYPE MÉCANIQUE.		
	Type alcool.	Type acétique.	Type éther.	Type aldéhyde.	Type acide.	Type oléfiant.	Type benzine.	Type acétone.
Série carbonique...	$C^4H^4O^2$...	C^4O^4......	C^4H^2O....	C^4O^2.....	»	C^4.......	»	»
— oxalique.	$C^4H^6O^2$...	$C^4H^2O^4$...	C^4H^4O....	$C^4H^2O^2$...	C^4O^3.....	C^4H^2....	H^2......	C^2O .....
— formique.....	$C^4H^8O^2$...	$C^4H^4O^4$ ..	C^4H^6O....	$C^4H^4O^2$...	$C^4H^2O^3$...	C^4H^4....	H^4......	C^2OH^2...
— acétique......	$C^8H^{12}O^2$ ..	$C^8H^8O^4$...	$C^8H^{10}O$....	$C^8H^8O^2$....	$C^8H^6O^3$...	C^8H^8....	C^4H^8....	C^6OH^6...
— butyrique. ...	$C^{16}H^{16}O^2$.	$C^{16}H^{12}O^4$..	$C^{16}H^{14}O$ ..	$C^{16}H^{12}O^2$..	$C^{16}H^{10}O^3$..	$C^{16}H^{12}$..	$C^{12}H^{12}$..	$C^{14}OH^{10}$.
— lightique......	$C^{16}H^{20}O^2$..	$C^{16}H^{16}O^4$..	$C^{16}H^{18}O$...	$C^{16}H^{16}O^2$..	$C^{16}H^{14}O^3$..	$C^{16}H^{16}$..	$C^{12}H^{16}$..	$C^{14}OH^{14}$.
— phocénique. ..	$C^{20}H^{20}O^2$.	$C^{20}H^{16}O^4$..	$C^{20}H^{18}O$..	$C^{20}H^{16}O^2$..	$C^{20}H^{14}O^3$..	$C^{20}H^{16}$..	$C^{16}H^{16}$..	$C^{18}OH^{14}$.
— fuselique.	$C^{20}H^{24}O^2$..	$C^{20}H^{20}O^4$..	$C^{20}H^{22}O$..	$C^{20}H^{20}O^2$..	$C^{20}H^{18}O^3$..	$C^{20}H^{20}$..	$C^{16}H^{20}$..	$C^{18}OH^{18}$.
—	$C^{24}H^{20}O^2$..	$C^{24}H^{16}O^4$..	$C^{24}H^{18}O$..	$C^{24}H^{16}O^2$..	$C^{24}H^{14}O^3$..	$C^{24}H^{16}$..	$C^{20}H^{16}$..	$C^{22}OH^{14}$.
— caproïque.....	$C^{24}H^{24}O^2$.	$C^{24}H^{20}O^4$..	$C^{24}H^{22}O$..	$C^{24}H^{20}O^2$..	$C^{24}H^{18}O^3$..	$C^{24}H^{20}$..	$C^{20}H^{20}$..	$C^{22}OH^{18}$.
— benzoïque....	$C^{28}H^{16}O^2$..	$C^{28}H^{12}O^4$.	$C^{28}H^{14}O$..	$C^{28}H^{12}O^2$..	$C^{28}H^{10}O^3$..	$C^{28}H^{12}$..	$C^{24}H^{12}$..	$C^{26}OH^{10}$.
— cinnamique...	$C^{36}H^{20}O^2$.	$C^{36}H^{16}O^4$..	$C^{36}H^{18}O$..	$C^{36}H^{16}O^2$..	$C^{36}H^{14}O^3$..	$C^{36}H^{16}$..	$C^{32}H^{16}$..	$C^{34}OH^{14}$.
— naphtalique. .	$C^{40}H^{20}O^2$..	$C^{40}H^{16}O^4$..	$C^{40}H^{18}O$..	$C^{40}H^{10}O^2$..	$C^{40}H^{14}O^3$..	$C^{40}H^{16}$..	$C^{36}H^{16}$..	$C^{38}OH^{14}$.
— camphorique..	$C^{40}H^{32}O^2$..	$C^{40}H^{28}O^4$..	$C^{40}H^{30}O$.	$C^{40}H^{28}O^2$..	$C^{40}H^{26}O^3$..	$C^{40}H^{28}$..	$C^{36}H^{28}$..	$C^{38}OH^{26}$.
— thérébique....	$C^{40}H^{36}O^2$..	$C^{40}H^{32}O^4$..	$C^{40}H^{34}O$..	$C^{40}H^{32}O^2$..	$C^{40}H^{30}O^3$..	$C^{40}H^{32}$..	$C^{36}H^{32}$..	$C^{38}OH^{30}$.
— piperitique...	$C^{40}H^{40}O^2$..	$C^{40}H^{36}O^4$..	$C^{40}H^{38}O$..	$C^{40}H^{36}O^2$..	$C^{40}H^{34}O^3$..	$C^{40}H^{36}$..	$C^{36}H^{36}$..	$C^{38}OH^{32}$.
— cétique.......	$C^{64}H^{68}O^2$..	$C^{64}H^{64}O^4$..	$C^{64}H^{66}O$..	$C^{64}H^{64}O^2$..	$C^{64}H^{62}O^3$..	$C^{64}H^{64}$	$C^{60}H^{64}$..	$C^{62}OH^{62}$,
— cédrique......	$C^{64}H^{52}O^2$..	$C^{64}H^{48}O^4$..	$C^{64}H^{50}O$..	$C^{64}H^{48}O^2$.	$C^{64}H^{46}O^3$..	$C^{64}H^{48}$..	$C^{60}H^{48}$..	$C^{62}OH^{46}$.

NOTE: Before Dumas was aware of Regnault's discussion of mechanical types, he used sheets at the back of a folio notebook (Arch. Acad. Sci., Fonds Dumas, Carton 8) containing research done in 1838, to draw up a complete chart of formulas for various types of compounds corresponding to the 16 hydrocarbons that could exist from C^4H^4 to $C^{64}H^{64}$ assuming increments of C^4H^4 :

Carbure	éther	alco ol	acide hydraté	résidu	acide anhydre	acidone	aldehyde	acidehyde
$C^{64}H^{64}$	$C^{64}H^{66}O$	$C^{64}H^{68}O^2$	$C^{64}H^{64}O^4$	$C^{60}H^{64}$	$C^{64}H^{62}O^3$	$C^{62}H^{62}O$	$C^{64}H^{64}O^2$	$C^{64}H^{60}O^4$
C^4H^4	C^4H^6O	$C^4H^8O^2$	$C^4H^4O^4$	H^4	$C^4H^2O^3$	C^2H^2O	$C^4H^4O^2$	C^4O^4

Thus removal of two atoms (four volumes) of carbonic acid (C^4O^4) from the acetic type left compounds whose formulas were equivalent to the olefiant type, and he classified them as the benzine type (134). Having exhausted other possibilities, he finally considered removal of one atom (two volumes) each of water and carbonic acid, from the acetic type. This gave him the acetone type, also equivalent mechanically. While it appears that the number of equivalents differ in C^8H^8, C^4H^8 and C^6OH^6 for example, it should be borne in mind that the hydrogen equivalent for carbon is changing from 1 to 2 to $1\frac{1}{2}$, so that the number of equivalents in the compounds is the same.

Early in 1837, while seeking to establish the molecular arrangement of sugar, Dumas and Péligot had discovered the carbomethylates and carbovinates (135). Using this information and new discoveries made in collaboration with Peligot, he strengthened his type theory (136) by showing that both alcohol and acetic acid could be regarded as derivates of a marsh gas pair, $C^4H^8.C^4H^8$, and demonstrated how the new compounds (e.g., carbomethylic acid, $C^4H^6.\underset{O}{C}^4O^4$ and sulphocarbomethylic acid, $C^4H^6.\underset{O}{C}^4S^4$) also fit the pattern. With this approach Dumas had subtly moved back to groups without any electrochemical overtones. Whereas it seems at first sight that his chart was a game already played by Laurent, the rules were different and the breadth much greater.

Some time in February 1840, a letter was communicated to Dumas from the Academy in which Laurent claimed as his own most of the ideas that the

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134. Though there was a hint at a pattern within any type if certain compounds within a type were selected, Dumas was not ready to take such a step publicly, though he did so in his notebooks.

135. Comptes-Rendus, 4 (1837), 433-34 and 563-65. They summarised their results in a memoir: "Carbo-vinates, Carbo-methylates and the True Constitution of Sugar", Ibid., 6 (1838), 217-25.

136. "Third Memoir on Chemical Types", Ann. Chim. Phys., 74 (1840), 5-17.

older chemist had developed in the 3 February memoir. Dumas requested that it be published, because of the "necessity of placing before the public eye, in the interest of truth, all contributions relevant to the great discussion preoccupying chemists" (137). In his response (138) to the "vehement and impassioned" letter he noted that he had given credit where credit was due (139), then defended his position:

1. Laurent had added nothing to the law of substitution as an empirical law. In his first memoir on substitution he (Dumas) had seen:

> "1°. that chlorine could replace hydrogen equivalent for equivalent;
> 2°. that chlorine could combine in quantities exceeding the hydrogen removed i.e., addition;
> 3°. that water or hydrochloric acid formed could remain united to the product;
> 4°. finally I have seen that chlorine could remove hydrogen without replacing it." (140).

But Laurent claimed that he had made these modifications thus giving credence to the substitution theory. The biggest problem in assessing his claim lies with deciding what he meant by the term since the manner in which he used it changed over the years. As Dumas put it: "At first M. Laurent made use of concepts taken from my memoir. ... then little by little he forgot the origins and finally persuaded himself that they belonged to him." (141)

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137. Comptes-Rendus, 10 (1840), 408-17 (408). The letter contained a detailed attack on aspects of Dumas' work in addition to the priority claims.

138. Ibid., 511-24.

139. "I have rendered full justice to M. Laurent in my memoir in saying that he had insisted on the role of chlorine and hydrogen long before it was experimentally verified. But this did not satisfy M. Laurent any more than my reference to his honourable part in the matter of organic radicals." Ibid., 523.

140. Ibid., 517.

141. Ibid.

2. Laurent indicated that he alone had developed the nomenclature associated with the theory, that Dumas had contributed nothing. While it is hardly necessary to draw attention to the memoir already mentioned in the present work in which Dumas and Péligot first used the suffix -ose to identify a derivative of cinnamon oil (chlorocinnose), and reserved others (-ase, -ese, etc.) to indicate numbers of atoms substituted, a system that formed the basis for much of Laurent's nomenclature later, it should be recalled that Dumas abandoned the system almost immediately (142).

3. In attempting to show that the type theory was in opposition to Dumas' earlier views, Laurent 'quoted' (143) from the Traité:

> "Alcohol, $C^8H^8 + H^4O^2$, when oxidised loses H^4 (from the bicarboned hydrogen) and gains O^2. Hydrated acetic acid is formed, which is represented by $C^8H^6O^3 + H^2O$." (144)

But Dumas had said:

> "In accepting that alcohol contains $C^8H^8 + H^4O^2$, oxygen must act by preference on the hydrocarbon, and if it removes H^4, this is replaced by O^2. Thus $C^8H^8O^4$ remains, that is to say hydrated acetic acid, which is represented by $C^8H^6O^3 + H^2O$." (145)

Laurent, using the anhydrous acid, compared C^8H^8 with C^8H^6 to show that the type was not conserved. But Dumas drew upon his original memoir, to show that he had suggested the following mechanism:

$$\text{"}\frac{C^8H^8 \atop H^4O^2}{C^8H^{12}O^2} + O^4 = H^4O^2 + \frac{C^8H^4O^2 \atop H^4O^2}{C^8H^8O^4}\text{"} \quad (146)$$

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142. Undoubtedly he saw the obscurity to which it was leading.

143. Dumas observed: "He has altered my text so that he could have the right to complain, and it is enough to reread the passage of my memoir to appreciate the value of his recriminations." Ibid., 523.

144. Comptes-Rendus, 10 (1840), 411.

145. Traité, Vol. 5, p.286.

146. Ann. Chim. Phys., 56 (1834), 144. Dumas believed that the oxygen only replaced hydrogen in the bicarboned hydrogen portion, leaving the water portion intact. The hydrogen leaving was oxidised to water.

Clearly the type had been conserved, and Dumas took this opportunity to remind his former student that liberties could be taken in a memoir that were not permitted in an elementary textbook, "where substances must be represented according to the general opinion of chemists." (147) He went on to point out that type had been conserved in his memoir on chloral; that even earlier he had been thinking along these lines when he considered that chlorocarbonic acid was analogous to carbonic acid (148). In 1833 he had classified chloroform, bromoform, iodoform and formic acid in a single group. To these and other responses to Laurent's claims, he added:

> "I know of no one before me who had proposed to group organic compounds experimentally into genera, using fundamental chemical properties of the order of those which I have attempted to put to good use. I know of no one before M. Regnault who had tried to classify organic compounds using a precise experimental study of certain physical properties." (149)

Finally, he reminded Laurent that Jean-Pierre Couerbe (1805-1867) had been the first to suggest the existence of a relationship between the properties of compounds and the physical form of their molecules (150), that Laurent

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147. Loc.cit.(8-144), 518.

148. In 1827 (Ibid., 520) Dumas gave the name chlorocarbonic acid to J. Davy's chloride of carbonic oxide because he saw it as a derivative of carbonic acid rather than carbonic oxide. He noted: "It is easy to see that chlorocarbonic acid corresponds to carbonic acid itself. Indeed in all its combinations, 1 vol. of chlorine replaces $\frac{1}{2}$ vol. of oxygen; thus it is as if carbonic oxide has been changed into an acid by replacing the $\frac{1}{2}$ vol. of oxygen that must be added by 1 vol. of chlorine. But chlorocarbonic acid is more powerful than carbonic acid because it saturates four times as much ammonia and decomposes the carbonate of ammonia by driving out carbonic acid." Traité, Vol. 1 (1828), p.513.

149. Loc.cit.(8-144), 520.

150. Dumas (Ibid., 523) quoted part of a footnote which Couerbe had added to his memoir on "Du Cerveau, considéré sous le point de vue chimique et physiologique", Ann. Chim. Phys., 56 (1834), 160-93 (189), in which he had said: "In an earlier memoir I attributed alkaline properties to the physical form of the molecule the form produced by grouping the elementary atoms of that molecule. I generalised this concept; form is the secondary, perhaps even primary cause of properties."

had no right to that claim (151).

There were two more memoirs on types, one on indigo and compounds derived from it (152), the other on what he called conjugated acids (153). By considering that polybasic acids were formed by combining two organic acids in such a way that one acid partially or fully neutralised the other he could explain the degree of saturation of those acids (154). Because tartaric acid formed potassium acetate and potassium oxalate on heating with potash, Dumas considered that it was a conjugate of one atom of acetic acid and two atoms of oxalic acid in which one atom of oxalic acid was neutralised, and the saturation of tartaric acid was therefore twice that of acetic acid (155). Thus he wrote the formula $C^8H^4O^3_{C^4O^2}.C^4O^3$ for the anhydrous acid, the hydrate containing four atoms of water. Although there was still a long way to go, this was another step towards the modern arrangement for tartaric acid, COOH.CHOH.CHOH.COOH and polybasic acids in general.

Comparing Dumas' formulas with modern notation reveals three major differences which have made the study of early organic chemistry difficult

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151. General interest in the whole debate on substitution and the type theory led Gustave Augustin Quesneville (1810-1889) to devote most of the first number of his new journal to presentations by those involved, Dumas, Laurent, Couerbe, Baudrimont and Pelouze. Rev. Sci., 1 (1840), 5-166, also 339-44.

152. Ann. Chim. Phys., 2 (1841), 204-32.

153. Ibid., 5 (1842), 353-95. The work, undertaken with a student, Raphael Piria (1815-1865), was interrupted in 1839 when Piria returned to Italy. Dumas finally decided to publish it as it was, which means that the notion of 'copulated' compounds probably originated with him.

154. A dibasic acid had a degree of saturation twice that of a monobasic acid, i.e., it was equivalent to twice as much base.

155. Vapour density measurements which made it possible for him to write a four volume formula for acetic acid were unavailable for oxalic acid, which decomposed before vapourising. Thus he had no reason to change a formula that was well established by other means. It was, unfortunately, a two-volume formula.

for historians: The atomic weight he used for carbon was half the modern value; he had not come to grips with the problems created by using some two-volume formulas in a four-volume system; he was unwilling to accept the theory of hydracids, though he gradually put more emphasis on the hydrated form of the acid rather than the anhydrous form which was more in conformity with the oxygen theory of acids. Nowhere is the latter change more evident than in the work that crowned his type theory and must be regarded as a decisive step forward in the classification of organic compounds. He was acutely aware of the simple relationship suggested by formic, acetic, lightic, valeric and ethalic acids: equal numbers of carbon and hydrogen atoms combined with four atoms of oxygen. A similar pattern could be seen in their corresponding alcohols and ethers as well as the olefiants, as he had shown. Hampered by inaccurate formulas given to several of the acids by Chevreul (156) that left many spaces between formic and ethalic acids, he could hardly have assumed that these compounds existed until he had found the correct formula for valeric acid (157). Involved in other research of considerable importance, he was unable to return to this problem until 1842, when he began to prepare the next volume of his Traité, which was to include a chapter on fats. By this time several new acids had been discovered that fitted the new pattern. On 21 November 1842 he read a brief memoir to the Academy

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156. In his discussion of fatty acids (Traité, Vol. 5, Chapter 5), Dumas used the proportions assigned by Chevreul to the following acids: butyric, $C^{16}H^{13}O^{4}$; caproic, $C^{24}H^{21}O^{4}$; capric, $C^{39}H^{31}O^{4}$; phocenic, $C^{20}H^{17}O^{4}$; stearic, $C^{70}H^{69}O^{3\frac{1}{2}}$; margaric, $C^{70}H^{67}O^{4}$. Since the number of atoms of hydrogen was nearly a multiple of four in each compound, when he included the first four in his chart in 1840, he adjusted their values accordingly. The other two were omitted.

157. Valeric acid, $C^{20}H^{20}O^{4}$, interrupted a different kind of progression suggested by $C^{4}H^{4}O^{4}$, $C^{8}H^{8}O^{4}$, $C^{16}H^{16}O^{4}$, $C^{64}H^{64}O^{4}$. The analogous progression for olefiant gases, $C^{4}H^{4}$, $C^{8}H^{8}$, $C^{16}H^{16}$, $C^{64}H^{64}$, appears frequently in Dumas' notebooks.

entitled "Loi de composition des principaux acides gras" (158). Its importance warrants its inclusion in full:

"Starting with margaric acid, $C^{68}H^{68}O^{4}$, so well studied by M. Chevreul, and subtracting carbon and hydrogen in equal equivalents $C^{4}H^{4}$, a series of seventeen acids is formed, of which nine are already known, containing the principal fatty acids relating by unforeseen links margaric acid to one that seems most remote from it, formic acid.

$C^{68}H^{68}O^{4}$	margaric acid
$C^{64}H^{64}O^{4}$	ethalic acid, from spermaceti
$C^{60}H^{60}O^{4}$	
$C^{56}H^{56}O^{4}$	myristic acid, from nutmeg (159)
$C^{52}H^{52}O^{4}$	cocinic acid, from coconut fat (160)
$C^{48}H^{48}O^{4}$	lauric acid, from laurel berries (161)
$C^{44}H^{44}O^{4}$	
$C^{40}H^{40}O^{4}$	
$C^{36}H^{36}O^{4}$	capric acid?
$C^{32}H^{32}O^{4}$	
$C^{28}H^{28}O^{4}$	oenanthylic acid (162)
$C^{24}H^{24}O^{4}$	caproic acid?
$C^{20}H^{20}O^{4}$	valeric acid
$C^{16}H^{16}O^{4}$	butyric acid?
$C^{12}H^{12}O^{4}$	
$C^{8}H^{8}O^{4}$	acetic acid
$C^{4}H^{4}O^{4}$	formic acid

It is worth mentioning that the anhydrous acetates (163) all have the pearly look characteristic of soaps.

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158. Comptes-Rendus, 15 (1842), 935-36.

159. Isolated by Playfair, Phil. Mag., 18 (1841), 102-13.

160. Dumas wrote: "According to M. Bromeis, the fat that we will designate by the name cocinine can be considered as a compound of glycerine and a particular acid." Traité, Vol. 6, p.661. It is not clear who isolated and analysed it, probably Johann Conrad Bromeis (1820-1862).

161. Isolated by Theodor Friedrich Marsson (1816-?), Annalen, 41 (1842), 329.

162. Isolated by Thomas George Tilley (?-1848 or 9) from castor oil, Dumas noted. Traité, Vol. 6, p.645.

163. This was Dumas' generic name for salts of the acids.

In this list the acids at the top of the list are less fusible, their fusibility increasing regularly from top to bottom.

The existence of an acid $C^{72}H^{72}O^4$, which is almost certain, means that the list does not end with margaric acid.

The greatest interest is attached to completing this series and comparing the physical properties of the substances in it, but also in comparing the alcohols, ethers and hydrocarbons that correspond to these different acids as ethal and cetene correspond to ethalic acid. This is what a more extensive study of fatty substances can lead to, as I soon hope to show.

In all these acids a hydrocarbon is found that is isomeric with olefiant gas, confirming and specifying the general relationship observed by our colleague, M. Chevreul in his truly classic research on fats." (164)

Within a few months Dumas had published the next volume of his Traité (165), containing this list of acids to which was added rocellic acid with a question mark (166) and some melting temperatures to show the progression of which he had spoken. Within a year Josef Udo Lerch (1816-1892) working in Giessen had verified the formula for caproic acid, changed the one for capric acid to $C^{40}H^{40}O^4$ and discovered an acid $C^{32}H^{32}O^4$ which he called caprylic acid (167). Also in 1844, Pelouze and Amédée Gélis (1815- ?) verified Dumas' formula for butyric acid (168). One of the lightest members of the series, $C^{12}H^{12}O^4$ was prepared in several ways (169) before Dumas, working

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164. Loc.cit.(8-157).

165. Traité, Vol. 6 (1843), p.577.

166. He had included rocellic acid in his discussion of acids in 1835. Ibid., Vol. 5, p. 294-96. He had observed that Friedrich Heeren (1803-1885) had discovered it and Liebig had found its formula to be $C^{34}H^{32}O^4$, though "he believed it should be $C^{32}H^{32}O^4$". Much later it was shown that his analysis was correct, but it was a two-volume formula, $C_{15}H_{30}(COOH)_2$, thus dibasic, and did not belong in Dumas' series.

167. Annalen, 49 (1844), 212-31.

168. Ann. Chim. Phys., 10 (1844), 434- 56.

169. The pseudoacetic acid (or butyroacetic acid) (Annalen, 38 (1841), 299) of Carl Nöllner (1808-1877) had not been accepted; Johann Gottlieb (1815-1875) prepared it by oxidising 'metacetone' and called it metacetonic acid (Ibid., 52 (1844), 177) which Joseph Redtenbacher (1810-1870) obtained by oxidising glycerol. Ibid., 57 (1846), 174.

with Malaguti and Félix Leblanc (1813-1886) on the preparation and hydrolysis of nitriles, obtained the acid by hydrolysis of ethyl cyanide in 1847 (170). Thus within two years after the publication of his list all but three of the seventeen acids had been isolated and identified.

In view of Dumas' interest in substitution it may well be asked why he did not prefer to think of all these compounds as derivatives of the series of compounds beginning with marsh gas, C^4H^8, rather than addition compounds of methylene, C^4H^4. He had listed four of the former in his 1840 chart, C^4H^8, $C^{12}H^{16}$, $C^{16}H^{20}$ and $C^{60}H^{64}$, but marsh gas was the only one known, and there was no indication that any would be found. On the other hand several olefiant gases had been isolated and there was hope for others in view of the analogies that were apparent. Though Dumas did not provide a general formula for the series he mentioned, it is quite evident that the notion of homologues, which will be met again in Chapter 10, is contained in this memoir. The two essential points are there: a continuous series varying from one member to the next by a constant group, C^4H^4, and analogous series having the same characteristic, a notion that he had barely hinted at in his type theory and now expressed clearly. Indeed it was the culmination of his type theory, and his desire for a rational method of classification in organic chemistry. Certainly there were many compounds not included but he had shown that a large number of compounds could be related meaningfully. Many hands were needed to develop these series and devise new ones for such a variety of existing substances that no one could have dreamed of fifteen years earlier.

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170. Dumas showed that pseudoacetic and metacetonic acids were the same as the one he and his colleagues had prepared. Rather than name it after sources, they called it propionic acid because it was the lightest of the acids that separated out as an oil upon its saturated aqueous solution. The word is Greek for first fat.

CHAPTER 9

DUMAS AND THE FACULTIES OF SCIENCES AND MEDICINE

"The essay that M. Boussingault and I are submitting for public scrutiny connects in a simple form the principal characteristics of plant and animal life considered from a chemical viewpoint.

It offers some new insights that will provide general physiology, medicine and agriculture with foundations that are suitable for guidance in the study of the chemical phenomena that are observed in living beings. ...

As to the published form of this work, the reader should note that once we had decided on our views, one of us expanded them in his course at the medical school and summarised them in a final lecture reported here verbatim." (1)

The year 1838 had marked a new phase in Dumas' search for a broader principle of organic classification based on molecular arrangement, but it was also the year during which he entered yet another teaching environment. This became possible as early as 1832 when the barrier that had prevented him from teaching in the Faculties of the University was finally removed, enabling him to earn doctorates in medicine and the physical sciences and to accept an appointment to the Faculty of Sciences all in the same year. Following upon success in a remarkable competition held in 1838, he was awarded a Chair in Organic and Pharmaceutical Chemistry in the Faculty of Medicine. In his course there and the research that accompanied it, he returned to the physiological studies begun in Geneva, but from a much more chemical viewpoint because of the great advances that had been made in organic chemistry during the interval. Studies undertaken in collaboration with Boussingault led to his "Lecture on the Chemical Statics of Living Beings", given in the Faculty of Medicine for 1841 (2), in which he indicated the complementary role played by plants as reducing agents absorbing energy, and animals as oxidising agents releasing energy, linked by their relationship to the substances contained in the earth and the atmosphere, the media in which these activities occurred. From the time that it was first published, the Statique chimique

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1. Dumas, J.B. and J.B. Boussingault, Essai de Statique chimique des Etres organisés, 3e Ed., Paris, 1844 (viii, 147 p.; Essay, pp. 1-48, documents, pp. 49-147) pp. iii-iv (Introduction to the 2e Ed., 88 p.). References will be to the 3e Ed. as Statique chimique. The original lecture was reproduced verbatim in all editions, but with each new edition more notes were added to defend their thesis.

2. This lecture, given on 20 August 1841, was his last of the school year 1840-41 and it was published (Journal des Débats, 20 August 1841 and Ann. Sci. Nat. (Zool.), 16 (1841), 33-61) with the title Leçon sur la Statique chimique des êtres organisés, which was subsequently issued as a pamphlet of 48 pages. The second and third editions of the pamphlet are described in Note 1.

assumed international importance and engendered a controversy that lasted for several years, gradually drawing chemists and physiologists on to a common meeting ground. About the same time he became dean of the Faculty of Sciences and member of the administrative council of the University, positions that led to a deep involvement in reforms of science education at all levels. Before Dumas' role in the two Faculties can be examined, some understanding of their place in the French educational system in the first half of the 19th century is necessary.

