

Theories of the constitution of gases in the early nineteenth century

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Introduction

The purpose of this thesis is to give a history of the theories of gases held by chemists between the years 1800 and 1860 and to show the influence of these ideas on the whole chemistry of the age, and their help in producing a systematic description of chemical compounds.

It begins with an account of the theories of Dalton and some of his predecessors; this is not intended to be comprehensive but to introduce the scientific phenomena which occupied the chemists of the time, to give an idea of the degree of naivety with which they approached them, and to show the origin of the confusion over the derivation of atomic weights from gas density measurements which is the main subject of this history.

A connection between gas density and atomic weight was admitted, but its interpretation (which depended on the recognition of the equality of the numbers of molecules of all gases in the same volume under the same conditions) was obscured by theories which gave a different size to the particles of different gases. These theories were based on misinterpretations of phenomena and also on the fact that the atomic theory came to be interlinked with the theories of gases so that mistakes in the one were reflected in the other and then served to consolidate the error of both. The difference between the theories always lay in simple numerical ratios.

The correct theory, which acknowledged the equal apparent size of all gas particles, was thought incapable of giving atomic weight values and was ignored until it was found useful. This thesis deals mainly with the errors which sustained the wrong theories and the errors which limited the correct one.

At the beginning of the nineteenth century those chemists who speculated on the microscopic nature of gases used a model based on small nuclei, different for each chemical element, to which only "imponderable" elements: heat, light, electricity or motion had to be added to provide all the physical properties of the gas, which thus consisted of a swarm of squashy or bouncing spheres with a small nucleus in the middle of each.

The supporters of kinetic theories made their particles vibrate, rotate or, more seldom, move longitudinally and at random, and there were some hybrid theories which included both motion and imponderable atmospheres.

The most popular device for accounting for the behaviour of gases was a sheath of *caloric* around each nucleus. This was an elastic, weightless fluid, the essence of heat, which gave a bogus simplicity to the phenomena of heat of reaction and heat of compression, but which nevertheless evaded all attempts to explain it by a quantitative theory.

Dalton was the first to treat the nucleus numerically but he obtained the wrong results by deriving the weights of the particles of elemental gases from the reacting weights of their solid compounds.

Dalton's atomic theory gave ambiguous values for atomic weights and some attempts to reduce the uncertainty involved using the relative densities of gases as an indication of the relative weights of their atoms. The atomic theory was correct, if imprecise; Dalton's theory of gases, which was intimately connected with it (he merely coated the atoms with caloric), was wrong but gave an undeserved authority to the values of atomic weight which it favoured.

The mistake lay in his wrong ideas on the size of the caloric envelope of his atoms (the nucleus comprised all the weight but none of the volume of his particles) and *this* was due to a number of mistaken ideas on the nature of heat of reaction, heat of compression, specific

heat and heat content (in an archaic sense defined later on) and to his belief that gas particles were more or less stationary. All these influences will be considered in detail in the next chapters.

Chemists showed a utilitarian attitude towards hypotheses and their scepticism seems to have been reserved for those devised merely to explain the behaviour of gases without helping the general progress of chemistry. Dalton's theory, supported by the laws of constant, multiple and equivalent proportions and based on the combining weight of solids, gave enormous help in the classification of chemical compounds and it was accepted too hastily, or at least, too completely.

Avogadro's theory, which distinguished between the atomic weights of the elements and the relative weights of their gas particles (which could contain many atoms) was neglected because there was no way of deciding how many atoms each particle contained; thus gas density gave no indication of atomic weight.

After the discovery of Gay-Lussac's law (that gases combine together in simple integral ratios by volume and give a volume of product gas which also bears a simple ratio to that of the reactants) Dalton's theory, which attributed volumes as various as atomic weights to the particles of gases, was no longer believed. But Berzelius perpetuated the idea that the gas particles of elements had one atom each and supported this view with his electrical theory, which made it unlikely that identical atoms could unite chemically.

The decline of the simple atomic theory and its replacement by Avogadro's hypothesis as the systematising principle of chemistry is one of the best documented episodes in the history of chemistry (second only to the study of its origin), but it is not directly relevant to the history of gas theories because, as the inconsistencies became more numerous with the increasing amount of quantitative data, chemists lost faith in both the practical usefulness and the physical reality of the atomic theory.