In 1806 the Emperor Napoleon I created an Imperial University, a composite public corporation including all educational institutions in France, "an organisation charged exclusively with public instruction and education throughout the Empire" (3). Governed by a University Council under the direction of the Grand Master of the University who was responsible only to the Emperor (4), this highly centralised educational unit was established as his effective "instrument of politics, power and rule" (5). The decree of 1808 that constituted the University, created five Faculties in Paris: Arts, Sciences, Medicine, Law and Theology (6). Because primary and secondary

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3. D'Irsay, S., Histoire des Universités, 2 Vols., Paris (P.U.F.) 1933-35, Vol. 2, p.171.

4. Later it was the Council of Public Instruction, directed by a Minister responsible to the government.

5. Ibid., p.172.

6. The Ecole de Pharmacie did not become the Faculty of Pharmacy until 1840. Some of the Faculties were instituted in other cities also in 1808, the rest only gradually over many years. The Faculty of Science was new. The other four had been suppressed in 1793 and re-established one by one. Ecoles de santé were created in 1794 because of the need for doctors but had no control over medical practice and could not check abuses. By a decree of 1803, the degree Doctor in Medicine was again made mandatory, to be conferred only after examinations, successfully passed after four years of preparation under the supervision of the teaching staff of one of the écoles de médecine founded at the time. The discussion in this chapter does not include the grandes écoles which had their own entrance requirements, nor the many private schools such as the Athénée which paid (cont.)

education was badly in need of reform, the primary purpose of these institutions was to set standards, that is, to examine candidates and confer degrees, although they did so at different levels. The baccalaureates in arts and sciences served a twofold purpose: For most they were terminal degrees; for some, however, they were an indication of readiness to enter the programmes leading to the licence and perhaps doctorate including the degree Doctor in Medicine and the new Doctor in Sciences. A notice circulated in 1820 pointed out: "The baccalaureate will open the door to all civil professions and will become for society an essential guarantee of the ability of those whom it will admit to its service." (7)

While any student with a certificate of attendance at lectures in rhetoric and philosophy at an approved secondary school could ask to be examined for the Baccalauréat ès Lettres, in practice only a few who had attended a Lycée did so immediately. Most waited for a year or more, often attending lectures in the Faculty of Arts. The Baccalauréat ès Sciences was obtained in a similar manner, usually requiring a year of preparation after the awarding of the Baccalauréat ès Lettres. Initially professors for the Faculty of Sciences were chosen from among those teaching in the Muséum, Ecole Polytechnique and the Collège de France. After that time new professors were presented by the Faculty, approved by the Council of the

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6. (cont.) a tax to be free of control. It is limited to the Faculties and the school system. The distinction will be emphasised in the present work by using English equivalents for the system except for the Lycée which does not have a suitable English equivalent.

7. Circulaire du 19 septembre 1820, quoted by O. Gréard, Education et Instruction, Paris, 1889, p.169.

University and appointed by the Grand Master (8). Political events retarded the growth of the system somewhat. Until 1826 less than 100 Baccalauréat ès Sciences diplomas were issued annually and the increase that occurred about this time must be attributed to the enforcement from 1823 of the law that the science diploma must be obtained to register in the Faculty of Medicine (9). On the other hand, attendance at lectures was not limited to students seeking the diploma and the size of the audience varied widely, depending very much on the ability of a professor as a lecturer as well as his subject matter (10).

From the outset regulations required that candidates for teaching positions in Lycées were to have a licence and in the Faculties they were to have a doctorate, but it was recognised that some time would be necessary to implement this fully (11). To prepare for it, a pensionnat normal was introduced in 1808, the first permanent Ecole Normale (12). Again political

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8. Some insight into the character of the Faculties may be gathered from the fact that the Academy of Sciences had a very strong voice in the presentation of candidates for chairs in the sciences in the grandes écoles, but had shown little interest in exercising this kind of control when the Faculties were instituted.

9. The decree of 1808 indicated that the Baccalauréat ès Lettres would be a prerequisite for entering the Faculty of Medicine from 1 October 1815. In 1820 the Baccalauréat ès Sciences was added, effective from 1 January 1823. Except for two brief periods (1831-36 and 1852-58) this requirement has continued to the present.

10. Ampère did very poorly at a time when science lectures were popular. Many hundreds attended those given by Thenard at the same time. At one point, his audience was so large that it was necessary to change the site of his lectures to the largest amphitheatre available, a new one at the Muséum. His son wrote: "He was often offered the assistance of the police, which he always refused." Thenard, op.cit.(3-81), p.103.

11. Those teaching in the Faculty at the beginning were given the necessary degree on the strength of their earlier work.

12. Though the Ecole Normale dates its existence from 1795, the attempt to form many teachers rapidly at that time ended in failure after a few months. The project of opening such a school was not revived until 1808, and it was undertaken on a very limited scale. The history of the Ecole Normale, containing a long discussion of that early attempt may be found in P. Dupuy, ed., Le Centenaire de l'Ecole Normale, 1795-1895, Paris, 1895.

events intervened, changing its format, curriculum and various regulations every four or five years, even suppressing it for a time, but by 1830 it had become solidly established (13). Students preparing to teach science attended many of the lectures in the Faculty of Sciences, complemented by seminars and routine laboratory experiments in physics and chemistry done in the Collège du Plessis where they stayed. While mathematics, physics and chemistry were emphasised, courses were also given in astronomy, mineralogy, geology, botany and zoology. The Baccalauréat ès Sciences was awarded after success in first-year examinations and the licence after passing those at the end of the second year. From 1828 those who were among the first ten at that time would be allowed to stay on and begin work on the doctorate as agrégés in one of three sections: mechanics and astronomy; physics and chemistry; botany, zoology and mineralogy. Two theses were required; if the major thesis was in chemistry, it was required that the other be in physics. Since the doctorate was obtained in the Faculty of Sciences, and was necessary to teach in it, a certain amount of inbreeding could have resulted if professors had not been teaching elsewhere. The same was true for the Faculty of Medicine.

After the success of the July Revolution, a commission was formed to examine all questions concerning the reorganisation of the Faculty of Medicine (14). Nine professors were replaced, permutations taking place among those

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13. "The Ecole Normale was among the institutions most favoured by the liberal government that issued from the events of 1830." Ibid., 228.

14. Arrêté of 23 August 1830. Members of the Commission included: Professors, Cuvier, Antoine Dubois (1756-1837), Duméril, Augustin Jacob Landré-Beauvais (1772-1840), Gabriel Andral (1797-1876); Agrégé, Cloquet; Doctors of Medicine, Armand Husson and Jules Guérin (1801-1886). Guérin submitted the 46-page report on 15 September.

remaining as in 1823 when 11 were retired (15). Four of the professors who had been retired in 1823 were invited to return, among them Deyeux (16) who was appointed to the Chair of Pharmacology (17). At this time Deyeux was 85 years old, so there can be little doubt about the honorary and interim character of the appointment (18). Another decision was made that effected the students and was of considerable importance for Dumas. At the request of the students, the Commission advised the abrogation of the law of 1820 that had required the Baccalauréat ès Lettres and Baccalauréat ès Sciences before registration in the Faculty of Medicine. The order accomplishing this was published 18 January 1831 (19).

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15. Events following a return to the 'right' had brought dissolution of the Faculty in November 1822. The professors retired in the reorganisation of February 1823 as honorary professors were replaced and a corps of agrégés was created to serve as substitute professors and to assist in examinations. Before the new professors were chosen, those remaining were allowed to take one of the vacant chairs if they wished. This was a permutation and one of them had brought Duméril, an anatomist, to the Chair of Physiology.

16. The others were A.L. de Jussieu and Marie Lallement (1750-1834), who declined; and Desgenettes who regained the Chair of Hygiene.

17. The history of this chair is somewhat complex. Deyeux had been the assistant to Fourcroy when the Chair of Medical Chemistry and Pharmacy was founded. He had taught the part of the course concerned with pharmacy. In 1811 Fourcroy was replaced by Vauquelin, who along with Deyeux was retired in 1823. At that time, the chair was divided; Orfila was appointed to the Chair of Medical Chemistry and Jean Nicolas Guilbert (1779-1835) to the renamed Chair of Pharmacology. Deyeux was appointed to the latter chair on 5 October 1830 as a result of Guilbert's revocation.

18. Until 1830 Deyeux had never been more than an assistant in the Faculty. Though it appears that he never had a substitute except for examinations, it has been suggested that his lectures were only attended by agrégés.

19. The authorities were reluctant to reject such requests during this highly sensitive period. An order of 9 August 1836 re-established both baccalaureates as prerequisites, effective 1 November 1837. Diplomas were presented before the first examination, which was after the eighth registration.

Within a short time Dumas registered for the Faculty of Medicine. For years he had been prevented from doing so because he had not completed his schooling in Alais and examination for the <u>Baccalauréat ès Lettres</u> was out of the question. He had now been in Paris for over eight years. Though he had been involved in many enterprises, only his position as <u>répétiteur</u> at the <u>Ecole Polytechnique</u> could be regarded as stable, and advancement depended on a decision by Thenard to retire. Dumas had relinquished his position at the <u>Athénée</u>, which had been an annual appointment anyway, and uncertain. Though he had been a substitute for Thenard regularly at the <u>Collège de France</u> since 1827 (20), this too depended upon an annual decision. The <u>Ecole Centrale</u> had begun in difficult circumstances, made worse by the events of 1830 and was not a source of income. It was the only school in which he held a chair. The industry that he had taken on from his brother had become a liability. It is quite probable that his decision to ask help from his father-in-law at this time was prompted by the opportunity to pursue the doctorate.

When the <u>Ecole de Médecine</u> was re-established in 1803, it was decreed that four years of course work were to precede the awarding of the degree. Evidence for the fulfillment of this requirement came in the form of sixteen registrations over a four year period. Some time after the eighth registration the student was required to sit an examination covering pharmacology and the medically related aspects of chemistry, physics and natural history (21). The second examination, on anatomy and physiology was given after the tenth registration; the third, on pathology, after the twelfth; the fourth, on hygiene, legal medicine, therapeutics and medical substances, after the

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20. See Chapter 3, notes 117-18.

21. These new examination requirements were set forth in a decree of 1825 discussed in A. Corlieu, <u>Le Centenaire de la Faculté de Médecine de Paris, 1794-1894</u>, Paris, 1896, pp. 84-85.

fourteenth; the fifth, on internal and external clinical medicine and maternity, after the sixteenth. At the last examination, the candidate was expected to discuss six observations made at sick beds, four of these in Faculty clinics. Finally, the candidate was examined on his thesis.

The standard dispensation from the baccalaureate given at this time was noted on Dumas' registration certificate (22). Information concerning his registrations and examinations, which appears to be unusual, is summarised in Table 9-1 (23). While the registrations, normally occurring at the

TABLE 9-1. Dumas' Registrations and Examinations in the Faculty of Medicine.

Registrations	1-8	9-10	11-12	13-14	15-16	Thesis
Date of Permission to register	2 Aug.	2 Aug.	12 Aug.	12 Aug.	12 Aug.	
Date Registered	31 Oct.	24 Nov.	30 Dec.	3 Feb.	22 Feb.	
Registration Number	5632	7494	7735	1764	1861	
Examination	1	2	3	4	5	6
Date Examined	9 Nov.	7 Dec.	28 Jan.	16 Feb.	21 Mar.	12 Apr.
Examination Number	1398	1548	193	298	443	67
Grade	T.S.	E.S.	E.S.	E.S.	S.	E.S.

22. "Disp. du B. le 2 août 1831", Certificats d'Inscription, Arch. Nat., Faculté de Médecine (non-cotés).

23. The information contained in the chart was compiled from three certificates: registration, examination, thesis examination. Ibid. The first two summarised in 1831-32 data contained in Registres d'Inscription and Registres des Examens. Reference to the Registre was by year and registration number or examination number. Apparently Dumas was dispensed from the registration fee (first year, 100 francs; second year, 120 francs; third and fourth years, 140 francs). His registration certificate bears the following statement: "12 Inscriptions all[ouées] le 2 août 1831, 4 autres all[ouées] le 12 août 1831." He did pay the standard examination fee of 30 francs per examination required by decree of 25 November 1823, (cont.)

beginning of each semester, were related to the lectures that the student was expected to attend, for Dumas they came in the middle of brief study periods and signified a readiness to be examined more than anything else. The extent of his success suggested by the results was confirmed by the "first" written on the thesis examination certificate.

The thesis, submitted in Latin or French at this time, was on a topic drawn from a prepared list or on the candidates own theme. In addition some Hippocratic aphorisms were required, or, from 4 February 1831, at least six propositions of medicine and surgery, on which the examiners would question him. Dumas' thesis (24), dated Thursday, 12 April 1832, was defended before Pierre Eloi Fouquier (1776-1850), professor of clinical medicine; Duméril, who had resumed the Chair of Medical Pathology in the permutations of 1830 after lecturing on physiology for seven years; Deyeux, professor of pharmacology and Adolphe Brongniart, Dumas' brother-in-law, who had been chosen agrégé (25) for the accessory sciences section in the competition of

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23. (cont.) which ensured the presence of examiners, who indicated that they were pleased (satisfait)(S), very pleased (T.S.) or extremely pleased (E.S.). No doubt it was his preparation for these examinations that prevented Dumas from replacing Thenard at the Collège de France in 1831-32 (see Chapter 3, note 118). Dumas' address on the registration certificate was: "Rue de Seine, St. Victor, 35 (at present the junction of the rue Cuvier and rue Linné).

24. Dumas, J., Propositions de Physiologie et de Chimie médicale (hereafter Props. Physiol.), Thèse présentée et soutenue à la Faculté de Médecine de Paris le 12 avril 1832 pour obtenir le grade de Docteur en Médecine, Paris (Didot le jeune), 1832.

25. Brongniart had just received his medical degree, a prerequisite to agrégation. Agrégés were created by an ordonnance of 2 February 1823. There were 36 places; 12 in training, 12 practising and 12 free. Each stage lasted 3 years, so that a doctor entering the programme normally remained in it for 9 years. Initially 24 were appointed and 12 chosen in competitions involving a written composition, lecture and thesis. Agrégés, between 25 and 40 years old when first chosen, were appointed as examiners for which they were paid, and had the right to be candidates in their section for a vacated chair. There were three sections: medicine, surgery, accessory sciences. The accessory sciences were: chemistry, physics, natural history and pharmacology.

1826 (26). Dumas dedicated it to his mother (27). He gave the following introduction to his 26 propositions, some of which were somewhat expanded:

> "For a long time I have been involved in physiological or chemical studies which have evoked some interest. I am taking the first opportunity available to discuss publicly the principal results and to reply to the objections which have been raised to some of them. Some of the propositions have never been made public because the pursuit of my physiological studies was interrupted by the demands imposed on me by my chemistry teaching." (28)

Dumas' suggestion that there was little new in his thesis, that he had largely summarised and defended work that he had done earlier, should be considered in the light of the general quality of medical theses at the time. It has been observed: "In 1829 there were 274 theses defended in the Paris Faculty of Medicine ... The Gazette Médicale evaluated them as follows: 38 good, 82 fair, 72 mediocre, 82 bad." (29) Certainly the comments of the

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26. The thesis certificate shows that Jean Jacques LeRoux des Tillets (1749-1832) and Jean Etienne Dance (d. 1832) had been assigned as examiners but did not sign it. Both were undoubtedly ill; LeRoux died just five months later. He was probably replaced by Deyeux who was not assigned originally, but who signed the certificate (twice!). The certificate was also signed by Guillaume Dupuytren (1777-1835), president of the Faculty. The printed copy of the thesis lists Orfila, professor of medical chemistry and dean of the Faculty as of 4 May 1831 and Auguste Félix Hatin, agrégé as substitutes, but they do not seem to have exercised their function. It also lists the complete Faculty and all agrégés at the time.

27. The date of his father's death is not available, but apparently he was not alive at this time.

28. Props. Physiol., Introduction.

29. Fosseyeux, Marcel, Paris Médical en 1830, Paris, 1930, p.13. The Gazette then pointed out that most of the latter were plagiarised, that in fact only the 38 listed as "good" met the standard demanded, i.e.: "work resulting from observations collected, at least in part, by the author". On the other hand, conditions were no better elsewhere according to Hérard, F., Doctrine médicale de l'Ecole de Montpellier et comparaison de ses principes avec ceux des autres écoles de l'Europe, Montpellier, 1819. It is reasonable to expect that there would not have been a significant change in just over two years.

examiners indicate that Dumas had surpassed the standard for he had not only presented his own work, but had extended some of the ideas that he had already published. It is not surprising that they wrote "extrêmement satisfait" in the printed form: "Because we have been extremely pleased with his responses, we advise the Faculty to award him the Diploma Doctor of Medicine."

The next day (13 April 1832) the Chair in Chemistry in the Muséum became vacant when André Laugier (1770-1832) (30) fell victim to the terrible cholera epidemic in Paris that claimed so many lives and nearly finished the Ecole Centrale (31). There was some hope that Dumas might be nominated for the chair, but other more prominent names were brought up in private conversations. A rather longer period of mourning than was usual gave way to a sense of urgency when the Academy convened on 21 May (32). At the request of the president, the chemistry section (33) met privately during the regular meeting, making possible the presentation of three names to the Academy that day, Serullas, Dumas and Robiquet, but clearly none of the three had been

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30. Laugier had succeeded Fourcroy as professor of chemistry in 1810.

31. The Procès Verbaux de l'Académie des Sciences show that reports on cholera, studies, methods of curing it, etc., poured into the Academy for some time. April and May were apparently the worst months.

32. Advised by the Minister of Commerce and Public Works to present a candidate "très promptement", Sylvestre François LaCroix (1765-1843), president of the Academy for 1832, urged the chemistry section to meet "sans retard"! PVAS, 10 (1832-35), p.63.

33. The six members were Deyeux, Chaptal, Thenard, Chevreul, Darcet and Serullas, but the latter two were absent. Serullas, head pharmacist at Val de Grâce hospital, had been named to a commission formed on 2 April 1832 to analyse the air because of cholera. He had shown some symptons of the disease at Cuvier's funeral the previous Wednesday, had in fact contracted it, and was in serious condition. Ibid., p.62.

contacted to obtain their agreement (34). A vote could not be taken until the following Monday, and during the interval Serullas died. A second presentation was required (35). After a delay of only two weeks, the names of Gay-Lussac, Dumas and Robiquet were presented in a closed meeting of the Academy on 4 June. As Gay-Lussac could not be present, he accepted the honour through an intermediary who added: "If he is nominated, he did not see how he would be able to retain one of his other two chairs in chemistry as well." (36) He was nominated in the following meeting (37) and subsequently the appointment was confirmed.

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34. This was an unusual procedure. One of the members of the Academy commented for the record: "MM. Dumas and Robiquet had been put on the list without being asked." Ibid., p.63. Probably Serullas had expressed his interest earlier. Brongniart, who seems to have been more worried about Dumas' future than Dumas, declared that he was "discouraged and disheartened" when Serullas was put on the first line. Launay, op.cit. (2-115), p.148. He may have discussed Dumas' candidacy privately with members of the chemistry section after Laugier's death. Because he, his son and Audouin all taught at the Muséum and Dumas resided there, he saw this as an ideal opportunity.

35. LaCroix announced to the Academy: "As the list of candidates presented in the last meeting is incomplete, the chemistry section is invited to meet again to proceed to a second presentation. Loc.cit.(9-31), p.64. Dumas read "Recherches sur la composition du minium" (ibid., p.66) which he may have had ready for such an occasion.

36. His two chairs in chemistry were in the Ecole Polytechnique and the Faculty of Sciences. He had already occupied the Chair in Physics in the Faculty of Sciences for several years when he began teaching Dulong's chemistry course in 1828 because of Dulong's illness. Crosland, op.cit. (1-28), p.227. If the statement quoted is taken literally, Gay-Lussac not only replaced Dulong who was an assistant professor, but a chair was created for him, since there was only one chair before that. Probably it should be position, not chair.

37. The nomination (loc.cit.(9-31), p.70), took place immediately after the report by Thenard, in his own name and that of Gay-Lussac, on a memoir read by Dumas "Sur les chlorures de soufre" on 7 May. Gay-Lussac received 35 votes, Robiquet 2. Dumas could not compete successfully against Gay-Lussac, but he was interested in the position Gay-Lussac was leaving even though he was not yet qualified for it.

While the medical degree meant that Dumas was qualified to teach in the Faculty of Medicine, it did not give the necessary credentials for teaching in the Faculty of Sciences. On the other hand, he had been dispensed from the baccalaureates, and the one stumbling block to the pursuit of advanced degrees in science had been removed. Furthermore there was a very real possibility that a position would be available in the latter Faculty in the not too distant future. Now a Doctor of Medicine, he turned immediately to preparations for receiving the degree Doctor of Sciences. He had been persuaded by Mitscherlich late in 1831 that the anomalous vapour density values for phosphorus, arsenic and sulphur should be published. As a result, he had written a brief article on phosphorus, with an emphasis on the experimental difficulties that he had encountered in measuring its vapour density (38). Now he gathered together all of the anomalous data he had obtained and prepared his first thesis (physics) for the science degree, which he read to the Academy of Sciences on 7 May (39). On 18 June, Thenard, in his own name and that of Gay-Lussac, read a long report on this "Dissertation on the Vapour Density of some Elements", (40). Dumas defended it before the Faculty of Sciences on 9 July, quite fittingly dedicating it to Gay-Lussac, "as a token of his deep admiration", since it was Gay-Lussac's research on vapour density measurements that had inspired his own work (41). Two days later he defended

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38. Ann. Chim. Phys., 49 (February 1832), 210-14.

39. Ibid., 50 (June 1832), 170-78. This work was discussed in Chapter 4, pp. 163-64.

40. Loc.cit.(9-31), 74-75.

41. "Dissertation sur la densité de la vapeur de quelques corps simples", thèse soutenue devant la Faculté des Sciences, Académie de Paris, le 9 juillet 1832 par J. Dumas, Docteur ès Sciences, Docteur en Médecine, etc., Paris (Mme V^{e} Thuau), 1832. The members of the Faculty were listed. Professors: Thenard (dean), LaCroix, Biot, René Louiche Desfontaines (1750-1833), Poisson, Gay-Lussac, Francoeur, Geoffroy Saint Hilaire, Beudant; assistant professors: Mirbel, Jean Nicolas Pierre Hachette (1769-1834), De Blainville, Dulong, Pouillet, Louis Constant Prévost (1787-1856).

the second thesis (chemistry), "Memoir on Plant Substances Related to Camphor and on some Essential Oils" (42), again very suitably dedicated, this time to De Candolle who had taught him botany in Geneva. Not only was this research concerned with compounds derived from plants, but also with a simple attempt to classify them (43). Dumas was awarded the degree Doctor of Sciences on 17 July (44).

Within a few weeks Gay-Lussac resigned his positions in the Faculty of Sciences (45). Soon afterward Dulong was appointed to the chair in Physics, and Dumas became assistant professor of chemistry. On 30 November he gave his first lecture in the Sorbonne (46). Thereafter he lectured for one and one-half hours, twice each week for about 15 weeks each semester. He was responsible for one semester each year, Thenard for the other, but ill health and other duties prevented the older professor from lecturing after 1837 (47).

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42. "Mémoire sur les substances végétales qui se rapprochent du camphre et sur quelques huiles essentielles". Except for the date the information was the same as in note 41. The dedication read: "In acknowledgment of my deep gratitude". Apparently the memoir was not read to the Academy, but it was published: Loc.cit.(9-39), 225-40.

43. Dumas noted: "The facts contained in this memoir are sufficient to establish, or rather to confirm the existence of two distinct classes of essential oils; those containing carbon and hydrogen only, and those containing oxygen in addition to these." Ibid., 239. He thanked those who provided compounds, observing that J.F. Bonastre "who had made very careful observations on products of this kind, had already placed his collection at my disposition, and I soon hope to be able to give an analysis of the products discovered by this capable chemist." Ibid., 240.

44. Chatelain, op.cit.(1-6), col. 130.

45. In a letter dated 14 August 1832 Abel François Villemain (1790-1870), member of the Council of Public Instruction, was asked by Amedée Girod de l'Ain (1781-1847), Minister of Public Instruction, to see to it that the Academic Council of the Paris Faculty of Sciences present a candidate for the Chair of Physics given up by Gay-Lussac. Arch. Nat., $AJ^{16}25$, Doss. 7.

46. Loc.cit.(9-44).

47. Dumas was obliged to substitute for Thenard, but the pressure of duties prevented him from lecturing for the whole year, so either Balard or Péligot substituted for him during one semester. Loc.cit.(9-45), Doss. 11, 12, 13.

Finally he retired from his chair on 9 December 1840 (48). In a meeting held on 28 December, the Faculty presented the names of Dumas and Péligot as possible replacements (49). Dumas was chosen by the Minister on 3 February 1841 (50). When Thenard gave up his duties as dean on 30 March 1840, Biot accepted them on a temporary basis (51). Dumas was appointed to succeed him on 8 March 1842 (52).

By now Dumas was an outstanding lecturer. On 9 December 1842, shortly after his arrival in Paris as a student at the Ecole Normale, Louis Pasteur (1822-1895) wrote an ebullient letter to his father in which he said:

> "I am attending the course given at the Sorbonne by M. Dumas, the famous chemist of our time. You cannot imagine the crowd of people present at this course. The room is immense and always full. One must go half an hour in advance to have a good place, absolutely like attending the theatre. In a similar manner, there is a good deal of applause. There are always six to seven hundred persons present." (53)

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48. Arch. Nat., F^{17}21776, No. 11.

49. Loc.cit.(9-45), Doss. 14.

50. The chain of decision was complex: Upon reception of the letter of retirement, the Faculty met to name at least two candidates for the position vacated. Their choices were then sent to the Minister of Public Instruction, who informed the Inspector General of the University (IGU) of them (Villemain did this in a letter dated 18 January 1841). The IGU in turn informed the Academic Council of the University, who, according to the terms of the Arrêté of 17 December 1833, could present the choices of the Faculty, in whole or in part, to the IGU as their own candidate(s) (the Council presented both Dumas and Péligot on 23 January). The IGU then informed the Minister, whose duty it was to make the final choice, if necessary, and to present that candidate's name to the IGU, who was expected to send out a notification of the choice to the dean and the successful candidate.

51. Loc.cit.(9-48). Poisson was appointed to replace Thenard but died 25 April. Biot was a reluctant replacement.

52. Loc.cit.(9-44).

53. Quoted in Valery-Radot, op.cit.(1-5), p.32. In Dijon Pasteur had earned a place in the Ecole Normale, but it was not high enough to satisfy him. He presented himself for the Baccalauréat ès Sciences again through the Lycée St. Louis and ranked fourth among those entering the Ecole.