But they continued to build their comprehensive systems of chemical generalisation, laying emphasis now on the fact that they were giving not an image of reality but a mere notation which correlated in the simplest way the phenomena of chemistry. Their notation unconsciously approached that of the modern molecular theory (founded by Avogadro) as they became better at generalising their growing number of facts, and eventually it became almost identical; but since they denied any attempt to present reality they can be credited only with the doctrinaire methods which arrived at the results, but not the physical concept, of Avogadro's theory. Nevertheless their reasoning shows that they did in fact allow reality to filter into their chemical notation and their cautious attitude may have concealed their true convictions.

The synthesis of Dalton's and Avogadro's theories was done by Cannizzaro in 1858. He fixed the number of atoms in the gas particles of all the elements and compounds by applying the criterion of the atomic theory (maximum simplicity in the numbers of combining atoms), and Avogadro's hypothesis, to the data on the reactions and the densities of gases.

The caloric theory

Many chemists date the beginning of modern chemistry from the work of Lavoisier, so his theory of gases will form a convenient introduction to the caloric theory, which reached the peak of its influence in the second decade of the nineteenth century. It was accepted by most chemists as a useful device rather than a reflection of the truth but their lack of criticism caused considerable confusion, which their gradual unconscious acceptance of its reality perpetuated.

Lavoisier's theory was that each particle of an element was surrounded by a layer of *caloric*, which was fluid yet elastic, and which was discontinuous (each particle had its own sphere of caloric) but transferable. When the air was compressed the caloric was squeezed out into whatever was squeezing it to give the sensation of heat or to expand the mercury in a thermometer.

One other phenomenon which Lavoisier explained in a similar way and which, though modified, remained the gravest mistake of the caloric theory was that the heat of combustion was due to the caloric which oxygen gas was forced to release when it became congealed in the solid state as an oxide.¹ Later, any change in volume became a convenient source of heat of reaction and when, as soon happened, it became necessary to extract heat of reaction from an *increase* in volume this was done by saying that the heat capacity of the product was less, although its volume was greater, than that of the reagents. This caused controversy over the size and density of caloric envelopes (since caloric had no weight its density was as elusive and irrefutable a concept as phlogiston).

The idea that the kind of heat which a gas acquired by being put in an oven and that which it gave out in chemical reaction were the same – both contained in the caloric flesh of the atom – was one of the most misleading ideas in the chemistry of the period.

Perhaps the reason for this mistake was the lack of interest in affinity, of which heat of reaction was the most obvious measure. The only person to make any progress in this branch of chemistry was Berthollet and *his* mistake, the denial of the law of constant composition, caused chemists to ignore the real advances he had made in the study of affinity.²

Ironically, the possibility that Berthollet was right and the the law of constant composition was based on exceptional rather than normal compounds, led chemists to concentrate their studies of the combining ratios of elements on gases, which would obey the law and simplify the calculations of the atomic theory; they reasoned that a compound $H_{200}O_{100}$ might exist in the solid state but would be too heavy to rise into a gas.³ This argument may however have been due to the affection of Berthollet's pupils rather than their scientific convictions. Berthollet himself, being ignorant of the atomic theory,⁴ saw neither the difficulty nor its happy outcome.

Many chemists had variations on the caloric theory. One of the more highly developed was that of Laplace (who collaborated with Lavoisier). After weighing the rival merits of the caloric and kinetic theories he favoured, with caution, the former, but he combined with it some kinetic ideas and he also differentiated between free and combined heat. Laplace attributed the expansion of gases to the mutual repulsion of the caloric envelopes of the molecules, and he deduced a formula for the pressure of a gas, although he was not certain if the nature of the nucleus affected the caloric atmosphere. The particles of gases were mixed and pushed around by the streams of radiant caloric, produced by its repulsion for itself, which left and re-entered the surface of each particle in an irregular way.⁵

The irregular nature of the release of caloric was both a cause and an effect of the movement of the particles, which made the pressure on any part of the particle's surface vary and thus allowed caloric to escape. The density of this radiant caloric was very small compared with

¹Laplace, 'Mémoire sur la chaleur' *Acad. royale des sciences de Paris*. 1780.

²*Essai de Statique Chimique* 1803.

³Gay-Lussac. *Mém. d'Arcueil* II (1809) 231.

⁴*Nicholson's* IV (1800) 377.