In 1895 he recalled with enjoyment his days at Collège du Plessis, the home of the Ecole Normale:

> "On the days when J.B. Dumas gave his course in chemistry at the Sorbonne, we were impatient to hurry to the amphitheatre, in which there would be seven or eight hundred people. The front places were reserved for the students of the Ecole Normale. I listened, I applauded, I left each lecture with my mind on vast projects." (54)

Hofmann, who suggested that "lecturing well on chemistry is as great an art as lecturing well on any other subject" (55), has much to say about Dumas' style and manner of presentation:

> "And that Dumas is a master in this art is unequivocally proved by the lively and lasting recollections which his lectures, addressed to such a diversity of audiences, have left in the minds of his hearers. Even those who have but had the good fortune of attending a single one of his lectures will ever remember the clearness and precision of his reasoning and the attractive grace of his delivery. ... [His] early efforts at classification, the value of which is but now fully appreciated, have left their stamp upon the present mode of teaching. ... the scientific physiognomy of these lectures presented moreover an artistic feature. Each lesson had its carefully matured plan, its introduction, and its conclusion. Dumas made but few experiments, but they were well chosen and executed with faultless elegance. They formed, so to speak, part of the reasoning of the lecturer. Everything foreign to his argument was carefully avoided; side paths, however seductive, would never induce him to leave the main road leading to his goal. ... it is as if he had always before his mind those golden words of Schiller: That which is wisely suppressed shows me the master of style. ... Dumas [skillfully] enlisted the sympathy and secured the mental cooperation of the students. From the very outset the height to be reached was seen looming in the distance, and when the difficulties in the way had been conquered and the point of survey attained, the student left the lecture-room in a measure convinced that it was by his own efforts that the ascent had been accomplished." (56)

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54. Dupuy, op.cit.(9-13), p.448. Pasteur was an agrégé when the Ecole Normale was moved from the ancient Collège du Plessis to new quarters in the rue d'Ulm.

55. Hofmann, op.cit.(1-6), xxxiii. This was in response to the allegation that "lecturing on chemistry is a comparatively easy task".

56. Ibid.

In the spring of 1836 Dumas was teaching courses in the Faculty of Sciences, Collège de France, two at the Ecole Centrale and was répétiteur at the Ecole Polytechnique. It is hardly surprising that he decided that he could no longer substitute for Thenard at the Collège de France when Thenard relinquished the first of his many teaching positions, the Chair of Chemistry in the Ecole Polytechnique, and Dumas succeeded him on 23 December 1836. Conditions had improved considerably at the Ecole Centrale since the near disaster of 1832, so that he was settling nicely into three established teaching positions when Deyeux fell ill in April 1837 and died a fortnight later (57). On 25 May, at Orfila's request, a Commission was formed "to give a report on the Chair of Pharmacy left vacant by the death of M. Deyeux" (58). After giving their report on 6 June, Pelletan, in the name of the Commission, proposed that it be renamed the Chair of Organic Chemistry and Pharmacy, a proposal that the Faculty adopted (59). Competition for the chair, open to French citizens (even those naturalised) who were at least 25 years of age and held a doctorate in medicine or surgery, was announced later that year (60). Five candidates registered: Baudrimont, Apollinaire Bouchardat (1806-

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57. Arch. Nat., Faculté de Médecine (Registres non-cotés), Procès Verbaux de l'Assemblée des Professeurs, Vol. 1835-38, pp. 178, 182.

58. Ibid., p.184. Members of the Commission were Achille Richard (1794-1852), Pierre Nicholas Gerdy (1797-1856), Pierre Pelletan fils (1782-1845), Duméril and Nicolas Philibert Adelon (1782-1862).

59. Ibid., p.188. It was made official by an arrêté of the Council of Public Instruction, 14 July. Ibid., p.205.

60. On 30 September the Minister of Public Instruction, Narcisse Achille de Salvandy (1795-1856) gave orders for the competition to begin on 1 February 1838, with announcements to be made by printed notices and in journals, but according to an attached note the letter had still not been sent to the Inspector General, Rouselle, who was responsible for the administration of the Academy of Paris, on 11 October. Arch. Nat., AJ^{16} 22. Salvandy was Minister 1837-39 and 1845-48.

1886), Bussy, Cottereau and Dumas (61). On 18 January 1838, the eight examiners, drawn from among Faculty members were named (62), and soon afterward the four external examiners, all members of the Academy of Medicine (63).

The competition did begin 1 February and continued until 26 March. A total of 27 meetings were involved. These included five kinds of tests:

1. A discussion, in the presence of the judges, of relevant articles and books written by the candidate, the services he had performed, etc.

2. An essay, written by all candidates during the same time period, on the same topic, drawn at random, in their presence, from a list known only to the examiners who had compiled it. The topic drawn was: "Salt forming organic bases considered from a chemical and pharmaceutical point of view." (64)

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61. Loc.cit.(9-58), p.226. The list, given in the Faculty meeting of 4 January, 1838, was forwarded to Salvandy for approval. Hofmann, op.cit. (1-6), xxxii, said that Dumas "was induced, chiefly by Orfila, to offer himself as a candidate for the chair". Cottereau withdrew before the competition began.

62. Corlieu, op.cit.(9-22), p.169. There were five by right: The professors of chemistry (Orfila), physics (Pelletan), natural history (Richard), general pathology and therapeutics (François Joseph Victor Broussais (1772-1838) and legal medicine (Adelon). There was no professor of medical and therapeutic substances at the time; he would have been the sixth by right. In his place Jean Bouillaud (1794-1881) was chosen by ballot from among the holders of the other chairs. A seventh examiner by right was elected as usual from among three professors: medical internship, pathological internship and pathological anatomy. The lot fell on the first of these, Auguste François Chomel (1788-1858). The final examiner by right was elected from among another three professors: medical externship, pathological externship and surgery. The lot fell on the last of these, Cloquet. Two substitutes were also elected at large, Jean Nicolas Marjolin (1780-1850) and Fouquier. The substitutes were bound to attend all of the meetings, but only had active voice if they replaced an examiner. Marjolin replaced Chomel.

63. Robiquet, Caventou, Antoine François Boutron-Charlard (1796-1878) and Mérat. DeLens was the substitute.

64. Loc.cit.(9-62), p.281. There is no indication that any restrictions existed with regard to consulting books or journals during the various tests.

3. A lecture with 24 hours preparation on a topic related to the chair. Dumas' topic was: "The Chemistry and Pharmacy of Sugars." (65)

4. A lecture with only three hours notice. Dumas' topic was: "The Chemistry and Pharmacy of Milk." (66)

5. The final test was the defense of a thesis. The usual pattern was a presentation of some general ideas about the chair, an outline of what the candidate planned to teach and his method of teaching it. The topics were drawn by lot, probably on or about 23 February and the theses were composed, printed and submitted within 10 days (67). During this brief time, Dumas prepared a 110 page dissertation on "The Action of Heat on Organic Substances" (68). While he was eminently qualified to prepare a good dissertation on

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65. Ibid. Each candidate spoke on a different topic drawn at random. The other titles, all considered from a chemical and pharmaceutical viewpoint: Bouchardat, Essential Oils; Bussy, Fats; Baudrimont, Alcohol and Alcoholic Fermentation.

66. Bussy lectured on the same topic on the same day. On another day Bouchardat and Baudrimont lectured independently on: "The Chemistry and Pharmacy of Gelatine and Albumine".

67. The theses, bound together as Concours, mars 1838, are in the library of the Faculty of Medicine (now Université René Descartes), catalogue number 90974. The title page of Baudrimont's thesis bears the statement: "Par un règlement de la Faculté de Médecine de Paris, les thèses sont tirées au sort, composées et remises imprimées en dix jours." According to Corlieu, op.cit.(9-21), p.210, the printed dissertation was to be sent to the examiners 20 days before the beginning of the competition, but more direct evidence to be presented later suggests that it was 20 days before the defense of the thesis, which was on 25 March.

68. Baudrimont's thesis was: "What is the Present State of Organic Chemistry, and what help has it received from Microscopic Research?" (123 pages). Baudrimont was forced to speak about Dumas' accomplishments, but instead of playing them down, he made the unfortunate error of attacking them. Bouchardat's 23 pages on "Blood and the Various Changes it Undergoes during Illness" seems to have been a token effort. Bussy added the following note to the title page of his 87 page thesis, "The Various Changes in Urine during Illness and Kidney Stones": "My position as candidate forces me to transcribe exactly the question which has fallen to me, such as I have received it from the hands of the president, bearing his signature and that of the secretary of the examining body; but I think I must remark that according to the decision of the royal Council, the competition was opened for a Chair of Pharmacy and Organic Chemistry."

any of the topics chosen by the examining body, undoubtedly he was best prepared for the one he drew, not only because he had done research on the topic as early as 1832 (69) but also because he was able to present a considerable amount of original material. He had been assigned as a member of two commissions to report on research involving pyrogenous reactions: A memoir by Edmond Frémy (1814-1894) entitled, "Some modifications made by the Action of Heat on Organic Acids" (70) and that of Pelletier and Walter on the products obtained by heating resin (71). Furthermore he had been collaborating with Liebig on research on acids, which had led to the acrimonious citric acid controversy with Pelouze (72). In a letter to Liebig, written sometime between the arrival in Paris of Liebig's well-known article on organic acids and its publication in the Annales de Chimie et de Physique, Dumas observed:

> "Forced to interrupt my experiments [on acids], I received a letter from you announcing that you were going to publish your memoir on acids with a note indicating that you were dissociating yourself from me. That letter of 19 February was confirmed by another of 10 March. On 25 March I defended a thesis in the Faculty in which I thought from that time that I had the right

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69. He correctly analysed pyroacetic spirit (acetone), Ann. Chim. Phys., 49 (1832), 208-10, and pyrocitric acid, Ibid., 52 (1833), 295-303. The theory of substitution took him in other directions from this time, but he maintained an interest in the topic which had been largely rationalised by Pelouze who had originated and refined the process of constant temperature distillations, Ibid., 54 (1833), 337-65. Dumas emphasised the importance of this discovery in his eulogy of Pelouze. Eloges, Vol. 1, pp. 147-49.

70. The memoir was read 4 September 1837 and an extract by Frémy appeared in the minutes of the meeting, Comptes Rendus, 5 (1837), 389-91. Pelouze and Robiquet were the other members of the Commission, but Dumas read the report.

71. See p. 186. He did not read the report to the Academy until after the competition.

72. Holmes, op.cit.(6-119), pp. 338-44, in discussing "The Problem of Acidity" from Liebig's standpoint gave a generally unbiased account of the events involved in the controversy. Ibid., p.342. A more detailed study is beyond the scope of the present work.

> to make use of some observations that I had made; if we had published something together, these could have been a part of our memoir. But there was no question of it in the note together.
>
> This thesis was not sent to you because it was not sent to anyone. A volume written and printed in 8 days could not deserve the attention of chemists." (73)

Despite these remarks, the thesis was outstanding and its defense brilliant. One of his students, Félix Leblanc, wrote in 1884:

> "His thesis, instead of being a simple dissertation, contained an exposition of important original work. The immense audience in the large amphitheatre of the Faculty of Medicine broke into applause at the reading of his thesis, on hearing his lectures, whose subjects had been imposed by the examiners." (74)

At the end of the long competition, the examiners placed Dumas first in each of the five tests. On 26 March 1838, he became the titular of the Chair of Organic Chemistry and Pharmacy at a salary of over 9000 francs per year (75). On 6 June he bought a complete set (1823-1837) of the journal Archives de Médecine (76). Later that year he retired from the Chair of Chemistry at the

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73. An undated, unpublished copy of the letter, Arch. Acad. Sci., Dossier Liebig (Fonds Dumas), gives some indication of the deep hurt experienced by Dumas at the unwarranted action taken by Liebig. Much of it was deleted, but Liebig would never have seen these portions and probably was never aware of Dumas' feelings. At the end of the letter he added "Permit me to recommend to your kindness M. Philippe Walter, a young chemist who was very strongly recommended to me by M. de Humboldt and who has fully justified [his recommendation] for several years."

74. Bull. Soc. Chim., 1884, 551.

75. In 1836 a fixed sum of 3000 francs was supplemented by a normally budgeted 4000 francs available from student fees for examinations and theses, though it depended on their number. This supplement was usually more than 4000, not less. In addition 1800 francs were given as droits de présence, and 300 francs for jetons de présence aux assemblées. In 1844 the former were raised to 3000 francs and the jetons were not mentioned. Thus in 1844 the minimum salary was 10,000 francs and continued to be that until at least 1849. Arch. Nat., AJ^{16}24.

76. The cost was 300 francs. It was listed in his accounts with Béchet Jeune (1835-1845). Arch. Acad. Sci., Fonds Dumas, Carton 1.

Ecole Polytechnique that he had had for only two years and was replaced by Pelouze (77).

Again Dumas was in a position to create a new kind of course. At the Athénée he had integrated theoretical and applied chemistry in a course that he was able to adapt for his students at the Ecole Centrale, where he brought an entire curriculum of chemistry into existence, directed towards industrial chemistry. At the Collège de France he had introduced lectures in chemical philosophy as a significant part of his course (78). Now, at the Faculty of Medicine, he had the opportunity to teach organic chemistry while bringing out its application to both pharmacy and medicine, and this included returning to physiology from a chemical point of view, i.e., a primitive course in biochemistry. In retrospect, one sees in the Traité the unfolding of Dumas' career in chemistry. In the beginning he had taught and done research in mineral chemistry and its applications which formed the first four volumes of textbook. In 1835 he completed volume 5, concerned principally with the theoretical and descriptive aspects of organic chemistry, again the fruit of his own research and teaching. Though he had also been involved with its

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77. "Démission acceptée 2 8[bre] 1838." Arch. Ecole Polytechnique, Carton 1824 (1), Doss. "M. Dumas, répétiteur, 1824-1838". He was four months short of the 15 years of service required for receiving a pension by decree of 28 September 1824. It was the second position in which he had been replaced by Pelouze.

78. In the Ecole Polytechnique and Sorbonne Dumas was limited by the type of student and the spirit of the school. The more advanced and free character of the Collège de France gave him a much greater latitude. As he continued to lecture there from 1827, the importance given to chemical philosophy in the course increased. It is of no small interest to observe that Thenard, whom Dumas replaced, including a section on chemical philosophy in the final edition of his Traité de Chimie, 5 Vol., Paris, 1836, despite the fact that he had had very little penchant for publishing theory, and had not made it a part of the first five editions of his textbook.

industrial applications, which would be part of the remaining volumes, he had not yet come to grips with the medical and physiological applications of chemistry. With his new appointment he entered on a new phase of teaching and research in preparation for the completion of his Traité.

While Dumas' research had been almost exclusively in chemistry, his interest in physiology was far from dead. He had continued to edit the Annales des Sciences Naturelles and after completing research on a physiological problem linked to maternity (79), his research began to appear frequently in the Journal de Chimie médicale, de Pharmacie et de Toxicologie (80). In 1831-32 he had been involved in studies for the medical degree. Soon after his election to the Academy in 1832 he was appointed to the Gelatin Commission (81) and as a member of several other commissions, he read reports from time to time on memoirs of physiological interest, most of them relating to nutrition (82). When the Ecole Centrale was founded in 1829 Dumas had

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79. "Sur la présence du pus dans les vaisseaux lymphatiques de l'utérus et dans les ganglions prélombaires à la suite des accouchements", PVAS, 9 (1828-31), p.389 (18 January 1830).

80. This journal was founded in 1825, but before 1830 only one note written by Dumas had been published in it. By 1835 he was listed on the editorial board which included Orfila, Pelletan, Pelouze, Richard and Lassaigne among others of no interest to the present work, twelve in all.

81. A good discussion of the work of this commission can be found in Holmes, F.L., Claude Bernard and Animal Chemistry, the Emergence of a Scientist, Cambridge, Mass. (Harvard Univ. Press), 1974. His implication (Ibid., p.16) that Dumas did nothing in physiology for 14 years (1822-36) is incorrect.

82. Prior to 1836 he gave the following reports on such memoirs: By Payen and Persoz, "De la diastase et de la dextrine", PVAS, 10 (1832-35), 287-91 (17 June 1833) (with Robiquet); Payen, "Théorie des engrais", Ibid., 409-12 (2 December 1833) (with Becquerel and René Joachim Henri Dutrochet (1776-1847); Louis René LeCanu (1800-1871), "Observations chimiques sur les corps gras", Ibid., 488-89 (7 April 1834) (with Chevreul); Couerbe, "Le Cerveau considéré sous le point de vue chimique et physiologique", Ibid., 566-68 (11 August 1834) (with Thenard and Chevreul); Payen, "Les Racines des plantes", Ibid., 644-45 (5 January 1835) (with Pierre Jean François Turpin (1775-1840); Roch Théogène Guérin-Varry, "L'Action de la diastase sur l'amidon de pommes de terre et les propriétés du sucre d'amidon", Comptes Rendus, 1 (1835), 81. He was on other commissions of this type without being asked to report.

tried to introduce an agricultural section, but finally agreed that it was too much to take on at that time. He maintained his interest in applying scientific principles to agriculture. Thus, when Boussingault, who had returned from South America to France in 1832 mentioned his discovery that guano was a good fertiliser and that it was high in nitrogen content, Dumas took notice. In 1833 Boussingault acquired a farm at Bechelbronn in Alsace and began experiments on a massive scale to study the nitrogen content of plants. There can be little doubt that Dumas was aware of this research and of its importance when the results began to appear. Though he could not participate in the labour involved, Dumas was able to give advice on the use of his analytical method for the quantitative determination of nitrogen in the crops, a central point in the experimental work. When it was observed that clover absorbed nitrogen from the air, they began to think in terms of discovering a master plan governing all living things. As Dumas observed in his lectures at the Collège de France in the summer of 1836:

> "If nothing stands in the way, I will devote a part of my lectures next year to the simplest, most general explanation of what takes place in living things while they are alive and after their death, drawing support from the conclusions of physiology and organic chemistry." (83)

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83. Leçons, p.426. Dumas referred to this passage in one of the documents in the third edition of Statique chimique (1844), p. 116-17, to show that they had been working since at least 1836, observing that "the principal rules drawn up in [the essay] were beginning to form in their minds". Ibid., 113. The French edition of Liebig's Die organische Chemie in ihre Anwendung auf Agricultur und Physiologie, Brunswick, 1840 (Chimie organique appliquée à la Physiologie végétale et l'Agriculture suivie d'un essai de Toxicologie, transl., C. Gerhardt, Paris, 1841), had appeared at about the same time as the Statique chimique, and there were priority problems. Dumas' statement was not intended as a proof, but as a further indication of an approximate starting date. There were enough documents available to provide the necessary evidence that they had arrived at their conclusions independently.

Boussingault had become a Doctor of Sciences (84), but his first position had been unsatisfactory because of the nature of his research at Bechelbronn (85). When Dumas' teaching schedule became overtaxed in 1836-37 because of Thenard's illness, he invited Boussingault to substitute for him in the Faculty of Sciences (86), thus strengthening their ties. By 1838 Boussingault was able to show that some plants absorb nitrogen from the air (e.g. clover), others absorb it from the soil, not the air (e.g., wheat) (87). It was at this time that Dumas began teaching at the Faculty of Medicine.

Notes taken by Félix Leblanc give an insight into what Dumas taught during his first year (88). Long before, Dumas had come to the realisation

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84. His theses, describing research done in South America, were defended on 5 June 1834.

85. Named to the newly constituted Faculty of Sciences in Lyon on 21 July 1834, he gave only 13 lectures (11 June to the end of July 1835) before he was replaced, finally by Bineau. He was unwilling to accept more than part-time teaching, since the experiments on his farm required close attention for much of the year. At the time he also raised the problem of finances: "I would very much like to know why an unhappy titular professor of the Faculty, because he is in the provinces, should be condemned to receive a quarter of the salary of an assistant professor in Paris." LaCroix, A., Notice historique sur Jean Baptiste Boussingault, Paris (Gauthier-Villars), 1926, p.35.

86. As an assistant professor Dumas was obliged to substitute for Thenard, but he was allowed to request a substitute himself. Holmes, op.cit. (9-81), p.17, citing LaCroix, loc.cit.(9-85), indicated that Boussingault substituted for Dumas at the Ecole Polytechnique, but LaCroix said only that Dumas "in his turn had immediately felt the need to ask for a substitute for the schoolyear 1836-37, and it was Boussingault". It seems very unlikely that he would have obtained an untried substitute in his first year as full professor at the Ecole Polytechnique. It is more probable that Boussingault taught at the Faculty of Sciences for a semester.

87. Boussingault, J.B., "Recherches chimiques sur la végétation, entreprises dans le but d'examiner si les plantes prennent de l'azote à l'atmosphere", Comptes Rendus, 6 (1838), 102-12 and 7 (1838), 889-891.

88. Arch. Acad. Sci., Fonds Dumas, Carton 10, "Cours de Chimie et de Pharmacie, 1838. Notes. F. Leblanc." Holmes, op.cit.(9-81), p.468, incorrectly ascribed these to Dumas.

that physiology could not be studied properly until the chemical constitution of compounds was known. Despite the great advances made in organic chemistry, classification was still primitive, and very few types of reactions were known. There was no way of studying reactions that went on in living beings in any detail. What was needed in his course was a study of the substances, particularly compounds, that were known to exist in these beings, and others that could be derived from them. Not surprisingly, he began with nitrogen containing compounds, first ammonia, amides and their salts, then the alkaloids. This led into a study of urine and urea, kidney stones, urinalysis and some conclusions about ones' health that could be derived from chemical analyses. The relationship of these considerations drew him into lectures on blood, which in turn took him into a discussion of respiration, where he did go into some theories regarding mechanism instead of limiting himself to simple observations and conclusions. After enlightening his students on the composition of bile, he went into some theories (including his own) about digestion (89). Foods occupied several days: A full lecture on gelatine because of its topical importance (this gave him an opportunity to talk about the composition of skin, bones and muscle); milk and eggs; starch, sugars; wine and beer (alcoholic fermentation). He then went into a study of alcohols and ethers, as a preparation for a long discussion of other foods, fats and oils. Finally, several lectures were built around organic acids. Although he did present some theories that other scientists had offered, he made it clear that the evidence was thin, that the only real advances in the chemistry of living things would be made at this time in the isolation and identification of compounds found in living things. The existence of a link between

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89. Leblanc wrote: "Dumas believes that gastric juice contains some particular principle capable of producing remarkable transformations; this is possible when one considers the action of diastase." Loc.cit.(9-88), Lecture 11.

physiology and chemistry was generally accepted; but it was still not possible to specify it by relating a physiological activity to one or more chemical reactions. On the other hand Dumas had already shown what a powerful tool his theories had been in the development of organic chemistry, even when they were provisional. Aware that Boussingault had "introduced the use of the balance in the study of questions of general physiology" (90), Dumas saw the possibility of formulating a theory based on observed data. Though the experimental work necessary was far from complete Dumas was constrained to present their ideas in his lectures to the medical students during 1840-41 and to summarise them in the final lecture on 20 August 1841. The lecture was published the same day in the Journal des Débats, a daily newspaper. As Dumas wrote later:

> "Convinced that it was necessary to base our rules on careful experiments before publishing them, we thought that it would be proper to issue them slowly to the extent that they were justified by the facts.
> To our great regret, we could not continue in this pathway. An early publication, at least in certain matters, of our personal views seemed completely necessary to us in 1841, exposed as we were to losing all our rights.
> That necessity, which we regretted very much, will serve as an excuse for having advanced some of our propositions before we had performed the experiments necessary to verify them." (91)

It was also published in the Annales des Sciences Naturelles, and in pamphlet form, which by the third edition had become so heavily documented that this section was twice as long as the essay itself (92). The necessity for the hasty publication and rapid documentation (93) was undoubtedly a letter from

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90. Comptes Rendus, 8 (1839), 54.

91. Statique chimique, p.113. Holmes, op.cit.(9-81), p.28, offered this as a possible reason without proof.

92. Consult the bibliography for further information on the various editions of the pamphlet.

93. The documentation appeared in several journals, including Ann. Chim. Phys., 4 (January 1842), 115-26, and in the second edition of the pamphlet, which was also published in January.

Liebig on "albumin, fibrin, the colourless substance from the blood corpuscles and casein" (94). A long, detailed, balanced discussion of the chemical approach to physiology exhibited by Dumas and Boussingault, Liebig and many other French and German chemists from 1836 to 1844, has been given by Holmes (95) who summed up Dumas' work:

> "The physiological aspects of Dumas' system became very influential during the years following its appearance. One reason for its popularity was that physiologists had previously been unable to explain, or even give a persuasive coherent description of, the incessant exchanges of matter which form so prominent a feature of animal life. Dumas not only portrayed the processes of nutrition and respiration as an integral series of events, but gave them a clear significance for the life of the animal and for its part in processes on an even grander scale. The outlines of the picture he sketched have remained basic to our understanding of the meaning of the chemical processes of living organisms. (96)

And what was Dumas' "system"? Dumas himself described it:

> "Thus the mysterious circle of organic life on the surface of the earth is closed. The air contains or engenders oxidised products, carbonic acid, water, nitric acid, ammonium oxide. Plants, true reducing agents, take hold of their radicals, carbon, hydrogen, nitrogen, ammonium. With these radicals, they fashion all of the organic or organisable substances that they give to animals. In their turn, the latter, true oxidising agents reproduce with their assistance carbonic acid, water, ammonium oxide and nitric acid which return to the air to allow the same phenomena to happen again and forever.
>
> And to this picture, already striking by its simplicity is added the undisputed role of sunlight, which alone has the power to set in motion this immense apparatus." (97)

Again he had provided the general framework within which the details could be worked out. While the real value lay in this "coherent description",

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94. This letter (Comptes Rendus, 12 (1841), 539-41), not mentioned by Holmes, gave some information about these substances that Liebig published later. Annalen, 39 (August 1841), 129-50. Holmes discussed the latter, but Dumas had not seen it before his 20 August lecture, while he had seen the former.

95. Holmes, op.cit.(9-81), Chapter 1 to 5 and passim.

96. Ibid., p.25.

97. Statique chimique, p.7.

there was another advantage, the possibility of designing physiological pathways that could be tested experimentally. By deciding that all reactions in plants involved reduction and all reactions in animals oxidation, Dumas was also obliged to limit synthesis to plants so that digestion in animals was either a physical reaction (decreasing particle size, followed by absorption) or an oxidation reaction (breakdown to smaller molecules, then absorption). Dumas chose the former (98). While the interaction of personalities complicated the first test of his hypothesis immensely, a problem was clearly delineated so that a definite answer could be obtained: Were fats simply absorbed, or were they produced in animals from simpler substances? The answer, slow in coming, was provided by Dumas and Milne Edwards when they proved beyond doubt that beeswax was formed from honey, a simple sugar (99). It was Dumas who had set the problem in stark terms:

> "M. Liebig thinks that herbivorous animals make fat with sugar or starch, whereas MM. Dumas and Boussingault assert as a general rule that animals, of whatever kind, do not make fat or any other organic alimentary material, but that they take all of their nutriments, sugar, starch, fat or nitrogenous substances, from plants." (100)

It was his next statement, however, that left him no way out:

> "If M. Liebig's assertion were well-founded, the general formula that MM. Dumas and Boussingault have given as a summary of the chemical statics of the two kingdoms would be false." (101)

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98. There were two reasons for his choice: It was far less complex and it kept the chemical reactions involved in the oxidation of food in the blood. Dumas accepted the opinion of Lavoisier and Laplace that animal heat was entirely due to oxidation in the blood resulting from absorption of oxygen during respiration, and used Despretz'measurements as evidence. Ibid., pp. 102-04.

99. "Note sur la production de la cire des abeilles", Comptes Rendus, 17 (1843), 531; 537-45.

100. Editorial footnote in an article by Liebig, Ann. Chim. Phys., 4 (1842), 186-211 (208) (~~authors'~~ Dumas' italics).

101. Ibid.

This statement was unfortunate, because it was not true. As a net description of the interlocked carbon dioxide and nitrogen cycles it was quite correct, so long as it did not descend to details. It did lead Dumas to more exacting research on protein that showed small but definite differences between the composition of fibrin on the one hand and casein or albumin (both with the same composition) on the other (102). Legumin too he found to differ in properties and composition. He suspected that albumin and casein combined with other highly nitrogenous substances to form fibrin or legumin.

While Dumas' studies provided some information about compounds existing in living beings, little new was learned about physiological pathways within the organism. But Dumas had generally circumscribed the limits imposed by nature on the overall chemical reactions involved. As time went on he began to appreciate the complexity of the internal reactions to some extent. Indeed, he began to see the importance of other approaches, the use of ferments for example, which he discussed at length in his textbook (103), and the _in vivo_ methods to which Claude Bernard turned. Ultimately, however, physiological problems had to be examined from both a chemical and a physiological viewpoint, with the emphasis dependent upon the particular problem under study.

Dumas continued teaching in the Faculty of Medicine until he was limited by the decree of 10 March 1852 to one teaching position. Invited to present three candidates, one of whom would replace him, he listed Charles Adolphe

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102. Dumas and Cahours, "Sur les matières azotées neutres de l'organisation, _Ann. Chim. Phys._, _6_ (December 1842), 385-448.

103. _Traité_, Vol. 6, pp. 302-84. In a ferment was an active compound which is now called an enzyme. Dumas considered fermentation in a general way including a statement of the conditions necessary: a temperature of 20-25°, water, air, a nitrogenous organic ferment and a substance to be fermented. He also discussed some specific examples, among them alcoholic, saccharic, lactic, acetic, benzoic, pectic, gallic and digestive fermentation and fermentation of fats.

Wurtz (1817-1884), Pierre Antoine Favre (1813-1880) (both his students) and LeCanu. Wurtz was chosen on 2 February 1853. When Orfila died a month later both his chair and that of Wurtz were suppressed. Two new chairs were created on 10 December 1853, one in pharmacy, given to Soubeiran and the other in organic chemistry and mineral chemistry given to Wurtz, who was succeeded by Armand Gautier in 1884.

Dumas was vice-president of the Academy of Sciences in 1842, when a place fell vacant in the Academy of Medicine. In the meeting of the latter on 15 November 1842, presided over by Fouquier, a letter from Dumas was read in which he submitted his candidacy for the place in the physics and chemistry section. He was placed on the first line and the others, Bouchardat, Boudet, Gaultier de Claubry, Lassaigne and Louis Mialhe were listed after him alphabetically. Of 115 voting, he received 85 votes in the meeting of 31 January 1843 and his nomination was approved by royal decree, sent by the Minister of Public Instruction on 7 February (104).

Soon after Dumas acquired a new sensitivity to the difficult conditions in which his colleagues had been obliged to teach for so long in the venerable but quite inadequate quarters of the Sorbonne (105). On 19 October 1837, an opportunity to take a step forward presented itself when Salvandy, the Minister of Public Instruction, addressed a letter to the Faculty, in which he

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104. Bulletin de l'Académie de Médecine, 8 (1842-43), 252, 649, 661.

105. The ancient buildings of the Sorbonne were nationalised by the Law of 18 August 1792 and given to the University by the Decree of 11 December 1808. "By the terms of the first article of this decree, all the buildings used for public instruction which had not been transferred or given over finally to another public service by a special decree were given to the University." Gréard, op.cit.(9-8), p.17, Note 1. Ordinances of 3 January and 27 February 1821 gave the use of the buildings to the Ministry of Public Instruction, who made it the home of the Faculties of Letters and Sciences and the headquarters for the Académie (educational district) of Paris.

"manifested the desire that the Faculty of Sciences of Paris indicate the improvements that were judged necessary for science teaching" (106). The Minister was especially interested in improving the provincial Faculties particularly those in science. Dumas was invited to prepare the report required. Making it clear that the Minister's desires were in accord with the long-standing wishes of the Faculty, he pinpointed the subjects that needed immediate attention, then the order in which they should be dealt with, finally, the way to do so. A summary of his well-organised discussion of the problems and the solutions offered will shed some light on another aspect of his life, an interest in the whole French educational system.

The Provincial Faculties of Sciences.

The severest problem plaguing provincial Faculties was the need for more teaching positions. If Dumas could point to the 14 in the Paris Faculty of Sciences (107) and insist that these were not enough, he had even more reason to decry the far greater deficiencies that existed in those in the provinces (Table 9-2). The three at Grenoble were the absolute minimum

106. From the report, presented by Dumas to a Faculty Meeting 15 November 1837, preparatory to forwarding it to the Minister. Gréard quoted it in full. Ibid., pp. 236-55.

107. "Consider that the Faculty of Paris, which most certainly does not yet have all the men and materials necessary, nevertheless has 14 chairs with separate functions and the same number of professors ..." Ibid., p.237. The term chair must be taken to mean here teaching positions. There were 10 professors and 5 assistant professors (A) at this time: Differential and integral calculus, La Croix, advanced algebra, Francoeur; calculus of probabilities, Guglielmo B.I.C. Libri-Carruci-Dalla Sommaja (1803-1869); astronomy, Biot; rational mechanics, Poisson; physics, Dulong, Pouillet (A); Chemistry, Thenard, Dumas (A); anatomy, comparative physiology and zoology, Geoffroy Saint Hilaire, Ducrotay de Blainville (A); botany, plant physiology, Mirbel, Auguste Saint Hilaire (A); mineralogy and geology, Beudant, C. Prévost (A). The five assistant professors were responsible for a particular section of the course. It is difficult to say which one Dumas did not include.

TABLE 9-2. Chairs in the Provincial Faculties of Sciences in 1837 (108).

	Lyon	Montpellier	Caen	Toulouse	Strasbourg	Dijon	Grenoble
1. Mathematics	1	1	1	1	1	1	1
2. Astronomy and Rational Mechanics	1	1	0	1	1	0	0
3. Physics	1	1	1	1	1	1	1
4. Chemistry	1	1	1	1	1	1	1
5. Anatomy, Comparative Physiology and Zoology	1	1	0	0	0	0	0
6. Plant Physiology and Botany	1	1	0	0	0	0	0
7. Mineralogy and Geology	1	1	1	1	1	1	1

required for the baccalaureate examinations. This meant that one professor taught all of the natural sciences; one taught astronomy and chemistry as well as physics; and the third all the mathematics and the rational mechanics. This was the worst of a bad situation. In most of the Faculties, to attain a standard equivalent to that offered in Paris in the natural sciences, for example, one man would have found it necessary to teach what six were teaching in Paris. Certainly the problem was most acute in the natural sciences because of their rapid development around the beginning of the 19th century. To make matters worse, the quality of a professor willing to accept a position in the provinces was not always the highest, and he was often required to do his own preparations for demonstrations. The laboratory at his disposal for this, and for whatever research he might have been interested in undertaking, was small and poorly furnished, with no funds for chemicals, apparatus or specimens. Thus teaching was often superficial. There was no time or money

108. New Faculties were created at Bordeaux, Besançon and Rennes, and reinstituted at Marseilles soon afterward.

and little incentive to do research. Thus it was not surprising that these Faculties were not the thriving centres of national attention that would attract students to share in the excitement provided by professors who were penetrating the boundaries of knowledge.

As a first step towards a solution, Dumas suggested that all Faculties should be brought up to the level of Lyon, which had just been reconstituted in 1833, and Montpellier. This should be done by creating the necessary chairs immediately, but not filling them until qualified personnel became available, men who could pass stiff examinations and submit original theses that could serve as good evidence of their scientific potential. A second area of concern was the need to attract candidates for teaching positions. He saw no reason why the educational system should not be state-operated, but it was important that the professors be properly paid. The disproportion between the salary of the professors of the Faculty of Sciences and those teaching in the Faculties of Law and Medicine was shocking enough, but there was no comparison at all with the salaries of their counterparts in "neighbouring countries", who were being paid by students who attended the universities there (109). Dumas observed:

> "Young men who are well-endowed and aware of their ability will not enter a career with neither a present nor a future. ... youth of the Départements will have a pretty poor opinion of the usefulness of sciences which treat learned men, teaching in the most prominent chairs, so poorly. ... As long as this condition lasts, the generous, wise and patriotic project of decentralising talented personnel will be nothing but utopian." (110)

His solution was simple: "We believe that 5000 francs is the least salary that can be offered to professors of the Faculties of Sciences of the

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109. Dumas referred to the German and English Universities, where salaries were considerably higher in many instances.

110. Ibid., pp. 240-41.

Départements, and we ask that it be fixed at that rate." (111) The last of the problems mentioned, because it required an urgent solution, was the need for new Faculties. Dumas advised that this step be taken as soon as possible after the existing Faculties had been given the material means for accomplishing their purpose.

The Paris Faculty of Sciences.

Using the material needs of the other Faculties as a springboard, Dumas launched into a long discussion of problems existing in the Paris Faculty. He began by defining its role:

> "Clearly its purpose is to prepare young men to be examined for the licence in sciences, the agrégation, and the doctorate in sciences by providing courses open to all without distinction. Beyond this, it exists to promote a knowledge of the exact sciences among the general public." (112)

While other professors required only lecture and examination rooms and a library, Dumas pointed out that professors of the sciences needed additional rooms and materials. The facilities about which he expressed particular concern included: a library; science materials; lecture, preparatory and storage rooms; laboratories; a botanical garden; and examination rooms.

1. The Library. Dumas pointed out that the library of the Faculties (113) was far from the amphitheatre where the science lectures were given, controlled by the Faculty of Letters, and closed in the evenings (114). Furthermore

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111. Ibid., p.240. It may have been Boussingault's complaint (see note 85) that touched off the desire expressed by Salvandy.

112. Ibid., pp. 241-42.

113. The Sainte-Geneviève Library, still in use.

114. "When one sees to what seductions of all kinds the young men who attend the schools of Paris are exposed, one cannot help regretting most strongly that nothing else has been done before now to prepare these young men to use their evenings well." Ibid., p.243.

its collection of science books was inadequate. Because of these difficulties, the library was not used by science students. He suggested that the Faculty of Sciences should establish its own library, under its own direction, in the centre of the study area, with its own librarian, open in the evening as well as during the day, for the use of those in the science courses. If the above was not possible immediately, he called for the modification of the existing library to provide a special room for the sciences only, under the direction of the Faculty of Sciences to be open at times convenient for the students and that a budget, administered by the administration of the Faculty of Sciences, be set up for the purchase of scientific works. This library was to be a reading room for students, not a reference room for professors. There they would find the most important scientific journals of Europe and America and the books necessary for their courses (115). The Faculty supposed that a capital outlay of 30,000 francs and an annual expenditure of 3000 francs would be sufficient.

2. Science Materials. Dumas indicated that the material needs for courses (specimens in the natural sciences, chemicals and equipment in the physical sciences) were far from being met by the incomplete collections then existing at the Faculty, which had to be supplemented from time to time by loans or donations from the advanced schools (116). He made it clear that these materials were not simply adjuncts to teaching but an essential correlative. Collections must be selective, vivid and well organised to complement the

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115. He noted that enough copies of each book should be available to meet the demand, and that permission to remove books from the library should be given to no one, not even professors.

116. There were those who felt that students ought, for example, to be content to study the specimens in the excellent Muséum collection. They held that there was no need for special collections at the Faculty of Sciences as well. Ibid., p.245.

"limited clear and concise teaching" (117) expected from the professors in the Faculty; supplies of chemicals for demonstrations must be increased to the level of need, and there should be samples on display, of which there are none; equipment must be purchased and maintained for physics and chemistry courses.

3. Lecture, Preparatory and Storage Rooms. He noted that storage areas were cramped and too far from the lecture amphitheatres, often resulting in the perilous transportation of sensitive and costly apparatus; preparation rooms were non-existent with the result that it was necessary to prepare demonstration experiments in full view of the public, allowing no assurance that the experiments would be successful; even though the Faculty was housed in a large and conveniently placed building, the layout was so poor that it needed immediate attention (118). Storage was a problem that needed urgent attention. Zoological specimens could no longer be left in humid areas. All storage should be in a gallery central to the teaching area. Some of these materials should be displayed in cabinets where they can be examined in detail, easily, and at the students' leisure.

> "In foreign establishments ... all the preparations are made in a laboratory contiguous with the amphitheatre, giving communication with it at will. The apparatus arrives on trolleys ... The professor can then assure himself before the lecture that all has been well prepared and the auditors, undistracted by circumstances foreign to the thought of the professor, can given him their undivided attention." (119)

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117. Ibid.

118. Among the lecture amphitheatres, there were two which bordered on the street, along which an omnibus line had been established, with a depot for changing horses right beneath the window. The heavy traffic was very distracting during lectures, and dangerous after them.

119. Ibid., p.246. Dumas pointed out that the administration of the Ecole Polytechnique was about to request such an arrangement for teaching chemistry. Though he was professor of chemistry there also, he believed that it was even more necessary at the Sorbonne.

4. Laboratories. The chemistry laboratory (a preparation room) was totally insufficient, and there were none for physics or zoology. Agrégés, future professors of the secondary schools, and Faculties (120), were given no laboratory experience. "In this respect the education of the Ecole Normale is, and will always be insufficient". (121) Dumas saw a need to associate the agrégés with the various courses as assistants, preparing lectures, working in the laboratory, doing research under the direction of the professors. He saw a need for two in chemistry, two in physics, one in astronomy (122) and three in natural history (123). He believed that these agrégés should be given a sufficient salary, with an increment each year equal to one-half of the initial sum. They should also be given the same privileges as the students of the Ecole Polytechnique (124). These efforts would prepare them properly for teaching in the Faculties, and for research as well (125). There were other items, the need for a botanical garden, a course in mathematical physics and one in experimental mechanics. Dumas devoted two pages to the last of these, emphasising the clear superiority of the English in

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120. Agrégés in science were preparing for the doctorate. Those in medicine had already earned it.

121. Ibid., p.248.

122. He should do practical work at the Paris Observatory if an observatory could not be built at the Sorbonne.

123. Botany, zoology, mineralogy-geology. Provisionally these should be laboratory work at the Muséum.

124. They should be allowed to go to the special schools of Mines, Ponts et Chaussées, Metz, etc. and be given 1200 francs per year over and above their salaries as agrégés.

125. "Briefly, this would ensure the continuation of education in the experimental sciences, a recent innovation (in secondary schools), but one which must be considered very important, given the state of our civilisation." Ibid., p.249.

mechanical arts. He pointed out that the French chemical industry was unmatched in the world because of the excellent chemistry courses that had been offered for 40 years in Paris, especially those at the Sorbonne.

When the report was made to the rest of the staff, prior to its submission to the Minister, it was modified in some aspects. Thenard objected to the establishment of a separate library because of the expense, to which Dumas replied:

> "The whole report is destined to establish the necessity of giving to the Faculty a locale separate from that of the Faculties of Letters and Theology, as are those of the Faculties of Law and Medicine; furthermore, the organisation of the library is such presently that one can consider this library as an establishment belonging to the Faculty of Letters." (126)

But Thenard made it clear that he would only support something that the Minister could give, and probably would. Therefore the report officially requested a room in the library and either a librarian or assistant librarian from the Faculty of Sciences, the other being from the Faculty of Letters.

The passage concerning practical activities for _agrégés_ was suppressed following the observation by Dulong that it would be expensive and difficult to organise. A long discussion on the course in experimental mechanics led to an agreement to request a new chair in the Faculty, because lectures in this science were now on a par with others in the Faculty (127). It was among the recommendations introduced (128). However, those that involved

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126. _Ibid._, p.252.

127. Research on the topic had been done by such _savants_ as Jean Victor Poncelet (1788-1867) and Claude Louis Marie Henri Navier (1785-1836), both members of Mechanics section of the Academy of Sciences.

128. _Arch. Nat._, _AJ16 25_, Dr. 10. Royal Ordinance, 12 December 1837. "A Chair of Physical and Experimental Mechanics has been created in this Faculty of Sciences and M. Poncelet, member of the Academy of Sciences, has been named to fill that Chair." This was quoted in a letter from the Minister of Public Instruction to the Inspector General of the University, a copy of which had been sent to Thenard, the Dean of the Faculty.

construction, especially expansion, could not be undertaken until the University became sole owner of the buildings in 1852 (129). During that time, representatives of both the University and the city continued to consider Dumas' clear, thorough report.

By 1845 Dumas had become dean of the Faculty of Sciences and a University Councillor. In a more liberal political regime Salvandy, who had left his position as Minister of Public Instruction, was reappointed. In this capacity he again visited the Sorbonne and immediately created a Commission to draw up a report detailing the means for a prompt, effective solution of the problems that had blocked the progress of science teaching in the Faculty (130). Once more Dumas was called upon to present the report (131), but this time he was in a much stronger position personally (132) and gave the opinions of a much more broadly based Commission (133), whose sole concern was the housing of the Faculties in Paris. Dumas made many of the same points that

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129. The Sorbonne had been put at the disposition of the Minister of the Interior by a decree of 19 Vendémiaire An X (12 October 1801) on a temporary basis for lodging. Because of this, a dispute arose concerning ownership when the University gave the use of the buildings to the Faculty in 1821. In 1845 litigation concerning the land was settled in favour of the University, but the city did not cede the buildings to the University until 1852. At the same time the City associated itself with the improvements recognised as necessary in the Ordinance of 6 November 1839. Gréard, op.cit.(9-8), pp. 17-18.

130. Arrêté, 17 November 1845. Gréard, op.cit.(9-7), p.18.

131. This report, dated 18 September 1846, is quoted in full, Ibid., p. 256-69. It was originally read to the Commission by Dumas on 9 March 1846. Ibid., p.20.

132. He was Dean of the Faculty and a Councillor of the University.

133. The members of the Commission were Rouselle, Rector of the University; Dumas, Joseph Victor LeClerc (1789-1865) (Dean of the Faculty of Letters); the Abbé Jean Baptiste Glaire (1798-1879) (Dean of the Faculty of Theology); Pouillet (Physics); Libri (Mathematics); Milne-Edwards (Natural Sciences). Ibid., p.18.

he had put forward in 1837: There was still need for a special library in the Faculty of Sciences, though some of the earlier problems had been eased (134). The amphitheatres were inadequate for a variety of reasons: bad lighting, absence of ventilation, high degree of humidity, poor location with respect to storage areas (135). The storage areas themselves were quite impossible: physical instruments crowded together, chemicals and apparatus overflowing their tiny cubicle into various nooks and crannies, thus endangering the whole establishment, natural history specimens destroyed in their humid quarters. Astronomical and mechanical instruments were needed but not purchased because there was no place to store them. Display space was urgently needed.

Dumas returned to these themes throughout the report, but there were two other points which he strongly emphasised: the need for laboratory instruction, which he had barely mentioned in the earlier report, and the importance of establishing a degree in the practical sciences, which he presented for the first time. He assured the Minister that lectures and examinations were not enough to bring students to a knowledge of the sciences (136). Abroad, Universities had adopted laboratory exercises as a standard procedure by which students could verify what was taught in their courses; learn how to observe and experiment; develop techniques for handling chemicals and apparatus, physical instruments and dissection methods. At home, the schools of medicine, pharmacy, and industry were all using this approach. "For a

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134. A special library was set up in the Geneviève, and after the Faculty of Sciences had hammered away for six years on the point, this library was kept open in the evenings.

135. Some of these points were determined by Dumas' students while they were doing research on the composition of air in various places.

136. He described this approach as the Faculties "old method of teaching". Ibid., p.260.

long time the Ecole Polytechnique has shown that if a system of practical instruction is added to lecturing, progress is certain and much more rapid." (137) He insisted that the Faculty must bring itself up to date, that laboratories were absolutely essential in all of the sciences if the professors were to fulfill the task set before them:

> "The laboratories requested by the Faculty are intended for laboratory exercises not only in chemistry but in physics and mechanics as well, for practical studies in mineralogy and geology, and finally for dissection of natural history specimens. It wants students to be trained in all the operations of practical chemistry, in the use of all precision instruments such as the balance and goniometer, of all the instruments of research: the microscope, etc." (138)

These practical studies would be directed by agrégés. They were not intended just for the elite at the Ecole Polytechnique and Ecole Normale, but for unregistered (139) students as well. "Laboratories are to science what studios are to the fine arts" (140), and should be open to anyone who is interested. Dumas continued:

> "The Faculty of Sciences will become a school and will draw students destined to take their place among the masters, if it can open to them its precious resources, those laboratories where all the great current discoveries will be reproduced and refined, where some will come to prepare themselves, others perhaps to be perfected." (141)

For some time Dumas had stressed the need for practical courses, even

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137. Ibid., p.258.

138. Ibid., p.261. Later Dumas emphasised that the Faculty had been asking for laboratories for more than ten years. Ibid., p.262.

139. The term used is 'libre' which here means students who were 'free' in the sense that they were not bound to attend the lectures, who only registered for the examination or, if they were not seeking a degree, not at all.

140. Ibid., p.262.

141. Ibid. (Dumas' italics).

courses of the industrial type (142). It was thus only a step to a very original idea, which he discussed for some time with the other members of the Faculty, and to which they had given their whole-hearted agreement: A licence or doctorate in practical sciences. The University should consider itself "obliged to do for the practical sciences what it has done for medicine or law, what the state has done for the navy or army, for roads and bridges or mines." (143) Railways and factories using various kinds of engines should have properly certified consultants and examiners. Architects having familiarity with the best methods of heating and ventilation could design these into their buildings, saving fuel, cleaning up buildings, improving public health. He noted that careers existed in industry for students who wanted to study practical sciences, particularly industrial chemistry, so that production could be improved and retail prices reduced, thus increasing the profits of the manufacturer and the well-being of the general public. In other words, with industry constantly growing, he observed: "it is absolutely necessary to introduce into society men guaranteed in the practical sciences by the _licence_ or doctorate" (144).

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142. He had been lecturing at the _Ecole Centrale_ for 15 years. In 1837 he had urged the introduction of the course in experimental mechanics in the Faculty, and in 1840 he had said: "Science has modified industry; industry in its turn has modified the conditions of science. At the University of London, students learn how to handle the principal tools (_outils_) in a special workshop; in Turin, University students study hydraulics in an establishment where all the experiments on the movement of liquids are performed. ... It is the professor's duty to place in the hands of students in some form everything that can help them to clarify their studies." _Ibid._, p.58.

143. _Ibid._, p.263. _The licence_ would be comparable to the _licence_ in law, the doctorate to the doctorate in medicine. Apparently "industrial consultants" had begun to spring up under the title of engineer, even carrying 'certificates of competency', who did not merit this guarantee. In part this was due to the value attached to a diploma from the _Ecole Centrale_ by manufacturers at this time, even though the government had not yet recognised it.

144. _Ibid._, p.264.

Dumas concluded that there was no way to accomplish all of this satisfactorily without a new building in which all the means of instruction could be brought together: amphitheatres, laboratories, storage rooms and galleries, a special library, rooms for regular and frequent examinations (145). It should include residences for the dean, secretary and some security personnel. It was felt that four to five thousand square meters of floor space would be adequate. The members of the Faculty were opposed to moving away from the Sorbonne. They wanted a new building physically contiguous with the existing buildings of the Sorbonne so that there would be interaction among the students taking classes in all three Faculties, Sciences, Letters and Theology (146)

The report and three plans (147) which had been drawn up by the Architect of the Minister of Public Instruction were submitted to the latter, who then formed a Commission which included officials of the city government to

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145. He wanted places where the examinations could be given "by the agrégés, so that the daily progress can be determined and guaranteed ... where the properly registered students will come for counselling, and to test their ability before presenting themselves for the final Faculty examination." Ibid., p.265.

146. Dumas made an issue of this point. His report was adopted by the Commission, and submitted to the Academic Council, which "recognised that it was urgent to erect a separate and complete establishment for the use of the Faculty of Sciences, and to construct for this purpose a new building which, attached to the Sorbonne, permits the union in one place of the Faculties of Theology, Letters and Sciences, the library of the University, a room for the distribution of the awards given in the General Competition, and the various offices of the Academy of Paris." Ibid., p.21.

147. The basis of the three plans, unanimously adopted, was "A main courtyard surrounded by open promenades; a great hall able to hold about 2400 persons for the distribution of awards given in the General Competition; a special courtyard around which are to be placed the preparation rooms and on the upper floors all the collections; finally, a part of the building reserved for the administration of the Faculty of Sciences and the lodgings of the dean." Ibid., p.20. The other Faculties would take over the existing buildings and make the few alterations necessary.

work out the final details (148). Hopes ran high for a time, but delays and political turmoil prevented construction from beginning until 1 September 1884, a few months after Dumas died (149).

Although Dumas retained his Chair at the Sorbonne until 1868, he retired as dean of the Faculty in 1849, and from 1853 Henri Etienne Sainte-Claire Deville (1818-1881) substituted for him as lecturer (150). On 22 February 1855 Milne-Edwards, who had succeeded Dumas as dean "announced, not without emotion, that a laboratory for development and research in chemistry had been created in the Faculty" after many years of waiting (151). Fittingly, it was Dumas who assumed its direction (152).

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148. Members of the Commission were: Thenard (Chancellor of the University), president; the Inspector General of the University; five members of the City Council; Dumas, LeClerc, Abbé Glaire, Pouillet, the Architects of the University and City.

149. Attempts were made again in 1852 (opening of rue des Ecoles), 1867 (Claude Bernard's report on Physiology) and 1874 before agreement was reached in the law of 22 August 1881. Complete rebuilding now became necessary; floor space doubled to 20,000 m^2 (60% for Faculty of Sciences); land value went from 2.5 to 3.6 million francs, but estimate of the remainder went from 2.5 million to 18.6 million francs! Ibid., p.20. Prior to this, at one stage (Procès Verbaux deliberations of the Faculty of Sciences 6 March 1849) Dumas suggested that the Faculty take over the Lycée Louis-le-Grand, which was just across rue St. Jacques from the Sorbonne.

150. Partington, op.cit.(1-14), p.497.

151. Gréard, op.cit.(9-8), p. 62-63. Fortoul, Minister of Public Instruction issued two Arrêtés that day, each of 3 articles. In the 2nd: "1. The laboratory of development and research of the Faculty of Sciences of Paris is installed provisionally in the Ecole Normale. 2. The students of the Ecole Normale will be admitted to it during their fourth year of studies. The licenciés ès sciences physiques can be admitted by authorisation of the Minister of Public Instruction for the preparation of their thesis for the doctorate. 3. M. Dumas, member of the Institute, is named director of the laboratory for development [and research] of the Faculty of Sciences in Paris." Quoted, ibid., p.63.