⁵*Mém. de l'Acad. Royale des Sciences*, Paris 1780, 2821. *Connaissance des Temps* 1825.

the density of caloric around the nuclei but its velocity was that of light. Its density was a measure of the temperature.⁶

All the *imponderable fluids*, heat light and electricity, were used to account for the physical nature of gases and before describing the most complete exposition of the caloric theory – that of Dalton – the electrical theories which followed the application of Volta's electric pile to chemistry must be mentioned.

Electrical theories

A hint that gases might owe their lightness to electricity was apparent in the experiments of Lavoisier and Laplace who generated gases on the top plate of an electroscope and observed the accumulation of an electric charge. They assumed that the gas must have escaped with the opposite charge.⁷ Boiling water gave the same effect so it seemed that the phenomenon was physical rather than chemical.⁸

The great encouragement to electrical theories was, however, the discovery of electrolysis by Nicholson and Carlisle; but the vast number of theories reflected the vivid imaginations rather than the diversity of genius among their originators.

The two phenomena which demanded unusual intricacy from theories of electrolysis were the appearance of hydrogen and oxygen – the products of the electrolysis of water – at widely separated electrodes and the generation at these points of acid and alkali, apparently formed from pure water, since the idea of a force powerful enough to break up a very dilute salt solution was at that time very strange.⁹

The first of these problems led chemists to believe that hydrogen and oxygen were not the generators of water but the product of the union of water with electricity and the second led them to believe that everything else was made from water too; and this idea was supported by some chemical evidence. German chemists took the most extreme view and five years before Dalton's atomic theory one of them wrote "I suppose I need not tell you that the atomistic system is almost entirely exploded in Germany ... in place of the term matter the phrase *spacefilling* is employed ... the only spacefilling in nature that gravitates is water which when united to electricity, furnishes the principle gases."¹⁰

Richter found that hydrogen and oxygen could be generated in two separate vessels connected electrically and concluded that the gases could not be the constituent parts of water, but must have been produced by the union of water with the galvanic fluid.¹¹ And an anonymous correspondent wrote: "The visionary hypothesis of oxygen and hydrogen being the basis of certain gases ... must now be abandoned ... Oxygen and hydrogen have the same basis, water." They were differentiated by the positive or negative electric fluids attached to them.¹²

Most of the theories were heavily dependent on the insensitivity of analytical techniques and not all demanded that electricity was indispensable to the gaseous state. So they will not be described.¹³ Ampère put the fundamental idea behind many of the theories succinctly:

⁶Davy, whose theory of heat was kinetic, also attributed rectilinear motion only to the imponderable particles of radiant heat. *Elements of Chemical Philosophy* p. 83.

⁷*Acad. des Sciences*, Paris 1781.

⁸Davy, *Elements of Chem. Philosophy*. p 138.

⁹Davy, *phil. Trans* XVI (1826) 388.

¹⁰Dr. G.M. Nicholson's IV (1800) 513.

¹¹Frulander, *Phil.Mag.* IX (1800) 225.

¹²*Ibid.* p 352.

¹³For a summary see *Phil. Mag.* X (1801) 89, Dumas, *Leçons sur la philosophie chimique*, 414.

"How does one, in fact separate molecules which are combined together? Give them their atmospheres. Well that is precisely what the [voltaic] pile does."¹⁴ Electrical theories were extended far beyond the confines of the electrolytic cell: Wollaston believed that as the formation of hydrogen in electrolysis was effected by electricity so was its production by all other methods.¹⁵

In later years a more vague, though no less speculative attitude prevailed and Grove, commenting on the gas galvanic battery said: "... a beautiful instance of the correlation of natural forces in which gases by combining and becoming liquid transfer a force which is capable of decomposing a similar liquid and causing its constituents to become gases; heat, chemical action and electricity being all blended and mutually dependent."¹⁶

Later still, in 1849, a fellow of the Royal Society wrote a book which, in between acrid comments on the more respected chemists of the age, expounded the theory that phlogiston was merely electricity – the decomposition of water resulted from a redistribution of its electricity: hydrogen containing a greater, and oxygen a lesser quantity of it.¹⁷

The importance of the electrical theories however lies less in their explanation of the nature of gases than in their indication that electrical effects were the only hope of those who attempted to explain the nature of affinity: the electrochemical series into which the elements could be placed was the only measure of their chemical affinity.

From electrolytic reactions Berzelius developed a general principle of chemical reaction which did much to delay the acceptance of the most accurate theory of gases of the age – that of Avogadro. These developments will be followed in a later chapter.

Chemical effects of electrolysis

Of even less direct significance was the electrolytic and chemical evidence on the *chemical* constitution of certain gases. But the disputes over the nature of chlorine and nitrogen were reflected in the theory of volumes of Berzelius and the theories of the constitutions of acids, both of which were influential.

The formation of acid and alkali at the electrodes during the electrolysis of almost pure water led chemists to believe that the elements of these compounds were nothing but those of water: Pacchiani for instance thought that hydrogen was susceptible to a very large number of degrees of oxidation – one of which was hydrogen chloride¹⁸ (he was soon contradicted by the Galvanic Society).

Even in 1801 Davy realised that dissolved gases from the atmosphere upset the volume relationship of the gases obtained by the electrolysis of water, but the recognition that the acids and bases formed came from the very impurities which made electrolysis possible was delayed much longer.¹⁹

Some other misconceptions over the chemical constitution of gases were longer lived:

The confusion of chlorine with oxygen was due to their chemical similarity and the evolution of oxygen from chlorine water in sunlight. The experiments of Henry suggested that hydrogen chloride gas contained an ineradicable portion of water.²⁰

¹⁴Dumas, *Leçons sur la philosophie chimique*, 414

¹⁵*Phil. Trans.*(1801) 427

¹⁶*Phil. Mag.* XXIV (1844) 268.

¹⁷W.F.Stevenson, *The composition of Hydrogen* 1849.

¹⁸*Annales de Chimie* LV (1805) 15, LVI 152.

¹⁹*Nich.* IV (1801) 277. *Phil. Trans.* CXVI (1826) 388.

²⁰*Phil. Trans.*XC (1800) 197

The elemental status of nitrogen was doubted, at least by Berzelius, for some time: he thought that ammonia must be an oxide because it reacted with acids.²¹ Cruickshank had attributed the corrosion of a silver electrode during the electrolysis of pure water to the formation of nitrous or some other acid.²² Priestley demonstrated that nitrogen came from water by repeatedly freezing it and obtaining an apparently endless supply of gas.²³ Harrup described a similar experiment but was unable to analyse the gas obtained as he lost it by accident.²⁴ Girtanner described a bizarre series of experiments from which he deduced that nitrogen emerged from water boiled in earthenware unglazed on the inside.²⁵ From the same evidence Harrington deduced that nitrogen came from earthenware.²⁶ Girtanner accounted for the predominance of oxygen in the air of the alps by suggesting that the snow prevented air from reaching cultivated earth which would absorb oxygen and form nitrogen.²⁷ It must be admitted that these last theories were soon refuted;²⁸ but the doubts continued.²⁹

The atomic theory

Dalton's atomic theory was that the smallest recognisable part of a chemical compound was its molecule, which consisted of a small number of the atoms of its constituent elements in close contact, surrounded by an atmosphere of caloric which separated the molecules from each other and so ensured their continuing individuality. In solids and liquids the caloric envelope was thin enough to allow a faint influence of atomic forces to attract the molecules to one another but in gases the thickness of the caloric prevented all communication and their physical properties became independent of their chemical constitution.³⁰

The existence of gases of different chemical properties had for a long time been concealed by the similarity of their physical behaviour but now the situation had been reversed by the work of the pneumatic chemists, Cavendish and Priestley, and the invention of the pneumatic trough and the eudiometer. In consequence Dalton's calculations were based on the chemical differences rather than the physical similarities of gases.

Dalton's atomic theory accounted for the laws of constant, reciprocal and multiple proportions. By giving a different weight to the atoms of different elements, which came together in small numbers to form compounds, he accounted for all the analytical data available and chemists accepted his theory very quickly. Its only fault was that it did not give an unambiguous value for the number of atoms of each element present in a compound. If, for instance, a water molecule were supposed to contain one atom of oxygen to one of hydrogen, then analysis would reveal that the ratio of their atomic weights was 1 to 8. If water were H₂O the ratio would be 1 to 16 and there would be no way of deciding which alternative (and there were also many others) was true.

Chemists searched to find other properties of matter than its weight to reduce the uncertainty in the atomic weight system and the most used properties, and those on which great reliance was put, were the reacting volume and the density of a gas.

²¹ *Journal de Physique* LXIII (1811) 283.