152. Dumas, as President of the Municipal Council, hearing that shanties at 112 and 122 rue Saint-Jacques were to be wrecked, asked that they be leased to the Faculty to establish laboratories there. Ibid., p. 24-25. These may well have been intended as additional research facilities.

Before this chapter can be concluded, one further report must be mentioned because it involved Dumas as dean of the Faculty of Sciences in the complete reform of science education in France. After commenting very favourably on Dumas' 1846 report concerning the needs of the Faculty, Salvandy wrote to the dean that he now saw the problem in a much wider context, that any reform of the Faculty must include a revision of science teaching at all levels, from the upper primary schools, through the colleges to the Faculties. Indeed he believed that it was necessary to examine science teaching itself to see "what it is, what it produces, how it answers the needs of society and how it should be complemented to lead the country forward in the way that it should go, in the pathways of industry, work and science." (153) The Faculty of Sciences elected a commission composed of Pouillet, Poncelet, Milne-Edwards and Urbain Jean Joseph Le Verrier (1811-1877), presided over by Dumas. After their report had been approved by the Faculty, it was presented to Salvandy on 6 April 1847 by the dean, who observed:

> "In order to fulfill the important mission confided to it by the Faculty, this Commission contacted the headmasters of our colleges, heads of some institutions, and important farmers, industrialists and business-men. They visited various colleges, schools or institutions, examing them with care, and thus formed the opinions contained in this report." (154)

The report was excellent (155) providing the basis for the system of

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153. Ministère de l'Instruction Publique, Rapport sur l'Enseignement scientifique dans les collèges, les écoles intermédiaires et les écoles primaires, Paris, 1847, (63 p.) pp. 3-4, Lettre de M. le Ministre de l'Instruction publique à M. le doyen de la Faculté des Sciences (28 December 1846).

154. Ibid., pp. 5-6, Lettre adressée à M. le Ministre de l'Instruction Publique, Grand-Maître de l'Université, par M. Dumas, conseiller de l'Université, doyen de la Faculté des Sciences de Paris.

155. It was the subject of lively comment in the press and much discussion both public and private. Dumas was the recipient of many favourable letters concerning the report.

bifurcation that was introduced during the Ministry of Fortoul in 1852 (156). The Commission advised introduction of the sciences at all levels of instruction, graded to the requirements of the students at each age level. The various curricula were spelled out in great detail. One comment is of particular interest to the discussion in this chapter:

> "Everyone is agreed in deploring the present organisation of studies during the year dedicated to philosophy and the sciences; for no one is unaware of the requirements of the baccalauréat ès lettres; fear of the test is always present in the minds of the young pupils of this class, depriving them of all the attention necessary for philosophy or science. ...
> Because of this, it is understood that the students of our colleges do little or no studying in the sciences, that it is reduced to some answers memorised for the baccalaureate examination and forgotten the next day. It is not surprising that the Faculties of Sciences and Medicine must repeat the teaching of elementary physics and chemistry that should be given in the colleges, to the great detriment of the more advanced or specialised teaching that they should be giving." (157)

Certainly Dumas envisaged the Faculty as an advanced school, not simply an examining board, the purpose that it still served in 1847, nearly forty years after its foundation. Such was the state of the lower levels of science education even at this time however, that nothing more could be done. For this reason, Dumas began to take an active interest in educational reform. Though bifurcation did not prove to be the answer (158), there was some improvement in attitudes towards science education, though it was sporadic,

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156. Regulation of 30 August 1852. After the 4[e], students chose to enter either of two programmes: The one primarily scientific with some arts classes; the other mainly literary with some science classes. It has been said "Fortoul's reform, fruit of a concept born during Salvandy's ministry, ... owes much to the ideas of the dean of the Paris Faculty of Sciences, Dumas, and to the astronomer LeVerrier." Prost, A., L'Enseignement en France, 1800-1967, Paris, 1968, p.57.

157. Ibid., p.25.

158. The reasons are beyond the scope of the present work, but Prost's comment that it "deserved a better fate", loc.cit.(9-156), is worth noting.

partly dependent on political events but more on the orientation of most French people towards a literary education. Even Dumas' oratory and the high positions that he held could not overcome their unwillingness to change in this regard.

CHAPTER 10

DUMAS' RESEARCH STUDENTS

"More than forty years ago, J.B. Dumas accepted some young men, both French and foreign, into his private laboratory in the rue Cuvier, directing them in their work, communicating to them the zeal that inspired him, giving them an example as the hardest worker of all. The most important representatives of foreign countries have visited this very unpretentious laboratory; they have shown a vivid appreciation for the work of the master. Personally, I will always remember with emotion the day when he was kind enough to accept me finally as one of his students, even though I had no background, but was simply and ardently animated by the desire to learn under his direction. His words still ring in my heart: 'Work, young man, and you will succeed.' No doubt he added to himself: '... because I will be there to encourage and to help you.' Apart from the public lectures given by this well-known teacher, indicative of such brilliance, his very friendly and engaging talks in the laboratory will remain deeply etched on the memories of all students who were lucky enough to hear them. In them, all of his teachings created a feeling for scientific research.

What philosophical insights, what intuitions, sanctioned later by experimentation, unfolded in these conversations, covering all the profound questions of natural philosophy! It was necessary to be there to understand the great significance of all this.

With profound emotion and a deep sense of gratitude I would like to add that, master in both the lecture hall and the laboratory, he was also a sure guide in the struggles of life, because he became the father of his students and showed them a real affection in all the circumstances of their life." (1)

While the discussion of Dumas' life and works in the earlier chapters has brought out his more important contributions to both physiology and chemistry, there has been little emphasis placed on the relationship between Dumas and his students. It is tempting to look for a Dumas "school". One of his students Félix Leblanc hinted at the existence of such a group when he said in 1884:

> "Certainly Dumas is the man who exercised the greatest influence on the science of his period. Instructor of hard-working young men, happy to show the way by supporting and encouraging young workers at the outset of their career, he contributed more than anyone else to the rise of that host of distinguished chemists who have each added their share to the efforts that have brought about the progress of chemistry during the past forty years. ... What the state had not yet provided for young scientists, Dumas tried to create, the first to open a free, private laboratory, a true school of chemistry, where every young man of talent was welcome." (2)

It would be possible to consider the French school to which other students, Péligot and Wurtz have referred and which has been the topic of a more recent paper by a French historian of science, who has put Dumas at its head (3).

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1. "Discours de M. Melsens" (at a meeting of the Academy three days after the death of Dumas), Comptes Rendus, 98 (1884), 944-45. Wurtz, who had also been a student of Dumas, was another of the five speakers. Ibid., 933-44. Melsens represented his foreign students, Wurtz the Faculties of Science and Medicine.

2. Leblanc, F., "Le laboratoire et l'enseignement de J.B. Dumas", Bull. Soc. Chim., 1884, 549-59 (553, 555).

3. In a memoir read on 5 April 1841, Péligot discussed the differences that existed between foreigners and the French school, Thenard, Gay-Lussac, Chevreul and Dumas, on the separate existence of NO and N_2O_3. Ann. Chim. Phys., 2 (1841), 58-68. In a discourse in 1884, Wurtz, loc.cit.(10-1), 941, noted: "The basic lines [of the substitution theory] are indelibly drawn, and it was the French school that drew them. M. Dumas was the head and support of that school." M. Daumas, "L'Ecole des chimistes français vers 1840", Chymia, 1 (1948), 55-65, has stated categorically: "The French chemists, students of professors with excellent reputations, Thenard and Gay-Lussac, were aware that a great tradition had been passed on to them; moreover, most were worthy of their predecessors. In 1840, Jean Baptiste Dumas' place at their head was not contested." Ibid., 58.

The delineation of such schools, if indeed they exist, is much more difficult than the identification of Liebig's school, whose members worked in an isolated laboratory in Giessen, a town with only one institution of higher learning (4). One would be obliged to consider many factors in Paris: The number and variety of educational institutions, the number of chemists, their place within or outside of the establishment that included not only chemists, but other scientists, their relationship with one another and with scientists outside France, their particular research interests, the complex problems associated with the need for financial support and laboratory facilities. And beyond these lies a more serious and direct problem: A young man with an interest in chemistry may have been influenced by many different chemists in Paris. He probably attended the lectures of several well-known professors and could easily have done research in more than one laboratory. He may even have worked with Liebig (5). For these reasons, no claim will be made in the present work that there was a distinct 'Dumas school'. However, an effort will be made to point out significant relationships that did exist between Dumas and some of his students, between his work and some of theirs.

Dumas had lived in Paris for more than a year before he became <u>répétiteur</u> at the <u>Ecole Polytechnique</u> and was given the care of a preparations

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4. Liebig's school has been discussed in a recent article by J.B. Morrell, "The Chemist Breeders", <u>Ambix</u>, <u>19</u> (1972), 1-46. A chart of Liebig's noteworthy students (and their students down to the fourth generation) has been given by R. Sachtleben and A. Hermann, <u>Grosse Chemiker</u>, Stuttgart, 1961, p.33. A more complete list of his foreign students, arranged according to nationality and the semesters spent in his laboratory has been prepared recently by Wankmüller, A., "Ausländische Studierende der Pharmazie und Chemie bei Liebig in Giessen", <u>Tübingen Apothekengeschichtliche Abhandlungen</u>, Heft 15, 1967.

5. Gerhardt worked in Liebig's laboratory in the winter semester, 1836-37 and Wurtz in the summer semester, 1842. <u>Ibid</u>. Both were students of Dumas afterwards.

room which he could use as a research laboratory (6). Over the preceding years he had been provided with facilities for carrying out his experiments by pharmacists, biologists and chemists in Paris as well as in Geneva. Following in the footsteps of these scientists, he too invited a few young men to work in this modest laboratory, to assist him in his research (7). When his status improved remarkably in 1832 (8) he was able to set up a new private laboratory in an annex of the school, where he was able to share his facilities with still others inculcating in them his spirit of research and introducing them to his methods. Because he was particularly interested in encouraging promising young men whose resources were limited, he charged no fee for this experience (9). During the ensuing six years, Dumas and his students made important discoveries in this laboratory before he left it in 1838, when he relinquished his position as professor of chemistry at the school. About the same time he was given the use of a house near the Muséum which he was able to convert to a research laboratory. One of his students noted in 1884:

> "Across the rue Cuvier from the Botanical Garden, in a small house with a garden put at his disposal by his learned and worthy father-in-law, the late Alexandre Brongniart (of the Institute), Dumas set up a research laboratory for his work and accepted some French and foreign students there who were

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6. A brief description of this laboratory has been given on pp. 109-10. It continued to serve as a preparations room as well.

7. Francillon, Boullay and Laurent were among them.

8. He became a Doctor of Medicine, Doctor of Sciences and a member of the Academy of Sciences that year and was appointed to a position as assistant professor of chemistry in the Faculty of Sciences. At the Ecole Polytechnique he had excelled as a substitute for Thenard on many occasions as Leblanc has indicated: "As répétiteur for Thenard's course at the Ecole Polytechnique he substituted for the well-known chemist frequently. Former students of the Ecole Polytechnique who knew Dumas at that time still remember his dedication to teaching, his advanced views and his talent for exposition." Loc.cit.(10-2), 550.

9. Students paid for the privilege of studying with Liebig.

> happy to assist him in his research and to study under his direction." (10)

Most probably he began thinking about moving into more spacious accommodations about the time Liebig visited Paris late in 1837 (11), for it was at this time that he also decided to compete for the position in the Faculty of Medicine. His success in obtaining the chair, his debate with Pelouze (still only a répétiteur at the Ecole Polytechnique) which had left them on somewhat less than amicable terms, the desire to get on with research in practical organic chemistry, especially related to agriculture and medicine all conspired to take him away from the military school and of course his laboratory there. Thus he most likely spent the summer of 1838 in house conversion, so that by the autumn he was ready to move his equipment from his second laboratory to its new home about half a kilometer away. There he continued research with students until financial difficulties arising from the political events of 1848 forced him to close it (12). Fortunately, as Dumas himself was able to note with pride, Deville, one of his students, took up the reins a few years later at the Ecole Normale:

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10. Ibid., 553. Dumas' residence was at 35 rue Cuvier. Gautier, op.cit.(1-1), p.45, gave 24 rue Cuvier as the address of the laboratory.

11. There is a rough sketch of the ground floor of the building housing Liebig's laboratory (Giessen) in Dumas' papers. Arch. Acad. Sci., Fonds Dumas, Carton 9. It is not dated, but there is little reason to believe that Dumas would have been interested at any other time.

12. Soon after the death of his father-in-law in 1847, Dumas left the Muséum to take up residence in the Brongniart home, 69 rue St. Dominique, on the other side of Paris. This may have provided another reason for closing the laboratory, though a much less important one than the problem of finances. Adding weight to his decision were the many administrative duties that he had taken on, and the pressure to enter politics that he had felt since 1845 (he finally agreed to stand and was elected to the legislative assembly as the representative from Valenciennes (Nord) on 13 May 1849). On 31 October 1849 he was made Minister of Agriculture. His political career, lasting just over twenty years, began during a revolution and was terminated by a war!

> "After 25 years of activity, I closed my laboratory of advanced chemical studies. Henri Sainte Claire Deville became my successor. ... he opened his laboratory with the assistance of the state ... and in his turn dedicated himself to it without reserve for the rest of his life." (13)

Though Dumas no longer maintained a private laboratory, his talent for directing young men interested in chemical research was far from wasted. In 1855, Hippolyte Fortoul (1811-1856) as Minister of Public Instruction authorised the foundation of an advanced research laboratory for the physical sciences, where students who had received the licence could undertake the experimental investigations necessary to complete their doctoral theses (14). It was installed in the Ecole Normale in 1855 and Dumas was named director, a position he retained until 1862.

Dumas lectured to thousands of students and presided over hundreds in general chemistry laboratories. Many of these pursued careers involving chemistry but were not part of Dumas' research programmes (15). The present work will be limited to those students who collaborated with Dumas, worked on his programmes of research (often in his laboratory), or entered upon related research after attending his lectures. These students have been identified in several ways, among them the following:

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13. Dumas, J.B., Eloge de Charles et Henri Sainte Claire Deville, Paris, 1884, p.22. This was the last of Dumas' Eloges. It was read to the Academy of Sciences on 5 May 1884, a few weeks after his death on 11 April, and was as much a memorial to him as to the Devilles. Henri succeeded Balard in 1851.

14. There can be little doubt about the part that Dumas played in this project as vice-president of the Council of Public Instruction, an appointment he had received on 9 March 1852, less than two months after he had been made senator of France by Louis Napoleon. Nor is it difficult to imagine that the success of this laboratory made feasible the decision by Victor Duruy (1811-1894), Fortoul's successor, to initiate a programme of advanced studies, the Ecole Pratique des Hautes Etudes, a few years later.

15. Many examples could be drawn from the letters Dumas received; his influence on Pasteur, often mentioned by the latter, has already been noted.

1. An explicit statement by the student that he had been guided by Dumas. For example, Péligot wrote in a journal article on 1833:

> "These analyses have been done in M. Dumas' laboratory, in his presence; he has followed them with special kindness; his advice and experience have often been useful to me on this occasion as on many others." (16)

Often such acknowledgments appeared in connection with work done for the thesis, and it was rarely repeated in subsequent work by the student, even though such guidance may well have continued. Other students, particularly those from other countries, who were not seeking the degree, usually mentioned it in their first published work after entering Dumas' laboratory. Thus Piria indicated in his memoir on salicine in 1838:

> "I would be neglecting a debt of gratitude were I to pass over in silence how much I owe to the goodness of M. Dumas, who has allowed me to carry out this long work in his laboratory and assisted me with his kind advice." (17)

2. A clear indication in a memoir, report or other work published by Dumas that a young man was his student. Occasionally his reference to the fact was explicit. Thus when he found that his analysis of camphor, repeated several times, was different from that of Liebig in 1832, he "had it done again by MM. Jacquelain and Laurent, two of my students who are very good at this kind of analysis" (18). More frequently the relationship was implied. In his textbook he wrote:

> "Furthermore, an observer whose precision is well known, Pelletier's father, has made an observation that P[olydore] Boullay could never reproduce in his attempt to do so in my laboratory, working on large quantities and with every variety of acid that he could prepare or obtain." (19)

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16. Ann. Chim. Phys., 52 (1833), 270.

17. Ibid., 69 (1838), 283.

18. Ibid., 50 (1832), 226.

19. Traité, Vol. 5, p.152. After discussing Pelletier's research on vinegar, Dumas added: "If what I have said proves to young chemists that, in spite of all the important work done on acetic acid, the substances that modify (cont.)

3. Appearance of his name in lists of Dumas' students left by some of these same students. For example, Leblanc noted:

> "Students who worked in this [his first] laboratory attained a high level of achievement in science: MM. Boullay, Péligot, Laurent, Malaguti. ... and in Dumas' private laboratory, MM. Piria, Stas, Melsens, Delalande, Wurtz, Lewy, Bouis, authors of important works who became members of the Academy, or professors. All have been students of Dumas and have worked in his laboratory. ... During the period when this laboratory [at the Sorbonne 1855-62] was in operation, there worked under Dumas' direction: MM. Schickkoff [sic] and Beketoff (Russia), Rosing (Norway) and at the same time or in succession the following French chemists: MM. Aimé Girard, de Luynes, de Clermont. M. Collinet was préparateur in this laboratory; his successor was M. Paul Bérard. Both of them helped M. Dumas in his work on the atomic weights of many substances. M. Alfred Riche was then head of the chemical work in the Faculty of Sciences. From 1862 M. de Luynes became head of the research laboratories in the Sorbonne and M. Paul Bérard succeeded M. Riche in his duties at the Faculty of Sciences." (20)

He also mentioned that Bineau d'Aligny was a student of Dumas at the Ecole Centrale (21). In 1836 Bineau listed several students, at the same time describing the close relationship they enjoyed with Dumas:

> "This phrase has raised protests against M. Dumas from M. Laurent. As if, in opening his laboratory to all young chemists, to the unfortunate Boullay, to M. Péligot, to M. Pelouze, to M. Laurent and many others, making them part of his experimental life, inspiring them again and again, M. Dumas had renounced the right to advise them. ... I hope M. Dumas, far from becoming discouraged, will always keep that unvarying kindness towards youth that has already placed him so high in public esteem and enabled this brilliant school of young chemists to spring up among us, the hope of science and of the country." (22)

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19. (cont.) its properties still need a deeper study, and if I thereby can encourage them to complete this point of science, I will have accomplished my purpose [in mentioning it]." Dumas frequently presented such vistas to his students.

20. Loc.cit.(10-2), 550, 553, 555 (footnotes). His later students included: Ljew Nikolajewitsch (Léon) Schischkoff (1830-?), Nikolai Nikolajewitsch Beketoff (1827-1911), Anton Rösing (1828-1867), Aimé Girard (1830-1898), Victor Hippolyte de Luynes (1828-1904), Philippe Henri Arnoult de Clermont (1831-1921), Collinet and Alfred Jean Baptiste Léopold Riche (1829-1908).

21. Ibid., 550.

22. Leçons, p.352, footnote 1.

4. Statements made by students in the dedication of their theses. Many of those who were presenting memoirs describing the research they had undertaken for the doctorate, took advantage of the opportunity to acknowledge those with whom they had some special relationship. Some were dedicated to parents (23), others to teachers, still others to those who directed their research. While the exact nature of this relationship is not always specified, the words used do give some concept of its character. Thus Bineau dedicated both of his to Dumas "as a token of the respect, affection and gratitude of his student" (24), and Boullay his second thesis "as an indication of gratitude and friendship" (25). A dedication to Dumas after he had been appointed dean of the Faculty of Sciences might have been less meaningful. Before then Gerhardt, Péligot, Frédéric Hervé de la Provostaye (1812-1867) and Hector Pierre Aubergier (1809-1884) had dedicated theses to him (26). Remarks in two other theses have a special interest. Malaguti, who worked in the

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23. Sometimes their fathers were also well-known scientists, P.F.G. Boullay, for example, to whom Polydore dedicated his thesis.

24. Sur quelques combinaisons ammoniacales et sur la rôle que joue l'ammoniaque dans les réactions chimiques; Recherches sur les densités de vapeur, Paris, submitted 25 October 1837. Since the theses under consideration were published in Paris, only their title and date of submission will be given. Published copies may be found in the library of the Sorbonne. In the physics thesis Bineau discussed some problems encountered in determining vapour densities of the compounds studied in the chemistry thesis. From this time it was not uncommon for a student to use vapour density studies as his physics thesis when the major work was done in chemistry, a further indication of the extent of Dumas' influence.

25. Ulmine (acide ulmique) et acide azulmique, 6 March 1830.

26. The first three did so "in acknowledgment of deep gratitude", and the last "in respectful homage". The title and date of submission for the thesis of Péligot and Gerhardt will be given later. The work done by Aubergier will not be discussed since it was not part of Dumas' programmes. Hervé de la Provostaye measured the crystallographic angles of many crystalline substances supplied by Dumas and his students but his research is outside the purpose of the present work.

laboratory of the porcelain factory at Sèvres, dedicated both of his to Alexandre Brongniart, but the following unusual note was added to his chemistry thesis which had been approved by Thenard as dean of the Faculty of Sciences: "I have read M. Malaguti's thesis and I find that it is very worthy of being submitted to the Faculty. J. Dumas." (27) Though it will become evident that Antoine Philibert Masson (1806-1860) certainly did his work in Dumas' laboratory, he made the following dedication: "To M. Thenard, baron, Peer of France, Member of the Institute, acknowledging the strong gratitude and deep devotion of his respectful student" (28).

5. Secondary sources. A biographer has indicated that Gerhardt, Deville and Cahours had attended Dumas' lectures together and "frequently pooled their resources to do research in Deville's laboratory" (29). Deville had not worked in Dumas' laboratory because he had set up his own, as Dumas observed later, "in a hovel in the rue de la Harpe, where he busied himself at first with experiments demonstrated in the courses he had attended and in studying all their details" (30), but where he soon undertook original research, including his thesis on turpentine (31). One of Deville's students,

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27. Dumas kept a copy of Malaguti's thesis in his papers. Arch. Acad. Sci., Fonds Dumas, Carton 5.

28. Apparently Masson worked in Dumas' laboratory but attended Thenard's lectures.

29. Grimaux, E., and C. Gerhardt, Charles Gerhardt: Sa vie, son oeuvre, sa correspondance (1816-1856), Paris, 1900, p.33.

30. Dumas, J.B., op.cit.(10-13), p.19.

31. Etudes sur l'essence de térébenthine, 13 March 1841. It was published (Ann. Chim. Phys., 75 (1840), 37-80) as was the part of his physics thesis concerned with the index of refraction of turpentine (Comptes Rendus, 11 (1840), 865-67. On 13 November 1840 Deville wrote to Dumas thanking him for conferring the licence and approving his chemistry thesis. After discussing refractive indices at length, he added: "May I also ask you at the present time for permission to profit from your kind offer to loan me some of the substances in your collection to determine their indices. I

Désiré Jean Baptiste Gernez (1834-1910), wrote in 1894:

> "Without mentioning the many others who owe the brilliance of their career to him [Dumas], the two greatest scientific glories of whom they [the students of the Ecole Normale] have a right to boast, both Henri Deville and his illustrious friend, M. L. Pasteur, have been directed, supported, encouraged and exalted by him." (32)

All of these methods take on added value when there is evidence that a young man has also been associated with one or more of Dumas' research programmes.

Because Dumas was such an effective teacher, his influence upon those who attended his lectures, and afterwards pursued a career in chemistry, was profound. While he insisted on the importance of gathering data by observation and experimentation, he impressed upon his students the need to seek progress in chemistry by using that information as a basis for theoretical considerations. He was particularly interested in classificatory theories. All of the students who attended his lectures were informed of the importance of elemental analysis and the importance of determining chemical and physical properties of compounds (particularly vapour density where this was possible); but those who also worked in his laboratory under his supervision learned his experimental techniques, absorbed his conceptual methods, were exposed even more fully to his ideas, thus forming a much deeper relationship with the one they frequently called '<u>le maître</u>'. While the term research student would apply more correctly to these, many of whom have been mentioned earlier in the present work, it will be extended to include those who worked elsewhere

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31. (cont.) have only one means, sir, of showing my gratitude for all your benevolence, that is to be ready and at your disposition at all times to determine the indices of liquid substances that you want examined, if you are interested in doing this." Unpublished letter, Arch. Acad. Sci., <u>Fonds Dumas</u>, Carton 9.

32. Gernez, D., "Notice sur Henri Sainte Claire Deville", <u>Annales de l'Ecole Normale Supérieure</u>, 3e Serie, <u>11</u> (1894), 3-70 (70). ~~of Deville.~~

for various reasons, but turned to Dumas for advice or were directly influenced by his work. Often their interest, born in his lectures, was continued in the research they chose to pursue, either by their own decision or on Dumas' advice. Bearing this in mind, it is possible to group his students, quite loosely, by associating them with his research programmes. Several of these will be identified for the purposes of this thesis: The ether theory (including the study of alcohols, organic acids and essential oils); the substitution theory (with emphasis on chlorination studies); the type theory and the law of fatty acids; the atomic weight of carbon; studies relating to chemical biology; and Prout's hypothesis and the determination of atomic weights.

The ether theory. Polydore Boullay was only 20 years old when he began working with Dumas on ethers in 1826 or early in 1827. Though the physiologist-turned-chemist was barely six years older, he had acquired a reputation in both sciences by this time and had been teaching at the Athénée for three years. His prowess as an analyst had come to light in 1823 when he collaborated with Pelletier, who made sure that his protégé met the important pharmacists in Paris, including P.F.G. Boullay. Undoubtedly he met Polydore at that time and may have encouraged him to undertake the work on iodides published by the young man in 1827 (33). Thus it was as a student that he came to Dumas' laboratory to collaborate with him in the study of ethers (34).

33. "Mémoire sur les Iodures Doubles", Ann. Chim. Phys., 34 (1827), 337-80. An extract appeared in 1826. J. Pharm., 12 (1826), 638-39. Dumas had done extensive work on iodine in Geneva and in 1825 was investigating the vapour density of volatile elements and compounds, including iodine.

34. Despite the age difference, a close friendship developed between the two, and the student-teacher relationship was never expressed by either of them. Boullay concluded letters written in 1831 and 1834 "votre bien affectioné". Arch. Acad. Sci., Dossier Boullay, (Fonds Dumas).

When they had completed the 1828 memoir, he began his doctoral research, successfully defending the two theses required on 20 February and 6 March 1830 (35). Only then did he accept Dumas' invitation to collaborate with him in a thorough study of acetic acid and related compounds (36). Unfortunately his career came to an abrupt end a few months later when he was severely burned in an ether fire on 23 October 1830 (37).