²² *Nicholson's Journal* IV (1800) 263.

²³ *Nicholson's Journal* IV (1800) 196.

²⁴ *Ibid.* V (1801) 247.

²⁵ *Ibid.* IV 167.

²⁶ R, Harrington *The death warrant of the French theory of chemistry*, 1804

²⁷ *Nicholson's Journal* IV, 270.

²⁸ *Ibid.* 371.

²⁹ *Letters of Berzelius and Schonbeim*. Some chemists modified Prout's hypothesis (see page 23) to make up all the elements from oxygen and hydrogen.

³⁰ *A new system of chemical philosophy*, I 212.

Dalton's atomic theory is generally supposed to have been designed to explain the properties of gases; its chemical implications are thought to have been only dimly perceived by its inventor, who was trying to discover the nature of the atmosphere.³¹

The mistakes on which his theory of gases was built were these: The heat of reaction was supposed to come from the same source as the latent heat and the heat given to a gas by warming. The caloric envelope was the only source of heat. The nuclear forces which caused chemical reaction provided none. Secondly, his gas particles were static; they sat in a heap which made the rapid mixing of gases difficult to explain. A third mistake, which helped to overcome the problem set by the second, but which was no nearer the truth, was that he thought that the particles of different gases differed in size. And lastly, his belief that chemical reactions were additive led him to assume that the molecules of the elemental gases contained only one atom each.

The mixing of gases

The ability of gases of different specific gravity to mix uniformly and of liquids to evaporate unhindered by the weight of the atmosphere, was difficult to explain by any static theory of gases. Some chemists relied on mild chemical forces, insufficient to harm the reactivity of the mixed elements, some on the basic identity of the elements of air, some on the evidence that the constitution of air was not constant with height. Some observers used balloons and Dalton characteristically drew a model of the atmosphere on paper at ground level and deduced the properties of the upper reaches of the stratosphere.³²

Berthollet accounted for the mixing, but gradual change of proportions of the constituents of air with height by attributing to them a very weak mutual attraction.³³ This view was supported by a number of chemists but the objection to it was that air pressure had no influence on the rate of evaporation of liquids – vapour pressure was the same in a vacuum as in air.

Other objections to the chemical theory of gas mixture were that all gases mixed uniformly but not all reacted chemically with one another. Also there was no temperature change on mixing and the refractive index was the mean of that of the constituents.³⁴

Dalton's explanation went through several variations. He first tried to bring one of all the particles of different weight in the atmosphere together and wrap a coating of caloric round the group so that differences of weight would disappear in the equal weight of all these composite particles.³⁵ Laplace also tried this method, in his case to explain the velocity of sound.³⁶ Dalton abandoned this idea when the very limited supply of water vapour particles gave out. (This idea of course involved some assumption about the number of particles in the equal volumes of different gases but even if he thought that equal volumes of all gases always contained the same number of particles he later abandoned the idea.)

After this the independence of mixed gases – their inability to affect the vapour pressure or the solubility³⁷ of others – suggested to Dalton that each gas was, but for its bulk and its inertia, unknown to the others, and also that gases could not occupy space continuously and must therefore consist of discrete particles. The particles of one gas repelled each other but

³¹L.K.Nash, *Isis* XVII (1956) 114.

³²*Phil. Trans.* CXVI, part 2 (1826), 174.

³³*Nicholson's* IV (1800) 219.

³⁴Gmelin, *Handbook of Chemistry* 22.

³⁵Ms, quoted by Nash, *Harvard case histories in experimental science*, J.B.Conant (ed.) (1957) I, 221.

³⁶*Connaissance des Temps*, 1822.

³⁷*New System* I, 181, 150, 202.

not those of any other gas. Nor was the weight of the particles of different gases apparent to each other.³⁸

There were many objections to this theory: the slow mixing of gases, the absence of a fall in temperature on expansion when one gas mixed with another, and the simple sound heard from a distant cannon when the different speeds of sound in the different gases should cause multiple cracks. Dalton brushed off this last difficulty by retreating to a distance of thirteen miles and analysing the diffused rumble of the gun into separate but overlapping components. The first objection was answered by an analogy – a fine example of Dalton's mechanical imagination and concrete theories: a small lead shot suffered more delay in falling through the air than a large one, so an atomic sized lead shot would be enormously slowed down and an atomic sized lead shot, being inert and inelastic would be exactly comparable to an atom of some foreign gas. So gases would mix rather slowly.³⁹