The seminal work on ethers opened the way for various studies pursued by Dumas' students. Part of his work had involved the confirmation of the formula for alcohol. In 1834 Dumas concluded that wood spirit contained a substance that was perfectly analogous to alcohol. He invited Péligot to help him prepare the compounds of this substance whose existence could be predicted because of the analogy (38). Péligot had begun the course in engineering at the Ecole Centrale but was drawn towards chemical research by Dumas' lectures and gave up his original goal. He had already proved himself by research on chromium compounds done in Dumas' laboratory in 1833 when Dumas' invitation was extended. Much later he said: "M. Péligot and I were occupied throughout the whole of the year 1834 with our work on wood spirit." (39) Towards the end of the year Péligot became a répétiteur at the Ecole Centrale and in

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35. See pp. 136-37 and 406.

36. Loc.cit.(8-85). Dumas probably had his textbook in mind when he undertook this research.

37. In an unpublished letter to Dumas dated 24 December, Boullay wrote: "Yesterday was the baneful monthly anniversary of my accident 14 months ago." Loc.cit.(10-34). Partington, op.cit.(2-17), p.345, gave 1830 as the year of the accident. Though he did not die until 1835, it appears that Boullay was no longer able to do laboratory work, though he seems to indicate that he was able to do editorial work. Letter of 1834, loc. cit.(10-34).

38. See pp. 257-60.

39. Ann. Chim. Phys., 49 (1857), 487-96 (491, footnote 1).

1836, after he and Dumas had shown that ethal was analogous to alcohol and methylene bihydrate (40), further confirming Dumas' hypothesis that a series of such compounds would be discovered, the founding professor of chemistry in the Ecole invited his collaborator to accept the Chair of General Chemistry there (41). Two years later Péligot defended his doctoral theses, in which he described work on sugars that he had done in Dumas' laboratory (42). These show clearly that he had absorbed his teacher's penchant for classification, his persistent use of analogy and his manner of writing memoirs.

In 1839 another analogue of alcohol, potato oil was identified by Cahours (43). The similarity of his approach to that used by Dumas and Péligot suggests that he was a research student of the former, for he did attend Dumas' lectures though he had not worked in his laboratory (44). In the memoir describing this investigation, he wrote:

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40. They showed that Chevreul's ethal was an alcohol, $C^{64}H^{64}.H^4O^2$, (cetyl alcohol, $C_{16}H_{33}OH$).

41. He relinquished the chair in 1843 when he replaced Dumas as professor of analytical chemistry, a chair that he retained until 1865.

42. Recherches sur la nature et les propriétés chimiques des sucres; Propositions relatives à la détermination des densités des gaz et des vapeurs, 19 March 1838. The first appeared in Ann. Chim. Phys., 67 (1838), 113-77. He continued to study sugars until 1840, then sporadically for the rest of his life.

43. Mémoire sur l'huile volatile de pommes de terre et ses combinaisons", Ibid., 70 (1839), 81-104.

44. Besides preparing ethers and salts using standard procedures, Cahours made a hydrocarbon by Dumas' method (but found by vapour density determination that it was $C^{40}H^{40}$ not the $C^{20}H^{20}$ that he had expected); chlorinated the alcohol and obtained an effect similar to that found by Dumas; determined the chlorine content of products using Dumas' method. As préparateur for Chevreul at the Muséum, Cahours had access to a laboratory there in which to do his research. Following Dumas' logic he called the substance amylene bihydrate. Balard was the first to call it amyl alcohol. Ibid., 12 (1844), 294-330. In 1891 Gautier indicated that Cahours began working in Dumas' laboratory after the young man had identified potato oil as an alcohol. He noted that Cahours was profoundly influenced by the "jeune maitre de la chimie française". Acad. Sci., Funerailles de M. Auguste Cahours, Paris, 1891, p.3.

> "These analyses confirm entirely the results obtained earlier by M. Dumas (45) and lead to the formula $C^{20}H^{24}O^{2}$ adopted by the learned chemist. The numbers obtained from vapour density determination give rise to the conclusion that the above formula represents four volumes; thus the formula can be rewritten $C^{20}H^{20}.H^{4}O^{2}$, and this substance can be considered to be formed from a hydrocarbon isomeric with olefiant gas, and water vapour." (46)

In a second memoir on the topic (47), Cahours drew up a chart in which he compared the various derivatives of alcohol and amylene bihydrate. In 1839 he became a répétiteur at the Ecole Centrale on the strength of this work, became adjoint to Dumas in the general chemistry course in 1845 when he was awarded the doctorate (48) and was appointed to the chair as professor of general chemistry in 1853 (49).

In 1830 Dumas' work on ethers led him to the discovery of oxamide and the formulation of an amide theory. Bineau, a student at the Ecole Centrale at the time, became interested in ammonia compounds as a result and chose them as the topic for his doctoral theses, defended in 1837 (50), indicating that his own efforts were based on Dumas' research: "M. Dumas was the first to think of comparing the action of ammonia on oxygenated compounds with that

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45. In 1834 Dumas had associated the alcohol with camphor. Ibid., 56 (1834), 318.

46. Loc.cit.(10-43), 85. He first indicated that the oil was analogous to alcohol in March 1837, but the work needed considerable amplification before he could definitely prove that it was an alcohol. Comptes Rendus, 4 (1837), 341.

47. Ann. Chim. Phys., 75 (1840), 193-204.

48. His theses were: Recherches sur les huiles essentielles et sur une classification de ces produits en famille naturelle, fondée sur l'expérience; Recherches relatives à l'influence de la température sur les densités de vapeur des corps composés; 15 May 1845.

49. He was also répétiteur (1840-54) and professor (1870-81) at the Ecole Polytechnique.

50. Loc.cit.(10-24). After graduating from the Ecole Centrale in 1832, he was made répétiteur there. In 1836 he edited Dumas' lectures at the Collège de France and in the autumn was appointed to the Faculty of Sciences in Lyon though he had not yet finished his theses. He completed them in Lyon.

of hydracids on metallic oxides. In attempting to apply and extend this comparison ..." (51). In Lyon he continued to do research along similar lines (52). Dumas' discovery of amides had a broader research value in that it extended the number of derivatives of acids that could be prepared. In 1834 Félix Darcet read a memoir to the Academy on succinic acid and its compounds, in which he noted: "This work has been done under the direction and in the laboratory of M. Dumas and I want to take this opportunity to acknowledge my gratitude to him." (53) Among the derivatives he was able to prepare (ethers, salts, chlorine and ammonia compounds) was succinamide. He also investigated their vapour densities (54).

Not all of Dumas' students continued in chemistry. In his chemistry thesis, Masson chose to examine critical points of the ether theory that had not been resolved. He observed:

> "For a long time the phenomenon of etherification has defied the intellectual efforts of the most distinguished chemists, for despite their many efforts they have not been able to explain the remarkable change in alcohol, nor to decide how the elements are grouped to form ethers. Under what conditions is alcohol changed into ethers? What is the role of the hydrocarbon in these substances? Chemists are still waiting for an answer to these two problems. In undertaking their study, I have not been so bold as to believe that I would overcome obstacles that have withstood the efforts of important men. My only desire has been to fulfill M. Dumas' wishes, to complete the part of the science with which that man of learning has occupied himself with such ardour and success. I would rather follow the route traced by such a master than to expose myself to unknown pathways, without a guide and without purpose." (55).

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51. Ann. Chim. Phys., 67 (1838), 225-51 (242). His second thesis was also published. Ibid., 68 (1838), 416-41.
52. Ibid., 70 (1839), 251-72.
53. Ibid., 58 (1835), 282-300 (282).
54. For reasons that are unknown, Darcet does not seem to have earned the doctorate.
55. Ibid., 69 (1838), 225-58 (225). The publication of this thesis (L'Action exercée par le chlorure de zinc sur l'alcool, 11 January 1839) two months before Masson had defended it was not unusual.

In his report to the Academy, Dumas mentioned: "Appointed by the Academy to examine the preceding memoir, I have performed two of the analyses reported, and others have been done by M. Masson in my laboratory." (56) The thesis in physics was of greater importance and he chose to pursue research in that area. When Regnault gave up his chair in physics at the Ecole Centrale in 1841, he was succeeded by Masson, who retained the chair until his death in 1860.

Dumas' interest in compounds isolated from plants, often obtained from pharmacists, stemmed from his training in Geneva. When he received samples from pharmacists, the donation was acknowledged in his memoirs. This interest carried over to his students. Dumas noted that Oppermann, one of Liebig's French students, had worked on camphor in his laboratory (57). Dumas had already studied camphor and continued to do so with success, encouraging some of his students to do so. He also isolated several essential oils and analysed them (58). Piria, who came from Italy to work under Dumas' guidance, chose to work on salicin (59). Using the benzogen hypothesis (60)

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56. Ibid., 258.

57. Dumas wrote: "M. Oppermann, having prepared his hydrocarbon in my laboratory from artificial camphor ...". Ibid., 52 (1833), 400-10 (404). Oppermann received his doctorate in 1845 from the Faculty of Sciences in Strasbourg.

58. The oils of turpentine, cinnamon, cloves and lemon were a few of those he analysed in his research, and from which he prepared derivatives.

59. "Recherches sur la salicine et les produits qui en derivent". Ibid., 281-325. Salicin was first investigated by Pelouze and Jules Gay-Lussac (1810-1877). Ibid., 44 (1830), 220-21.

60. The first paper that Dumas read as a member of the Academy was a note on the composition of benzoic acid. PVAS, 10 (17 September 1832), 125. In it he gave his own interpretation of the arrangement suggested by Liebig and Wöhler. Annalen, 3 (1832), 249-82. He saw an analogy between the hypothetical benzoyl radical ($C^{28}H^{10}O^{2}$) and carbonic oxide ($C^{2}O^{2}$). To the hydrocarbon portion ($C^{28}H^{10}$) he gave the name benzogen. A few years later he wrote: "Although the existence of such a radical has not been proven, certainly the following facts become so easy to present that we will adopt this nomenclature completely." Traité, Vol. 5, p.205.

Piria offered some attractive theoretical conclusions:

> "Some years ago M. Dumas put forward a hypothesis according to which benzoyl and anhydrous benzoic acid were regarded as two oxides of the hypothetical hydrocarbon which he called benzogen. As a consequence of this hypothesis, benzogen forms four different compounds with oxygen; and this relationship makes it comparable with the best known elements.
> The series of these oxidations can be expressed as follows:
> $C^{28}H^{10}O^{2}$ benzoyl [the radical]
> $C^{28}H^{10}O^{3}$ anhydrous benzoic acid
> $C^{28}H^{10}O^{4}$ salicyl [the radical]
> $C^{28}H^{10}O^{5}$ anhydrous salicylic acid." (61)

By determining vapour densities, Piria was able to show that "salicyl hydride is isomeric with hydrous benzoic acid" (62). Through Dumas' help he became proficient in the application of other experimental procedures as well (63). While Piria was pursuing this research, Dumas visited Johann Samuel Friedrich Pagenstecher (1783-1856) in Berne and found that the Swiss pharmacist had extracted an oil from the flowers of spiroea ulmaria (64) resembling closely salicyl hydride, one of the substances that Piria had obtained in his research on salicin. Dumas commented:

> "The identity of the two substances would certainly have been demonstrated by new tests requiring more material than what I had available to devote to such tests; then M. Piria's work would have attracted the attention of chemists for two reasons: because of the products with which he has enriched the science, and by another example of the creation of an organic material, using procedures that are doubtless quite analogous to those

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61. Loc.cit.(10-59), 283. The modern formulas (C = 12) are: C_6H_5CO-; $(C_6H_5CO)_2O$; $C_6H_4.OH.CO-$; and $(C_6H_4.OH.CO)_2O$.

62. Ibid., 291.

63. Among those he mentioned were the process developed by Dumas for determining nitrogen and the standard process of using the lead salt for organic analysis introduced by Berzelius and used by Dumas.

64. Pagenstecher mentioned in a letter that in 1835 Carl Jacob Löwig (1803-1890), a chemistry teacher in Zürich, had described it as a hydracid having the formula $C^{24}H^{10}O^{4}H^{2}$. Ibid., 331-45.

that nature often uses. Nothing could be more encouraging for young chemists than such successes, which presage many others." (65)

In 1884 Cannizzaro described the relationship that had existed between Piria and Dumas:

"The letters of [Piria] and Stas which I published in the discourse about Piria (that I read in Turin) give evidence of the kindness and generosity shown by Dumas when he encouraged these young students by indicating pathways for research.
The limits of this notice do not permit us to list the valuable scientific discoveries made in [Dumas'] laboratory, by Dumas, working alone, with his students and with his collaborators." (66)

Cannizzaro, who credited Piria with founding the Italian school of chemistry, spoke of the ways in which Dumas' influence on Piria effected that school:

"The Italian school of chemistry, founded by [Piria], can be considered as an offshoot of the Dumas school of chemistry, a branch that developed independently afterward.
At another time (67) I recalled how Piria had followed Dumas in his formal teaching, and how he had opened new pathways towards the present views of chemistry by working on the type theory and bringing it into agreement with the concept of fixing molecular residues. I think I have also shown how the education received by Piria made it possible for us to arrive at the atomic and molecular theory in general use today; and this was accomplished without any abrupt change in the development of thought." (68)

In August 1840 Cahours invited Gerhardt to collaborate with him in research on essential oils in his laboratory at the Muséum (69). The work

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65. Ibid., 326-31 (327).

66. Cannizzaro, loc.cit.(1-100), 135.

67. In a footnote (Ibid., 140) the translater Leblanc wrote: "In an important discourse by the author of this notice on the occasion of the inauguration of the bust of Piria in the great hall of the University of Turin in 1883." Dumas had intended to write an article about it in the Journal des Savants, but his death intervened.

68. Ibid. Cannizzaro added: "I will never forget the pledge of affection given by Dumas to his former student and collaborator; it reveals the nobility of his character. With what joy he received the news of the honours given to the memory of Piria in Turin! What sentiments of noble friendship are contained in the letter (published in my discourse) and the telegram sent to Turin on the very day of that solemn inaugural meeting!"

69. Their memoir was read to the Academy on 30 November 1840. Ann. Chim. Phys., 1 (1841), 60-111.

is of particular interest because it provides a good example of the way in which research done by Dumas' students interlocked. Soon after Piria returned to Italy, Z. Delalande, who had just finished his studies at the Ecole Centrale was invited to take his place in Dumas' laboratory (70). Within a few months he had done important research on camphor (71) and coumarin, and had devised a new way of preparing phosphoric acid anhydride continuously on a large scale (72). Delalande's untimely death led Dumas to publish his work posthumously in four articles (73). The third article began:

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70. Several drafts exist of an article "Recherches sur la coumarine ou stearoptène des fèves de tonka, faites au laboratoire de M. Dumas par Z. Delalande, ancien élève de l'Ecole Centrale". Arch. Acad. Sci., Fonds Dumas, Carton 8, Dossier "Notes d'expériences/Analyses de Z. Delalande ...". In an early one, the young man wrote: "Salicylic acid, discovered recently by M. Piria, my learned predecessor in the laboratory of M. Dumas, has the following composition ...". The early drafts have many personal references such as: "Moreover, I only undertook it because of the prompting of my good and renowned teacher; I owe everything to his generosity and advice." These were all removed in the final draft prepared by Dumas for publication. Ann. Chim. Phys., 6 (1842), 343-51. In it Delalande showed that the relationship between coumaric and cinnamic acids was the same as between salicylic and benzoic acids.

71. "Recherches sur l'action que la potasse exerce sur le camphre". Ibid., 1 (1841), 120-27. Delalande began: "In sharing the point of view that guided MM. Dumas and Stas in their beautiful experiments on alcohols, I have sought to find out whether camphor, which undergoes some reactions analogous to those of that class of substances, acts the same under the influence of potash."

72. Ibid., 117-19. In it he described the method for preparing the acid that had been used in Dumas' laboratory. The acid was an important reagent in organic chemistry.

73. Apparently Delalande, in his early twenties, died just before the February issue of the Annales de Chimie et de Physique was published, for it included a brief note in which he said: "A young chemist, full of promise, who was taken from science and his friends prematurely by death, M. Delalande, was given the task of pursuing research on substances closely related to ordinary alcohols. ... His work, which opens a new pathway in this kind of study, will be published in a future issue." Ibid., 73 (1840), 165.

> "It is known that the name camphogen has been given by M. Dumas to a hydrocarbon derived from camphor by distilling the latter with phosphoric acid anhydride. Since I had learned how to prepare this carbide in greater quantities than had been made up till now, and with some facility, I submitted it to a few investigations." (74)

Gerhardt and Cahours, who discovered an important relationship between their own work and that of Delalande, were given access to some of the manuscripts before they were published and added a note to the third article "in which they said:

> "In the work that we published recently (January issue 1841) on the essence of cumin, we described cymene, a hydrocarbon $C^{40}H^{28}$ = 4 vol. of vapour, which seems to us to be identical with the camphogen of M. Dumas, studied by M. Delalande. Since the publication of our memoir, we have had occasion to determine the density of this hydrocarbon in the liquid state; we found that it was 0.861 at 14°. M. Delalande had found 0.860 at 15° for camphogen. The coincidence of the two densities is perfect. We have also determined the boiling point of cymene with the aid of the same thermometer used by M. Delalande; we have found it to be 175°, that is to say, the same point at which camphogen boils.
>
> Cymene and camphogen have thus the same composition, the same vapour and liquid densities, the same boiling point, the same chemical properties; everything leads us to believe that they are really identical." (75)

The substitution theory. August Laurent probably attended one or more of Dumas' courses at the Athénée and the Collège de France while he was an external student at the Ecole des Mines. It is generally agreed that he was attracted to a career in organic chemistry by his contact with the chemist, both as a student and as a répétiteur at the Ecole Centrale. Many of Dumas' attitudes towards chemical theory became his own and were developed while he continued his research. He was particularly impressed with the ether and amide theories, the core of his teacher's investigations at the time. Working in a laboratory of the Ecole Centrale under Dumas' direction, he mastered

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74. "Un acide nouveau dérivé de camphogène". Loc.cit.(10-71), 368-72 (368).

75. Ibid., 372.

the analytical and research techniques necessary for research in organic chemistry, particularly the vapour density determinations that were indispensable for obtaining correct molecular formulas for organic compounds. There too he became proficient in the use of chlorine, bromine, iodine, nitric acid and various oxidizing agents, whose reactions with naphthalene and benzene provided him with material not only for a doctorate but the work of his brief lifetime. It was Dumas who directed him towards the chlorination of naphthalene and gave him a place at the Ecole Centrale to undertake the unpleasant task of isolating large quantities of naphthalene from coal-tar by chlorinating it. But more than anything else, it was Dumas' substitution theory that guided Laurent so effectively in the preparation of hundreds of compounds, a theory to which he made his own contributions that led to his method of organic classification (76).

Forced by political events of 1831 to flee from Italy, Faustino Malaguti was accepted by Gay-Lussac in his laboratory as an assistant to Pelouze while he attended lectures at the Ecole Polytechnique. There Dumas came to appreciate his ability and when Laurent left his position at the porcelain factory in Sèvres, it was given to Malaguti. Much of his research there was on organic acids and ethers initially, in which he accepted Dumas' theories, but in 1837 he read his first memoir on the chlorination of ethers and for many years this was his major research interest. In 1839 he completed his thesis for the doctorate on the topic (77). In it he indicated

76. The role played by Laurent in the development of the substitution theory and his relationship with Dumas have been discussed in Chapter 8.

77. Action du chlore sur plusieurs substances ethérées et sur le méthylal, Paris, 15 April 1839. Ann. Chim. Phys., 70 (1839), 337-406. His physics thesis was related: Premier mémoire sur la faculté qu'ont certains liquides de retarder les effets chimiques de la lumière diffuse, Paris 26 July 1839. Ann. Chim. Phys., 72 (1839), 5-27.

the reason for his study of ethers for four years:

> "I was sustained, too, by the hope that the new facts that I happened to discover in the course of my experiments, whatever their importance may have been, may also have been useful in the examination of the question of ethers which has fixed the attention of chemists so profoundly in recent times." (78)

Malaguti's work did little to clarify the ether theory, but it did provide further proof for the substitution theory, and Dumas did not fail to capitalise on this in his dispute with Berzelius (79).

In 1822 Humboldt had directed Dumas' steps to Paris. Now the chemist was given the opportunity to reciprocate the kindness by accepting a Polish youth, Philippe Walter, in his laboratory at Humboldt's request. After unofficially assisting at the Ecole Centrale for a time he was made head of chemical work. That year he began research on a chromium compound that was useful as a reagent in organic chemistry (80). In 1840 he discovered a new kind of substitution reaction, in which anhydrous sulphuric acid (SO^3) displaced carbonic oxide (C^2O^2) from anhydrous camphoric acid. Walter noted: "This reaction ... is without analogy in organic chemistry in this, that substitution for carbon occurs, not hydrogen ..." (81). Unfortunately, before Walter published the remark, Dumas had used it to indicate that even carbon could be replaced by substitution and he soon regretted it (82).

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78. Ibid.

79. See pp. 325-26. In 1842 Malaguti left Sèvres and in 1845 he accepted a chair in the Faculty of Sciences in Rennes.

80. Walter acknowledged: "If I have dared to approach this topic, if I have undertaken some research to complete the history of this substance, I owe it to the encouragement of one of these chemists [Dumas] who has honoured me with his kindness and friendship." Ann. Chim. Phys., 66 (1837), 387-96.

81. Ibid., 74 (1840), 38-52 (39).

82. See Chapter 8, footnote 125.

Undoubtedly this work was to be part of his doctoral thesis, but he died before it was completed and apparently never earned the doctorate.

Charles Gerhardt became enamoured of Dumas' substitution theory almost from the time of his arrival in Paris. In a memoir on helenin he indicated his appreciation of the theory:

> "These facts are new evidence in favour of two fundamental propositions of organic chemistry that M. Dumas has already pointed out: They are wholly in conformity with substitutions and demonstrate the constancy of chemical properties in derived substances of a type by substitution. Indeed, helenin unites directly with chlorhydric acid; chlorinated helenin by substitution remains combined with hydrochloric acid from the moment that the latter is formed." (83)

In the article immediately following, Gerhardt mentioned that water was formed whenever acids reacted with neutral organic substances (84). Thus nitric acid, in reacting with benzene, formed water along with nitrobenzene. Later he studied these as double decomposition and elimination reactions.

Another application of the law made by a student must be considered. In 1844 Melsens was able to reconvert chloracetic acid into acetic acid, thus confirming that hydrogen and chlorine were 'playing the same role'. Melsens observed:

> "In taking the theory of types and the law of substitution as guides, acetic acid should necessarily be produced by substituting hydrogen for chlorine in chloracetic acid. This prediction has been verified by experiment." (85)

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83. Ann. Chim. Phys., 72 (1839), 163-83 (178). In his thesis he extended the work: Recherches chimiques sur l'hellénine, principe concret de la racine d'aunée, et sur quelques composés congénères, Paris, 8 April 1841.

84. Ann. Chim. Phys., 72 (1839), 184-215 (188).

85. Ibid., 10 (1844), 233-37 (233). He added: "This salt [silver chloroacetate] was prepared from the potassium chloroacetate that M. Dumas had analysed in the past, and had the kindness to put at my disposal." Ibid., 234. Melsens passed nascent hydrogen over the acid to bring about the reaction. Partington, op.cit.(2-17), p.364, used this work to indicate that Melsens had been a student of Liebig. In that light, the following unpublished letter from Melsens to Dumas is of some interest: "Giessen, (cont.)

On 20 November 1843 a memoir by Leblanc was read to the Academy on chlorine derivatives of acetic ether (86) in which he reviewed its origins:

> "The roots of the research in this memoir will be found in the period when the attention of chemists was irresistably drawn towards M. Dumas' work on chloracetic acid and that of M. Regnault concerning the action of chlorine on ethers. ... By envisaging that compound ethers are formed of ordinary ether combined with an acid, arguments are found in the facts established by M. Malaguti that are favourable to the opinion that chlorine, in the dark, reacts with the base of compound ethers and not with the acid part. From that time there was interest in obtaining the successive products of the substitution of chlorine for hydrogen, and in seeking to recognise by reactions how the division of the fixed chlorine among the elements of the ether and those of the acid was brought about. M. Dumas was kind enough to encourage me then to undertake some investigations in his laboratory, starting with this viewpoint. ... In this work, I limited my task to the addition of some new facts to the history of acetic ether. If I am not deceived, these facts agree with the views introduced into the science by M. Dumas, and with the beautiful analogies indicated by M. Malaguti." (87)

Leblanc may have been planning to use this work as part of his thesis for the doctorate, but apparently he never completed it (88). He was made

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85. (cont.) 24 August 1841. My dear master: When I received your letter of 29 July I was preparing to leave for Bonn. ... Now I must tell you where I am at concerning my diploma. I could only obtain the diploma of Doctor in Bonn by sending them an original thesis in latin. I would have done it, but finding that I was very near to Giessen, I decided to find out how examinations are given there, if there were any. First I went to the professor of the Faculty of Philosophy, then to the dean and finally to M. Liebig. M. Liebig asked me to return the next day for an interview; following our conversation he told me that I could tell the dean of the Faculty that he dispensed me from any further examination, and that if the Faculty agreed, he could grant me the doctorate without any other examination. The dean asked me to return today and advised me that everything would go as I wished, but that certificates of the courses I have followed would be necessary. I am writing, my dear teacher, to ask you for this certificate. I hope that I will receive it as quickly as possible, so that I can leave Giessen to spend a few more weeks with my family before returning to my studies. ... This will be yet another kindness to add to those for which I am already indebted to you." Arch. Acad. Sci., Dossier Melsens (Fonds Dumas).

86. Ann. Chim. Phys., 10 (1844), 197-221. An earlier version appeared in Proc. Verb. Soc. Philom., 1842, 117-20.

87. Loc.cit.(10-86), 197, 198, 220.

88. Leblanc noted that Malaguti's research on chloroxalic ether had reduced the importance of his own work.

répétiteur at the Ecole Centrale and the Ecole Polytechnique in 1845. In 1854 he became head of chemical work at the former, where he was appointed assistant professor of analytical chemistry in 1865 and professor in 1873.

The type theory. Laurent's crystallographic background had led him to reject Berzelius' electrochemical dualism as a useful tool by 1836 when he announced his theory of fundamental radicals (89). Thus Laurent adopted a unitary approach at least two years before Dumas had on the strength of his preparation of chloracetic acid in 1838. When Dumas announced the type theory a little later and described it in 1840, Laurent objected strongly that he had been given no credit for his research, that the type theory was no more than a restatement of the ideas associated with his fundamental radicals. Giving reasons for his rejection of Laurent's radicals before 1838, Dumas pointed out that he still could not accept them (90). He continued the development of his type theory with the help of three of his students, Stas, Péligot and Piria who collaborated with him on particular aspects of the investigation (91). The two dimensional organisation of what are now called aliphatic acids and

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89. The fundamental radical was the hydrocarbon from which a compound was derived by replacing one or more of its hydrogen atoms with another element (e.g., Cl) or radical (N^2O^4).

90. Comptes Rendus, 10 (1840), 521-23. It is now known that naphthalene forms both substitution and addition compounds, as does ethylene. Dumas recognised a difference in 'saturation', but could not explain it. Without an understanding of the cause for this difference, Laurent's position was not a strong one.

91. See Chapter 8. Piria, who had already assisted Dumas in testing Laurent's ideas on fundamental radicals (Ibid., 522), left Paris in the summer of 1839, just after Dumas' first memoir on types appeared. Piria wrote from Naples on 9 October 1839: "For three months I have toured Sicily ... I would very much like to do some experiments to finish what remains for us on tartrates, but it is not at all possible because I do not have a laboratory and do not know how long it will be before I will be able to do an analysis." Arch. Acad. Sci., Dossier Piria, (Fonds Dumas). Publication of their research on the topic was delayed in the hope that they would be able to complete it together, but Dumas finally accepted the fact that (cont.)

their derivatives received the final extension given by Dumas in his law of fatty acids (92). Undoubtedly Laurent referred to it when he drew up his classification of organic compounds two years later (93). Gerhardt was not sensitive to the value of Dumas' law when he first encountered it, suggesting that it was no law at all, but in 1845 he 'originated' a system of homologous series based on the same principles, using C = 12 and two volume formulas so that the difference from one member of a series to the next was CH_2 rather than C^4H^4 (94).

The atomic weight of carbon. As Dumas became more involved with the investigation of organic compounds having high molecular weights, he found that Berzelius' value for the atomic weight of carbon was becoming more difficult to accept. When he finally undertook the correction of this value, several of his students were among those who undertook fresh analyses of many of those compounds already studied, while the new value was used in their still unpublished research. In a note added to the posthumous publication of Delalande's research on the action of potash on camphor, Dumas wrote that

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91. (cont.) this would not happen, and published it as a fifth memoir on types. In it he included some work by Cahours, Melsens and Walter that had been done in the interval and made some other minor additions.

92. One of Dumas' students, Fleurant Victor André Edouard Gillot Saint Evre (1817-?), used the law in 1847 to correct the formula of an acid from cocoa-fat ($C^{44}H^{44}O^4$) so that it fitted into the series just before lauric acid. Saint Evre's doctoral thesis was Recherches sur l'huile essentielle de sasafras, 23 March 1846. Preliminary research for it was published, Ann. Chim. Phys., (1844), 107-13.

93. Laurent, "Classification chimique", Ibid., 19 (1844), 1089-1106.

94. Ibid., 14 (1845), 107-14. For the remaining ten years of his life, Gerhardt directed his efforts towards the development of the notion of homologous series, and his type theory as bases for a natural classification of organic compounds. A brief discussion of this aspect of his research has been undertaken recently by Fisher, N., "Organic Classification before Kekulé", Part 2, Ambix, 20 (1973), 209-33.

Berzelius' weight for carbon had been retained only because "we have changed nothing in editing it for we have no doubt about the formula that he adopted for campholic acid" (95). Gerhardt, Cahours, Walter, Deville, Laurent and Leblanc quickly published memoirs in which the new value was used. Bernhard Karl Lewy (1818-1863), a student of Dumas from Copenhagen wrote:

> "The modification of the atomic weight for carbon by MM. Dumas and Stas and the improvements made in organic analysis introduced by these chemists have led me to analyse [paraffin] again. ... All the analyses that I am reporting have been done in M. Dumas' laboratory; I owe the various samples of paraffin used for the analyses to his kindness. Some of these samples were prepared by M. Malaguti ... and others I purified myself." (96)

As late as 1844 research on helenin was undertaken by Gerhardt because of the change in weight of carbon (97).

The chemistry of living things. From the time he began teaching in the Faculty of Medicine, Dumas again exhibited a special interest in the chemistry of living things, collaborating with Boussingault on several memoirs. Among them was one on the composition of air, one of the media linking plants and animals in a chemical cycle. This work involved research by Marignac in Geneva (98), Piria in Italy (99), Stas in Brussels,

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95. Ibid., 1 (January 1841), 127.

96. "Note sur la composition de la paraffine", Ibid., 5 (1842), 395-99 (396). A vapour density oscillating between 10 and 11.8 made a decision on the formula impossible though he suggested some possibilities. He did not realise that he was working with a mixture of hydrocarbons with close melting points.

97. Ibid., 12 (1844), 188-92. It also allowed him to change his formulas for helenin and related compounds to his new notation.

98. Marignac wrote to Dumas: "I wanted to write to you a long time ago, but I waited until I could tell you that I was ready to begin the work in which you have invited me to take part. My preparations have taken a long time ... but everything is finally ready and I have already obtained results from three analyses of the air in Geneva. I did them to get used to this kind of experiment." Arch. Acad. Sci., Dossier Marignac, (Fonds Dumas).

Lewy in Copenhagen (100) and Leblanc (101). Very likely a study in silviculture done in Dumas' laboratory by Jean Pierre Eugène Napoléon Chevandier de Valdrome (1810-1878), a student at the Ecole Centrale and répétiteur in chemistry there (1833-34), was related to it (102). Dumas had planned to do

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99. After he had been invited to participate, Piria wrote on 29 June 1841: "Count on my cooperation. I even hope to be in a position to send you numerical results on the composition of air in Naples following the very simple and ingenious procedure that you have indicated." Arch. Acad. Sci., Dossier Piria (Fonds Dumas). On 4 August he sent a long letter writing about the need for a balance, since the one offered by the Naples Academy of Sciences was useless. After discussing the problems involved, he ended with the good news that the Academy had just voted to set aside money for instruments and the first purchased would be a balance to be bought in Paris so that he could participate in the project of the Paris Academy of Sciences under Dumas' direction.

100. Lewy had worked with Dumas in 1840 and 1841. In a long letter from Copenhagen on 19 August 1841 he wrote to Dumas: "I will never forget the kindness with which you welcomed me from the first day that I had the pleasure and honour of meeting you; I have lost my father, but God has given me you. Though I have travelled all around Europe, I have never found anyone who has done as much for me as you have." Arch. Acad. Sci., Dossier Lewy (Fonds Dumas). In this and the remaining letters that year, he described the difficulties that he was having, but finally on 7 August 1843, Lewy read a memoir to the Academy on the composition of air: "Deeply aware of the honour accorded me by the Academy when I was given the task of analysing the air in Copenhagen and over the North Sea, I am giving an account today of the results I have obtained. I am happy to be able to add that M. Dumas kindly had me analyse air collected in Guadeloupe ...". Ann. Chim. Phys., 8 (1843), 425-62 (425). His results agreed with those of Dumas, Boussingault, Stas, Marignac, Carl Emanuel Brunner (1796-1867) in Berne and Verver in Groningen. In 1846 he determined the composition of the gases in seawater at various times of day.

101. Leblanc did a number of analyses of confined air in Dumas' lecture hall, in the Sorbonne under various conditions and in other closed rooms of different kinds (the opera, a bedroom, military stables, etc.). The gases were collected in large glass bottles and analysed in the laboratory. Leblanc noted: "This research has been done in M. Dumas laboratory, in his presence and with his kind support." Ibid., 5 (1842), 223-68 (223). They were partly designed as air pollution studies to assist Péclet in his research on ventilation. Later Leblanc greatly simplified the procedure so that gases could be collected and analysed on the site, very quickly.

102. Ibid., 10 (1844), 129-62. His purpose was to find the average annual yield of a hectare of forest in terms of carbon, hydrogen, oxygen, nitrogen and ash. He noted that he had undertaken the work "with the guidance and kind support of M. Dumas ... All the chemical parts of the research has been done in the presence of M. Dumas, who very kindly put his laboratory at my disposal, and with the collaboration of M. Melsens." Ibid., 130, 132.

an intensive study with Boussingault of neutral nitrogenous substances as part of the physiological aspects associated with this research, but when his friend was unable to join him, he invited Cahours to collaborate with him in over 200 analyses of these substances. Another of Dumas' students, Saint Evre, helped them in this difficult and wearisome work. As another part of the programme, the chemical statics of living beings, Dumas endeavoured to show that fats are absorbed from plants by animals and produced by them. He invited Lewy to assist him in his important experiments with bees in 1843, including the determination of the amount of wax present before and after feeding.

Prout's hypothesis. His discovery that the atomic weight of carbon was an integral value, and that of hydrogen very close to it led Dumas to a deeper interest in Prout's hypothesis in 1843 and he called upon all chemists, but particularly his students, to test the theory in the laboratory. Even before this invitation was expressed publicly, Péligot, in his research on uranium had determined its atomic weight and commented:

> "This number is 750 [O = 100]; consequently it is a multiple by 60 of the proportional number of hydrogen as M. Dumas has established; the question of whether proportional numbers are multiples of hydrogen is today a controversial one; beyond doubt this work provides evidence favouring the affirmative." (103)

Jacquelin was another of Dumas' students who redetermined an atomic weight (zinc) before Dumas had formalised his request (104). Not long afterward Favre, "who had been inspired by Jean Dumas' lectures in chemistry at the

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103. Ann. Chim. Phys., 5 (1842), 5-47 (29).

104. Ibid., 7 (1843), 189-207. As préparateur at the Ecole Centrale from 1832 until his retirement in 1873, Jacquelin published many articles on various topics, but never earned a doctorate. In a memoir on starch in 1840 he wrote: "The work I am honoured to present to the Academy is only a rough draft, I hasten to say, through which I have tried to show my deep gratitude to M. Dumas in putting his teaching to use." Ibid., 73 (1840), 167-207 (167). His experiments were done in his own preparations laboratory at the Ecole Centrale. The same year Louis Alphonse Salvetat (1820-?), a graduate of the Ecole Centrale in 1841 and from 1846 a professor there, reported research "sur le poids atomiques du calcium, du barium et du strontium", Comptes Rendus, 17 (1843), 318-19.

School of Medicine in 1840 to turn to chemistry" (105), continued the examination of the weight for zinc:

> "Doctor Prout's hypothesis, taken up again from an experimental viewpoint by M. Dumas, has raised in the hands of the latter chemist, a question of the greatest importance. I have decided to undertake this work because of the experiments published by M. Jacquelain, done to find the equivalent of zinc. ... Certainly only theories sanctioned by experimentation should be accepted; but since experiments have already favoured the theory of equivalent multiples of hydrogen for many substances, new research on the equivalent of zinc was necessary, I believed, in order to confirm or weaken this theory. ... Since the equivalent of carbon has been well established by M. Dumas, I have tried to find the equivalent of zinc from that of carbon." (106)

He emphasised the need for absolute dessication in one part of the procedure, which "is almost impossible if one does not take the precautions indicated by M. Dumas" (107).

Marignac was a student at the Ecole Polytechnique in 1835-37, the two years during which Dumas was professor of chemistry there. After graduating at the head of his year, Marignac spent two years at the Ecole des Mines and did the required year abroad in Sweden, Norway, Denmark and Germany. In addition to meeting Berzelius and Wöhler, he stayed in Giessen for the winter semester (1840-41), then replaced Malaguti at Sèvres for six months before returning to Geneva to become professor of chemistry in the Academy. At Dumas' request he began studies on atomic weight determinations that occupied the rest of his life. On 27 April 1841 Dumas wrote to Auguste De la Rive:

> "I have made the analysis of Iceland spar with great care and using many precautions, as a means of verifying the atomic weight of some metal. It contains 56 lime, 44 carbonic acid, which gives 350 for the atomic weight of lime, i.e., for

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105. Kuslan, L., DSB, Vol. 4, p.554.

106. Ann. Chim. Phys., 10 (1844), 163-74. Favre was préparateur for Péligot at the Conservatoire and worked in Péligot's laboratory. He was a lecture student of Dumas and a second generation research student.

107. Ibid., 170.

> calcium exactly 20 times the atomic weight of hydrogen: 12.5 x 20 = 250. I have used 60 gr. of spar for each analysis and I can only be wrong in the centigrammes. M. Berzelius is mistaken by 2% in the atom of lime.
>
> You see why I wanted to make the metals that you would like to have; they were necessary for my experiments; but maybe you can also see why I could not do it. Anyway, Marignac has the task and he will expedite it. Arrange Marignac's affairs in Geneva so that he will have a peaceful existence and the time to work. You are too demanding when it comes to lectures and too tight-fisted in the matter of salaries." (108)

Many of Marignac's memoirs appeared in Swiss journals. Berzelius wrote of his work:

> "I place the highest value on your experiments concerned with atomic weights; the patience with which you repeat each experiment many times, the wisdom with which you vary your methods and the conscientious manner with which you report the numbers obtained from the balance must assure you of the complete confidence of chemists." (109)

He found atomic weights for 28 of the elements, always working alone with no collaborator, assistant or even a laboratory boy. He began his studies with an inclination towards Prout's hypothesis. For a long time he could find no evidence certain enough to cause him to reject it until values obtained by Stas led him to doubt its validity.

Stas too had put the determination of atomic weights at the centre of his research activities. Such was the respect for his ability engendered among chemists that the weights for the 12 elements that he found in the period prior to 1865 were accepted for nearly half a century (110). Following Dumas, he began his studies with "an almost complete confidence in the

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108. Bibl. de Genève, Collection De la Rive, Lettres adressées à Auguste De la Rive, Ms 2315, fol. 301-02.

109. Ador, op.cit.(1-35), p.15.

110. Ibid.

exactness of Prout's principle" (111), but his experimental measurements gradually forced him to reject it. Nevertheless, in 1887, when John William Mallet (1832-1912) "urged upon him the improbability of the near approach to integer values for so many atomic weights being due to chance", Stas responded: "One must believe that there is something behind it." (112)

Finally, analyses done by Edmé Jules Maumené (1818-?) in 1846 should be mentioned because he summarised the work of others who had experimented on chemical equivalents after the new weight had been assigned to carbon. He noted that the modification of some of the equivalents had brought them "appreciably closer to the values predicted by the theory" (113). He acknowledged his debt to Dumas:

> "I did not have the pleasure of working under the immediate direction of M. Dumas, but I have asked for his advice on many occasions; he has given it with such kindness that I would fail in my duty were I not to indicate here how grateful I am to him." (114)

In referring to the memoirs of Pelouze and Marignac, he wrote: "It seemed to me that the deductions presented by these well-known chemists did not rest on absolutely indisputable foundations." (115) The values he obtained seemed to indicate that he had been successful (chlorine 71, potassium 78, silver

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111. Partington, op.cit.(2-17), p.876, notes that the research was summarised in two publications "Recherches sur les rapports réciproques des poids atomiques", Bull. Acad. Roy. Belg., 10 (1860), 208-336 and "Nouvelles Recherches sur les lois des proportions chimiques sur les poids atomiques et leurs rapports mutuels", Mém. Acad. Roy. Belg., 35 (1865), 3ff.

112. J. Chem. Soc., 63(1) (1893), 35.

113. Ann. Chim. Phys., 18 (September 1846), 41-79 (41). This was his thesis: Mémoire sur les equivalents chimiques du chlore, de l'argent et du potassium, 24 August 1846.

114. Loc.cit.(10-112), 79.

115. Ibid., 43.

216), but Stas showed later that these were inexact.

Until 1862 Dumas continued guiding students in the research laboratory founded for the Faculty of Sciences in 1855 and put under his direction (116). He never ceased his efforts to discover new sources of error in measurements of atomic weights. When in 1880 he discovered that some metals retain gases by occlusion (117), his former student, Stas, wrote to him expressing both admiration and great interest (118).

By 1846 there had been enough changes in atomic weights to suggest that a re-examination of their relationships with atomic volumes would be profitable. This was done by another of Dumas' students, Jean Pierre Edouard Bernard Filhol (1814-1883) who took as his objectives a summary of the works of those who had examined the relationships involved (119) and the validity of their claims, especially those of Kopp and to present some of his own ideas (120). Although small adjustments in densities would have greatly enhanced the value of his conclusions, he avoided taking that step:

> "In my opinion, the best means of arriving at the truth consists in abstaining as much as possible from hypotheses,

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116. See note 20.

117. "Sur les gaz retenus par occlusion dans l'aluminium et le magnésium", Comptes Rendus, 90 (1880), 1027-29.

118. Arch. Acad. Sci., Dossier Stas (Fonds Dumas).

119. Dumas, Boullay, Adolph Theodor Kupffer (1799-1865), Persoz, Heinrich Georg Friedrich Schröder (1810-1885), Kopp and Christoph Friedrich Ammermüller (1809-?). Gerhardt, J. Pharm., 11 (1847), 381-85, studied the atomic volume of some isomorphic oxides, probably as a result of Filhol's memoir, Ann. Chim. Phys., 31 (1847), 415-39 (415-16).

120. This was a development of his second thesis: Etudes sur les changements de volume qu'éprouvent les corps pendant la combinaison, Paris, 21 October 1844.

> trying above all to determine very exactly the densities that must serve as a basis for calculation." (121)

Though it is not easy to consider Wurtz's relationship to Dumas in one of the categories used, it would be unpardonable to omit his name from our discussion. As one author has put it: "Dumas was the Victor Hugo of chemistry and Wurtz was his Sainte Beuve." (122) Wurtz studied in the Faculty of Medicine in his native Strasbourg where he was head of chemical work from 1839 to 1844. During the summer of 1842 he began research on the acids of phosphorus in Liebig's laboratory and in 1843 became Doctor of Medicine (123). After translating Gerhardt's Précis de chimie organique into German (124), he sought the author's guidance on how to begin a career in chemistry. In 1844, on Gerhardt's recommendation he went to live in Paris. Under Dumas' direction he continued studying the acids of phosphorus and in his article describing the research he wrote:

> "I have been doing this work in M. Dumas' private laboratory for a whole year. I have been able to undertake and complete my research because of the support and kindly advice of that well-known savant. It is with pleasure that I take this opportunity to offer him publicly my deep gratitude." (125)

In 1845 Wurtz became préparateur for Dumas' course in the Faculty of Medicine and obtained the use of a small room that he was able to convert into a

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121. Loc.cit.(10-119), 438.

122. Urbain, G., "Jean Baptiste Dumas (1800-1884) et Charles Adolphe Wurtz (1817-1884): Leur rôle dans l'histoire des théories atomiques et moléculaires", Bull. Soc. Chim., 1 (1934), 1425-46 (1427).

123. Part of his thesis, on fibrin and albumin studies, was published. Ann. Chim. Phys., 11 (1844), 253-55 and 12 (1844), 217-23.

124. Gerhardt, Précis de chimie organique, 2 Vols., Paris, 1844-46 (German transl., 2 Vols., Strasbourg, 1844-46).

125. "Recherches sur la constitution des acides du phosphore", Ann. Chim. Phys., 16 (1846), 190-231 (191).

laboratory. Appointed head of chemical work at the Ecole Centrale (1846-51), he soon became an agrégé in the Faculty of Sciences (1847). By this time Dumas had begun work on the hydrolysis of cyanides with Leblanc and Malaguti (126) and similar studies were taken up by another of his students, Dominique François Jules Bouis (1822-1886) (127). In 1849 Wurtz discovered methylamine and ethylamine, thus paving the way for Hofmann's important identification of the ammonia type, and eventually Gerhardt's more general type theory. Wurtz's interest in the aliphatic organic compounds, especially the alcohols and glycols (he first prepared ethylene glycol) gave rise to his most important discoveries. He also devised the method of synthesis named after him whereby alkyl halides are combined by reaction with metallic sodium. As Dumas' successor in 1852 he retained the chair of chemistry in the Faculty of Medicine until his death. He is regarded as the principle founder of the Société chimique, and Dumas was its first president. Just before his own death in 1884, he gave a discourse in praise of Dumas in the name of the University. In it he recalled his days in Dumas' laboratory:

> "He appeared to us to be like a courageous athlete, a conqueror when we gathered around him in his modest laboratory in the rue Cuvier which he had set up at his own expense, and from which flowed many memoirs and followers." (128)

For twenty years Dumas attracted young men to careers in chemistry by his teaching. Many of them began chemical research under his direction, often

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126. At the time Dumas had finished his Traité and had begun to do research on reactions of phosphorus pentoxide with ammonia salts, alone and with his two students. The work led to the synthesis of propionic acid. Comptes Rendus, 25 (1847), 383-85; 442-44; 656-60; 781-84.

127. The chlorination of mercury cyanide. Ann. Chim. Phys., 20 (1847), 446-59 and 21 (1847), 111-19. "Given by Dumas the task of studying some ethers derived from wood spirit ..." Ibid., 112.

128. Comptes Rendus, 98 (1884), 940-44 (942).

in his laboratory and continued to pursue the kind of studies they had begun there. In doing so, sometimes quietly, sometimes with daring, they built on the foundations of theoretical organic chemistry that had been laid by Dumas. Most of them went on to lecture to a new generation of students, guiding some of them in research, and in this respect Deville, the practical inorganic chemist, and Wurtz, the theoretical organic chemist, excelled. It is, however, most fitting to end with part of a discourse given by Melsens to his students at the State School for Agriculture and Veterinary Medicine in Belgium:

> "For those of us who modestly aspired to be worthy of the title 'student of Dumas' one day, it was not enough to admire that very large and vigorous group; to understand the bold but sure views of that noble and lofty intelligence, that guide who has illuminated the pathway to truth. We were also expected to make every effort to pass on a little of the knowledge we had received in such great measure in his inimitable lectures (129). This was the serious obligation that we had even when we were students. It carried with it a great responsibility ...
>
> Admire his unchanging kindness towards youth, but count the sacrifices that it cost him. In opening his private laboratory to young chemists, he knew how to encourage them by his example, by his love for work; he knew how to guide them in their research, but this guide both in work and in study became their friend, their mainstay in life; he encouraged them with a single word, with that superiority that is characteristic of a superior intelligence joined to a great spirit, a pure heart. ... For you and for us, I will try to bear with honour the title of student of Dumas." (130)

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129. Among the opportunities they were given to transmit information was through the translation of foreign articles into French for publication in the Annales de Chimie et de Physique. Walter, Melsens, Leblanc and Saint Evre were among those who were invited to do so.

130. A copy of this discourse, given on 2 February 1847, was included with a letter to Dumas dated 10 February. Arch. Acad. Sci., Dossier Melsens (Fonds Dumas).

TABLE 10-1. Dumas' Research Students Mentioned in this Thesis.

Name	Birth	Death	Doctorate	Academy of Sciences
Bineau, Amand	1812	1861	1837	
Boullay, Polydore	1806	1835	1830	
Bouis, Jules	1822	1886	1855	
Cahours, Auguste	1813	1891	1845	Mem.,Chem., 1868
Chevandier, Eugène	1810	1878		Corr.,Econ.Rur.,1857
Darcet, Félix	1807?	1846		
Delalande, Z.	?	1839		
Favre, Pierre	1813	1880	1853	Corr.,Chem., 1863
Filhol, Edouard	1814	1883	1844	
Gerhardt, Charles	1816	1856	1841	Corr.,Chem., 1856
Hervé de la Provostaye, Frédéric	1812	1863	1840	
Jacquelin, Victor	1804	1885		
Laurent, Auguste	1808	1853	1837	Corr.,Chem., 1845
Leblanc, Félix	1813	1886		
Malaguti, Faustino (naturalised)	1802	1878	1839	Corr.,Chem., 1855
Masson, Antoine	1806	1860	1839	
Maumené, Jules	1818	?	1846	
Péligot, Eugène	1811	1890	1838	Mem.,Econ.Rur.,1852
Sainte Claire Deville, Henri	1818	1881	1841	Mem.,Miner., 1861
Saint Evre, Edouard	1817	?	1846	
Salvetat, Alphonse	1820	?	1843	
Wurtz, Adolphe	1817	1884	1844 D.M.	Mem.,Chem., 1867

Lewy, Bernhardt	1818	1863	Denmark	
Marignac, Charles	1817	1894	Switzerland	Corr.,Chem., 1866
Melsens, Louis	1814	1886	Belgium	
Piria, Raphael	1815	1865	Italy	
Stas, Jean	1813	1891	Belgium	Corr.,Chem., 1880
Walter, Philippe	1810	1847	Poland	

BIBLIOGRAPHY

PRINCIPAL BIBLIOGRAPHICAL SOURCES

Maindron, Ernest, L'Oeuvre de Jean Baptiste Dumas, Paris, 1886. Prepared at Dumas' request, Maindron's list includes 853 books, articles, reports, discourses and other publications by Dumas, most of them scientific or science related. There are a few duplications, omissions (e.g. the article by Dumas and LeRoyer on atomic volumes) and errors (e.g. the source and date for the article with Guillemin on hybrids) but the list is generally reliable and must serve as a foundation for any serious study of Dumas' work. Maindron normally refers to only one source when locating a printed work, a French publication by preference. Only the first page of the work is given.

The Royal Society Catalogue of Scientific Papers, (1800-1900), 19 Vols., London, 1863-1925 (lists the more important journal articles complementing Maindron by listing other journals in which the article was reprinted (with or without translation) or abstracted. The 187 listings included 46 for which Dumas collaborated with others, half with students. Final pages are given.

Général J.B. Dumas included and extended Maindron's list in his biography of Dumas (q.v.).

The catalogues and card files of the Bibliothèque Nationale and the Bibliothèque de l'Institut contain some works of Dumas not listed by Maindron or Général Dumas.

MAJOR PUBLISHED SCIENTIFIC WORKS

Traité de Chimie appliquée aux Arts, 8 Volumes, in 8°, Atlas in 4°, Paris (Béchet jeune; printers: Cosson 1-5; Locquin 6-7; À Bailly 8).

Volume 1: Pp vii-x (Preface) + xiii-xv (Table of Contents) + i-lxxx (Introduction) + 689. 25 October 1828.

Volume 2: Pp vii + 808. 3 July 1830.

Volume 3: Pp vii + 784. 15 October 1831.

Volume 4: Pp vii + 744. 20 July 1833.

Volume 5: Pp viii + 819. 18 April 1835.

Volume 6: Pp vi + 752. 8 April 1843.

Volume 7: Pp ix + 716. 22 June 1844.

Volume 8: Pp viii + 760. 25 April 1846.

Atlas: Pp 252 + 148 figures. With Volumes 1, 2, 4, 6, 8.

Other Editions and Translations: Only one edition of the Traité was published in France. The work was subdivided into books. Volume 8 consisted of two books, XII and XIII and these were also published as separate works in 1846, retaining the original pagination: Book XII (pp. 1-416) as Précis de l'art de la teinture, Paris (Béchet jeune), 1846 and Book XIII (pp. 417-760) as Chimie physiologique et médicale, Paris (Béchet jeune), 1846. In 1847 part of Volume 1 was reprinted and all of Volume 2. In 1847 a Belgian edition appeared (Liège) with the atlas in two volumes. A German translation was made by Büchner, (Nürnberg, 1843-50, in 8°). Hoffman noted that a German translation was made by Gottlieb Alexander and Friedrich Engelhart and that the Traité appeared "in several languages". There was no English translation.

Leçons sur la Philosophie chimique, professées au Collège de France par M. Dumas, recueillies par M. Bineau, Paris (Ebrard), (1837), pp. 430, in 8°. An edition appeared with Béchet as publisher.

Other Editions and Translations:

__,_ Bruxelles, Société Belge de Librairie (Hauman et Comp^e.), 1839, pp.367.

__,_ Paris (Gauthier-Villars), 1878, pp. 470, in 8°.

__ par J.B. Dumas, Avant-propos par M. Georges Urbain, Paris (Gauthier-Villars), 1937, pp. xxviii, 270. Les Classiques de la Découverte Scientifique. Original text, preceded by a favourable critique, with particular stress on Dumas' attitude towards atomism and affinity.

__,_ Bruxelles, (Editions Culture et Civilisation), 1972. An exact reprint of the 1839 edition with a 19 page introduction by Albert Bruylants (pages not numbered).

A German edition (transl. Rammelsberg) was mentioned by Hofmann who indicated that the work had appeared in several translations.

Essai de statique chimique des êtres organisés. This work first appeared in the Journal des Débats the day it was given, then in the Annales des Sciences Naturelles (Zoology), 16 (1841), 33-61. At the same time it was published as a pamphlet:

Leçon sur la statique chimique des êtres organisés, professée par M. Dumas le 20 août 1841 pour la clôture de son cours à l'Ecole de Médecine, Paris (Fortin Masson et Cie), 1841, pp. 48, in 8°.

Other Editions and Translations:

Essai de statique chimique des êtres organisés, leçon professée par M. J. Dumas le 20 août 1841, pour la clôture de son cours à l'Ecole de Médecine, deuxième édition, augmentée de documents numériques, Paris (Fortin, Masson et Cie), 1842, pp. viii + 88, in 8°.

___, par MM. Dumas et Boussingault, leçon professée par M. Dumas, le 20 août 1841, pour la clôture de son cours à l'Ecole de Médecine, troisième édition, augmentée de nouveaux documents, Paris (Fortin, Masson et Cie), 1844, pp. viii + 147, in 8°.

An exact reprint of the second edition was included with the Leçons in the 1972 edition. An English translation of the third edition appeared in 1844: Chemical and Physiological Balance of Organic Nature: an Essay, Third edition, London, 1844, pp. , in 8°. The translator is unknown. An Italian edition, Pavia, Stamp, Fusi, s.d., exists, and both Hofmann and Leblanc have noted that the Essai was published in many foreign languages.

Mémoires de Chimie, par M. J. Dumas, Membre de l'Institut, Paris (Béchet jeune and Fortin, Masson et Cie), 1843, pp. x + 412, 7 figures. The introduction by Dumas preceded the following collection of his memoires:

Theses published by Dumas:

For the diploma Doctor of Medicine: Propositions de Physiologie et de Chimie Médicale, Thèse No. 67. Présentée et soutenue à la Faculté de Médecine de Paris le 12 avril 1832, pour obtenir le grade de Docteur en Médecine, Paris (Didot le jeune), 1832, pp. 23, in 4°.

For the degree Doctor of Sciences (Two were required): Dissertation sur la densité de la vapeur de quelques corps simples, Thèse No. 28. Présentée et soutenue à la Faculté des Sciences de Paris le 9 juillet, pour obtenir le degré de Docteur ès Sciences, Paris (veuve Thuau), 1832, pp. 15, in 8°. Mémoire sur les substances végétales qui se rapprochent du camphre et sur quelques huiles essentielles, Thèse No. 28. Présentée et soutenue à la Faculté des Sciences de Paris le 11 juillet 1832 pour obtenir le degré de Docteur ès Sciences, Paris (veuve Thuau), 1832, pp. 23, in 8°.

In competition for a chair in the Faculty of Medicine: De l'action du calorique sur les corps organiques. Applications aux opérations pharmaceutiques. Thèse présentée et soutenue à la Faculté de Médecine de Paris, le ? mars 1838, concours pour une Chaire de Chimie Organique et de Pharmacie, Paris (Rignoux et Cie), 1838, pp. 110, in 4°.

Periodical Publications

Though many memoirs, journal articles and notes by Dumas have been mentioned in the present work, the following were of particular importance (they are listed chronologically):

1. "Essai sur le volume de l'atome des corps", J. Phys., 92 (1821), 401-11. With Le Royer.

2. "Examen du sang et de son áction dans les divers phénomènes de la vie", Bibl. Univ., 17 (1821), 215-29 and 294-317; 18 (1821), 208-20. With Prevost.

3. "Nouvelle théorie de la génération", Ann. Sci. Nat., 1 (1824), 1-29 and 274-93; 2 (1824), 100-20 and 129-49; 3 (1824), 113-38. With Prevost.

4. "Recherches sur la composition élémentaire et sur quelques propriétés caractéristiques des bases salifiables organiques", Ann. Chim. Phys., 24 (1823), 163-92. With Pelletier.

5. "Mémoire sur les combinaisons du phosphore, particulièrement sur celles de ce corps avec l'hydrogène", Ann. Chim. Phys., 31 (1826), 113-54. In this thesis it has been called the January Memoir.

6. "Mémoire sur quelques points de la théorie atomistique", Ann. Chim. Phys., 33 (1826), 337-91. The October Memoir.

7. "Mémoire sur la formation de l'éther sulfurique", Ann. Chim. Phys., 36 (1827), 294-310. The August Memoir. With Boullay.

8. "Mémoire sur les éthers composés", Ann. Chim. Phys., 37 (1828), 15-53. The December Memoir. With Boullay.

9. "Sur l'oxamide, matière qui se rapproche de quelques substances animales", Ann. Chim. Phys., 44 (1830), 129-43.

10. "Lettre à M. Ampère sur l'isomérie", Ann. Chim. Phys., 47 (1831), 324-35.

11. "Recherches de chimie organique", Ann. Chim. Phys., 56 (1834), 113-54. This memoir on the substitution theory was virtually unchanged when it was printed in Mém. Acad. Sci., 15 (1838), 495-556, an oft-quoted source.

12. "Considérations générales sur la composition théorique des matières organiques", J. Pharm., 20 (1834), 261-94. This was in the May issue and was the third of the articles that were to comprise the first three chapters of his Traité, Vol. 5. The first was in the March issue (pp 129-56) and the second in the April issue (pp 185-223).

13. "Mémoire sur l'esprit de bois et sur les divers composés étheres qui en proviennent", Ann. Chim. Phys., 58 (1835), 5-74.

14. "Rapport sur un mémoire de MM. Pelletier et Ph. Walter relatif aux produits pyrogénés de la résine", Comptes Rendus, 6 (1838), 460-69. Dumas' research in connection with this report led to 19 (below) and thus to much of his research thereafter.

15. "Réponse à la lettre de M. Berzelius [à Pelouze], Comptes Rendus, 6 (1838), 689-702.

16. "Mémoire sur la constitution de quelques corps organiques et sur la théorie des substitutions", Comptes Rendus, 8 (1839), 609-22.

17. "Mémoire sur la loi des substitutions et la théorie des types", Comptes Rendus, 10 (1840), 149-78.

18. "Première mémoire sur les types chimiques", Ann. Chim. Phys., 73 (1840), 73-100.

19. "Deuxième mémoire sur les types chimiques", Ann. Chim. Phys., 73 (1840), 113-66. With Stas.

20. "Recherches sur le véritable poids atomique de carbone", Comptes Rendus, 11 (1840), 991-1008, expanded in Ann. Chim. Phys., 1 (1841), 5-58. With Stas.

21. "Recherches sur la véritable constitution de l'air atmosphérique", Comptes Rendus, 12 (1841), 1005-1025, expanded in Ann. Chim. Phys., 3 (1841), 257-305. With Boussingault.

22. "Loi de composition des principaux acides gras", Comptes Rendus, 15 (1842), 935-36.

23. "Recherches sur la composition de l'eau", Comptes Rendus, 14 (1842), 537-47, comments added in Ann. Chim. Phys., 8 (1843), 189-207.

24. "Mémoire sur les matières azotées neutres de l'organisation", Comptes Rendus, 15 (1842), 976-1000, expanded in Ann. Chim. Phys., 6 (1842), 385-448. With Cahours.

25. "Note sur la production de la cire des abeilles", Comptes Rendus, 17 (1843), 531 and 537-45. With Milne Edwards.

26. "Mémoire sur les équivalents des corps simples", Ann. Chim. Phys., 55 (1859), 129-210.

MAJOR REPORTS ON EDUCATION BEFORE 1850

Extrait des Procès-verbaux des délibérations de la Faculté des Sciences. Agrandissement de la Sorbonne. Séance du 15 novembre 1837. Rapport présenté par M. J.A. Dumas pour être adressé au Ministre de l'Instruction publique au nom de la Faculté des Sciences.

Extrait des Procès-verbaux des délibérations de la Faculté des Sciences. Agrandissement de la Sorbonne. Séance du 18 septembre 1846. Rapport présenté par M. Dumas, conseiller de l'Université, doyen de la Faculté des Sciences de Paris, au nom de la Commission chargée d'examiner la question d'agrandissement des bâtiments de la Sorbonne.

Rapport au ministre de l'Instruction publique, tendant à introduire plusieurs modifications dans l'enseignement de la Faculté des Sciences. Sur la création de plusieurs grades dans la Faculté des Sciences, Paris, 1846.

Ministère de l'Instruction publique, rapport sur l'enseignement scientifique dans les collèges, les écoles intermédiaires et les écoles primaires, Paris, 1847. Présentée à M. le Ministre, le 6 avril 1847.

DISCOURSES AND EULOGIES GIVEN BY DUMAS

Discours et Eloges Académiques, 2 Volumes, Paris (Gauthier-Villars), 1885, in 8°. Those included in these volumes were read to the Academy of Sciences unless otherwise noted:

Volume 1, pp. lii + 314.

Préface (J. Bertrand) v
Discours de réception à l'Académie Française le 1er juin 1876 xi
Auguste Bérard (Faculté de Médecine de Paris, 16 November 1846) 1
Michel Faraday (18 May 1868) 49
Jules Pelouze (11 July 1870) 125
Isidore Geoffroy Saint Hilaire (25 November 1872) 199
Arthur Auguste De la Rive (28 December 1874) 249

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Aléxandre Brongniart et Adolphe Brongniart (23 April 1877) 1-52
Antoine Jérome Balard (10 March 1879) 81-114
Victor Regnault (14 March 1881) 151-200
Charles et Henri Sainte Claire Deville (lu par M. Bertrand, 5 mai 1884) 281-328

Other discourses and eulogies of members of the Academy by Dumas that were of interest to the present work (Institut de France, Académie des Sciences, Funérailles de M.

Pelletier (22 July 1842)
Geoffroy Saint Hilaire (22 June 1844)
d'Arcet (5 August 1844)
le Baron Thenard (23 June 1857) (also Bull. Soc. d'Enc., 4 (1857), 568).
le général Poncelet (24 December 1867)
Claude Bernard (16 February 1878)

Médaille d'honneur offerte à M.

Chevreul (2 September 1872)
Milne Edwards (1881)

Inauguration de la statue de

Thenard (1861) (also Bull. Soc. d'Enc., 8 (1861), 404).
Pasteur (26 June 1882)
Becquerel (24 September 1882)

Funérailles de M. Hippolyte Fourtoul (Moniteur Universelle, 1856, p. 773).
Développements qu'ont reçu quelques-unes des principales découvertes de Thenard (Soc. des Amis des Sciences, Paris, 1861, in 8°, Séance de 22 mars 1861).
Discourse on Faraday, the First Faraday Lecture, 17 June 1869.
Notice sur Antoine César Becquerel (Soc. des Amis des Sciences, Paris, 1880, in 8°, Séance de 31 mars 1880).

MANUSCRIPTS

Archives de l'Académie des Sciences

In 1938, Général Dumas donated most of his grandfather's papers to the Academy of Sciences and Pierre Gauja arranged them in 31 Cartons. An index of the contents of the cartons has been prepared, but greater detail would be necessary to make possible more exact references to the contents. There are few letters written by Dumas in the Archives, but his correspondence must have been voluminous judging from the number of those he received. Besides the three Cartons (28-30) that contain only letters, there are many dossiers of members and corresponding members of the Academy containing letters written by them to Dumas. There is a complete index of all these letters, but there are copies of letters from Dumas and some letters to him in other Cartons, usually in connection with particular work that he was doing at the time. There are also some in Cartons containing information relating to Commissions of which he was a member (e.g., the Gelatin Commission).

The following documents have been specifically referred to in the present work:

Fonds Dumas

Carton 1: Dossier "Marriage, Médaillon, Retraite, divers", Accounts with Béchet Jeune, 1835-45 totalling 2,671.85 francs. Dossier "Annales de L'Industrie, Annales des Sciences et Annales de Chimie", Contracts for publication of the Annales de l'Industrie and the Annales des Sciences Naturelles.

Carton 3: Dossier "Etude microscopique du sang", Article, Développement du coeur et du sang. Dossier "Résection des reins". Notes d'Expériences fait à Genève [Notebook A].

Carton 4: Unpublished memoir, early draft of Memoir 1 (p. 438). Dossier "Mémoires de Dumas sur les Atomes; Mémoire sur l'acide acétique", Unpublished, unfinished "Mémoire sur l'acide acétique, les acétates, l'ésprit pyroacétique, la liqueur fumante de Cadet et la fermentation acétique. Par MM. J. Dumas et Polydore Boullay."

Carton 5: A hard cover 'dossier' containing many loose sheets, among them Malaguti's doctoral thesis.

Carton 7: Dossier "Ether nitrique", a density determination of "éther nitrique bien pur" dated 2 March 1821. Many loose sheets of similar format, some dated, written by Dumas when he was préparateur at the Athénée.

Carton 8: Dossier "Notes d'expériences/Analyses de Z. Delalande ..." A proposed table of contents for the Traité; various drafts of a memoir by Delalande and some of his notes and analyses.

Carton 9: Dossier "J.B. Dumas, Notes d'Expériences". Unlabelled, undated, unpaginated, folio notebook of experiments beginning with research on "Acide carbazotique de Jacquelain".

Carton 10: Dumas' "Cours de Chimie et de Pharmacie, 1838. Notes. F. Leblanc".

Carton 11: Notebook "Cours de chimie appliquée aux arts" (notes taken during Clément's lectures at the Conservatoire, 1823-24.

Dossiers: Boullay, Laurent, Lewy, Liebig, Marignac, Melsens, Pelouze, Piria, Stas, Thenard. Many others were consulted but not cited.

Archives de l'Ecole de Médecine

The contents of the Archives are being transferred to the Archives Nationales at present and are not classified.

Procès-verbaux de l'Assemblée des Professeurs.

Registres d'examen.

Registres d'Inscription.

Archives de l'Ecole Polytechnique

Cartons 1820, 1823, 1824 (1), 1825, 1827, 1830, 1832.

Livre des Cours, 1823-24.

Registre des Plans et Croquis.

Registres du Conseil d'Instruction, 15 May 1821 to 6 December 1827.

Archives du Collège de France

Affiches Générales, D-I-b.

Etats de Traitemens dûs aux Professeurs, C-VII-c.

Registres de Présence, C-VII-d.210.

Registres des Procès-verbaux d'Assemblés, G-II-4.

Archives Nationales

AJ^{16}22: Faculté de Médecine, Concours, 1838.

AJ^{16}24: Faculté de Médecine, Comptes , 1836.

AJ^{16}25: Dossiers 7, 10, 11, 12, 13, 14.

F^{17}21776: Démission, No. 11.

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Correspondance Adolphe Brongniart: Ms 1969.

Geneva: Archives d'Etat de Genève

Etrangers: Ea 1, p. 96, No. 479.

Recensement: F.3, Douane, 1822.

Geneva: Bibliothèque ~~de Genève~~ publique et universitaire de la Ville de Genève.

Collection de B. Reber: Ms 2146; Ms 2145 (Corr. P. F. Tingry).

Collection De la Rive: Ms 2315, fol. 293-94 and 301-02.

Correspondance générale de Daniel Colladon: Ms fr. 3747, fol. 229-33 et v°; Ms fr. 3745, fol. 132-33.

Correspondance de Th. de Saussure: Letter of 25 March 1836.

Manuscrits adressés à Prevost: I, fol. 281-82.

Manuscrits Saussure: 189, pp. 147-48.

Minutes de la Commission chargé de l'Impression des Mémoires de la S.P.H.N. de Genève: SP 30.

Papiers Gosse, Correspondance de Louis André Gosse: Ms. 2662, fol. 130-31; Ms 2663 (H-R), fol. 74-75.

Procès-verbaux de la Societé de Philosophie, Ms. fr. 1679, Note 3-11.

Registres des Séances de la S.P.H.N. de Genève, SP 29.

Unclassified letter (see note 2-75).

BIOGRAPHIES

At the end of his list of Dumas' works, Maindron gave a bibliography of "Notices publiées sur Jean Baptiste Dumas ou sur ses travaux" extending to the end of the year 1885. Of the 46 mentioned, 16 were written before 1884, half of these on the occasion of his reception as a member of the Académie Française. Three of those remaining were versions of Hofmann's monumental biography and the others were brief résumés. Only two are listed below along with a selection from the works listed by Maindron that were written in 1884 and 1885 as well as from the more important notices that have appeared since. Partington, op.cit.(2-17), p. 338, lists others.

1. Hofmann, August Wilhelm, "Scientific Worthies XIV: Jean Baptiste André Dumas", Nature, 21 (Extra Number, 6 February 1880), pp. i-xl. (Though listed as XIV, it should have been XV.) Within a short time the article

was translated into French and appeared in two journals:

a) Chimistes français. Jean Baptiste André Dumas, par A. W. Hofmann. La Revue scientifique, No. 37 (13 mars 1880) and No. 39 (27 mars 1880) in 4°.
b) Les Savants illustres. Jean Baptiste André Dumas, par A.W. Hofmann, Traduit du journal anglais Nature par Charles Baye. Moniteur scientifique (Quesneville) (avril 1880). At the request of Dumas' relatives, Hofmann completed the biography after Dumas' death:
c) Complément de la biographie de Jean Baptiste André Dumas, par M. A. W. Hofmann, Moniteur Scientifique, (mars 1885). Hofmann translated the work into German (with some additions to bring it up to 1884), when Dumas died (Berichte, 17 (1884), 630R ff.). Finally he incorporated the "complément" and made some minor modifications before including it in his Zur Erinnerung an Vorangegangene Freunde, 3 Vols., Brunswick, 1888, Vol. 2, p. 207-397.

Considerable correspondence with Dumas was involved (Arch. Acad. Sci., Fonds Dumas (Dossier Hofmann) indicating that Dumas provided him with many of his papers and read at least parts if not all of the manuscript before it was published. In one of his letters to Dumas he indicated how he came to undertake the task: "In a letter accompanying the portrait [of Dumas], M. Lockyer told me that it would be published in his journal "Nature" and he asked me to write a biographical memoir. I am aware of both the difficulties of such a task and the responsibility of the one who assigned it, but I could not resist the allurement that the thought of such a task has for my imagination. Therefore I have accepted, and I am doing preliminary studies now." (Letter of 20 May 1878). Three months later (August 22) he wrote: "Had I known M. Dumas as I know him today, I would probably have hesitated to undertake a task that I fear is beyond my powers." It was well over a year before he completed the work. There is little to fault in his data. Hofmann was a first rate chemist and cared about accuracy. The style is characteristic of the time, and there are some areas over which he has passed quickly. Despite the lack of supporting references, this must be considered to be the most important biography of Dumas to date. The author of the present work has yet to find a serious error.

2. "Jean Baptiste Dumas", Larousse, op.cit.(3-42), p. 1377-78. ~~Papillon, F.~~
Papillon, F.,

3. "J. Dumas, secrétaire perpétuel de l'Académie des Sciences. Sa vie, ses travaux, son influence", Histoire de la philosophie moderne, 2 Vols., Paris, 1876, Vol. 1, pp. 309-48.

4. Institut de France, Académie des Sciences, Funérailles de M. J. B. Dumas, Paris, 1884, particularly the "Discours de M. Wurtz" and the Discours de M. Melsens". Comptes Rendus, 98 (1884), 933-45.

5. Combérousse, C. de, J. B. Dumas (1800-1884), Paris, 1884, pp. 40. Taken from Le Genie civil.

6. Discours prononcé par M. S. Cannizzaro à la memoire de J. B. Dumas dans la séance du 4 mai 1884 de l'Académie R. des Lyncéens (Lincei). Traduit de l'italien par M. Félix Leblanc. Bull. Soc. Chim., 1884, 130-41. Maindron listed the original.

7. Riche, A., "J. B. Dumas", J. Pharm., 9 (1884), 369.

8. Leblanc, F., "Le Laboratoire et l'enseignement de J. B. Dumas", Bull. Soc. Chim., 1884, 549-59.

9. Grimaux, E., "Note sur l'Oeuvre de M. Dumas", Association française pour l'avancement des Sciences, Compte Rendu de la 13e session: Blois, Paris, 1885, pp. 32.

10. Ronna, A., "J. B. Dumas, agronome", Paris, 1885, pp. 21. Taken from Le Génie civil.

11. Gautier, Armand, Institut de France, Académie des Sciences, Inauguration de la statue de J. B. A. Dumas, Paris, 1889, pp. 49. The text, pp. 1-37, and explanatory notes written afterward by Gautier contain many quotations, particularly from letters written by Dumas to his family, that have been invaluable in the early part of the present work. It was the main discourse during a festival in Alais from 19 to 21 October 1889 (Pasteur was another of the seven speakers from Paris) during which the Lycée J. B. Dumas was also inaugurated.

12. Van Tieghem, Philippe, Notice sur la vie et les travaux de Jean Baptiste Dumas lue dans la séance de l'Académie des Sciences du 16 décembre 1912, Paris (Gauthier-Villars), 1914. See also Mém. Acad. Sci., 52 (1914), xliii-lxxx.

13. Dumas, le général Jean Baptiste, La Vie de J. B. Dumas, 1800-1884, par son petit fils, Paris, 1924, pp. 230, miméograph, folio. While drawing heavily on earlier secondary sources, especially Hofmann, Dumas' grandson has added family details not found elsewhere. His 'quotations' convey the meaning intended, but are often paraphrased for stylistic reasons.

14. Tilden, W., Famous Chemists, London (Routledge), 1921, pp. 205-15.

15. Ranc, A., J. B. Dumas, savant et administrateur, 1800-1884, Paris, 1934. This was an address given at the Congrés de chimie industrielle, Paris, 21-27 October 1934.

16. Tiffeneau, Marc, J. B. Dumas, Paris (Laboratoires G. Beytout), 1934, pp. 12.

17. Urbain, Georges, "Jean Baptiste Dumas (1800-1884) et Charles Adolphe Wurtz (1817-1884): Leur rôle dans l'histoire des théories atomiques et moléculaires", Conférence faite devant la Société Chimique de France le 8 mai 1934. Bull. Soc. Chim., 1 (1934), 1425-47.

18. Châtelain, Y., "Jean Baptiste André Dumas", Dictionnaire de Biographie française, Paris, 1933-, Vol. 12 (1968-70), Col. 129-33. His care in proper dating adds value to this work.

19. Kapoor, Satish, "Jean Baptiste André Dumas", DSB, Vol. 4 (1972), pp. 242-48. Kapoor's account is not well balanced; although it brings out Dumas' major contributions in the area of classification (over 80% of the article), he neglects almost entirely Dumas' contributions to physiology, his role as a teacher and the interplay of his scientific work with external factors that made their influence felt, points that Hofmann did not fail to mention. Kapoor did not include Hofmann's work in his very limited bibliography.

DOCTORAL THESES SUBMITTED BY SOME OF DUMAS' STUDENTS

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Bineau d'Aligny, A., *Sur quelques combinaisons ammoniacales et sur le rôle que joue l'ammoniaque dans les réactions chimiques*; *Recherches sur les densités de vapeur*, pp. 28, 25 October 1837.

Laurent, A., *Recherches diverses de chimie organique*; *Sur la densité des argiles cuites à diverses températures*, pp. 119, 28 December 1837.

Péligot, E., *Recherches sur la nature et les propriétés chimiques des sucres*; *Propositions relatives à la détermination des densités des gaz et des vapeurs*, pp. 76, 19 March 1838.

Masson, A., *Théorie physique et mathématiques des phénomènes électro-dynamiques et du magnétisme*, pp. 92; *Mémoire sur l'action exercée par le chlorure de zinc sur l'alcool*, pp. 38, 11 January 1839.

Malaguti, F., *Action du chlore sur plusieurs substances éthérées et sur le methylal*, pp. 76, 15 April, 1839; *Premier mémoire sur la faculté qu'ont certains liquides de retarder les effets chimiques de la lumière diffuse*, pp. 26, 26 July 1839.

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Aubergier, H., *Recherches sur les camphènes*, pp. 16; *Recherches sur le lactucatium*. *Faits pour servir à l'histoire des eaux sulfureuses*, pp. 12, 16 February 1841.

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Gerhardt, C., *Recherches sur l'hellénine, principe concret de la racine d'aunée, et sur quelques composés congénères*; *Des densités*, pp, 40, 8 April 1841.

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Saint Evre, F., Recherches sur l'huile essentielle de sasafras; Recherches sur les indices de réfraction, pp. 35, 23 March 1846.

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Many of the periodicals consulted have maintained continuity while changing titles or editors whose names were attached to them. Listings will be given for the period of interest to the present work. An asterisk ~~are used to~~ indicates that the periodical was published at an earlier date.

Ambix, Journal of the Society for the ~~Study~~ History of Alchemy and Chemistry, Cambridge, 1937-.

* Annalen der Pharmacie (Liebig), Lemgo and Heidelberg, Vol. 1-32 (1832-1839); Annalen der Chemie und Pharmacie, Heidelberg, Vol. 33-168 (1840-1873); Justus Liebig's Annalen der Chemie, Leipzig, 1874-.

* Annalen der Physik (Gilbert), Halle, Vol. 1-76 (1799-1824); (Poggendorff), Berlin, Vol. 77- (1824-).

Annales de Chimie, Paris, 96 Vols. (1789-94 and 1797-1815), then

Annales de Chimie et de Physique, Paris, 2e Sér., 45 vols. (1816-1840), 3e Ser., 69 vols. (1841-1869); 30 vols. every 10 years.

Annales scientifiques de l'Ecole Normale Supérieure, Paris, 1864-

Annales de l'Industrie française et étrangère, Paris, 6 vols., (1828-1830).

Annales de l'Industrie nationale et étrangère, Paris, 1820-1826.

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* Bibliographie de la France, ou Journal général de l'imprimerie et de la librairie, Paris, 1815-1856.

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* Bulletin de la Société Philomatique, Paris, 11 vols. (1814-1824); Nouveau Bulletin ---, 4 vols. (1825-1826 and 1832-1833).

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* Journal de Pharmacie et des Sciences Accessoires, Paris, 27 vols. (1815-1841); Journal de Pharmacie et de Chimie, 1842-.

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* Journal de Physique, de Chimie et d'Histoire naturelle, Paris, 53 vols. (1794-1823).

* Le Journal des Débats politiques et littéraires, Paris, 1815-.

* Journal für praktische Chemie (Erdmann), Leipzig, 1834-.

* Journal of the Chemical Society, London, 1849-.

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* *Mémoires du Muséum d'Histoire naturelle de Paris*, Paris, 1815-1832; *Nouvelles Annales du ---*, 1832-35; *Archives du* ---, 1839-61.

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