To the second objection Dalton replied that gases did not expand when mixed at constant pressure because although gases of different species did not repel one another their bulk was mutually effective – like the action of lumps of inert material mixed up with a heap of magnets.⁴⁰

After answering all these objections, apparently to his own satisfaction, Dalton changed his theory to one in which gases mixed because of the instability of a heap of spherical atoms of different sizes: the different sized particles of different gases would, spontaneously, mix until uniform.⁴¹

The possibility that gas particles had different sizes was raised by other phenomena – the fact that hydrogen and oxygen united to give water vapour whose density was less than that of oxygen, and that nitrogen and oxygen combined to give an equal volume of nitrous oxide which must have contained only half the original number of particles.⁴² Both these examples were embarrassing to the theory which attributed heat of reaction to the denuding of the caloric envelope, but they certainly indicated that compound particles were bigger, which was a very reasonable idea and supported the belief that compound gases were of a greater order of complexity than the elements; in other words that the elementary gases had atomic particles.

Dalton also believed that the different heat conductivities of methane and oxygen, to both of which he gave the same molecular weight, indicated a difference in the number of particles of each in a given volume. But this evidence was contested by Dulong and Petit.⁴³

Perhaps Dalton developed his ideas on particle size at the same moment that he turned from designing a theory of gases to an atomic theory based on the combining weights of compounds, obtained from the normal analytical techniques.

Nash has suggested that Dalton invented his atomic theory to account for the solubility of gases in water. Dalton said that he started with the opinion that all gases might well have particles of the same size but that he later gave a different size to each gas species. And from the solubility of gases in water he deduced that the diameter of a gas particle was proportional to the cube root of the product of the atomic weight divided by the specific gravity. For example, the ratio of the diameters of the particles of oxygen and hydrogen

³⁸*Nicholson's V* 242.

³⁹*New System I*, 157–185.

⁴⁰*New System I*, 157.

⁴¹*Ibid.* I, 190.

⁴²*Ibid.* I, 70.

⁴³*Ibid I*, 123.

was 0.794 to 1.⁴⁴ He found that light gases and elementary gases were the least soluble in water and that heavier gases were more soluble. He also believed that the ratio of the gas density in solution to that in the gas was constant (Henry's law 1802) and that these ratios were, for all gases that did not react with water, 1/8, 1/27, 1/64 &c.⁴⁵ These figures applied also to other non-viscous solvents. The denominators were the cubes of small integers and Nash suggests that this gave Dalton the idea that a mechanical explanation involving packed spheres of different sizes would be appropriate.⁴⁶ Perhaps Dalton wanted to use a mechanical explanation and forced these simple ratios by a liberal indulgence of experimental error, nevertheless this may have been the point at which he brought the combining weights of elements into his gas theory. He was of course unable to obtain the weights of gas particles from the gas density because their unknown sizes concealed their relative numbers in equal volumes.

The article on the atmosphere in 1826 suggested that he later returned to his previous theory.⁴⁷ In it he admitted that the particles of carbon dioxide and hydrogen were nearly, or exactly, equal in size. His explanation of the way gases mixed in the atmosphere was based on his second theory. Even in the second volume of his *New System* (1810) he withdrew part of the evidence on which he may have based his third theory of mixed gases – that most unviscous liquids absorbed the same quantities of the various gases as pure water.⁴⁸

Properties of caloric

The connection between the volume and the quantity of heat belonging to the particles of a gas was necessarily obscure. Chemical evidence had become less tractable since the time when Tilloch had written that the decrease in volume on chemical reaction was exactly equal to the heat given out.⁴⁹ Lavoisier's idea that heat of combustion came from the condensation of volume of oxygen and the release of the greater part of its caloric had been extended to general gas reactions; but it had been destroyed by the detonation of gun-powder, which gave much gas and a large amount of heat,⁵⁰ and by the decomposition of nitrogen chloride to give a greater volume of gas, and heat.⁵¹

The theory was modified and heat of reaction attributed with no greater success to the change in specific heat from product to reagent.⁵² If the specific heat of the product was smaller, then since the total heat content of the molecule was proportional to the specific heat, the total heat must have diminished, and this quantity of heat set free was sufficient to account for the most spectacular reactions. But there were exceptions – the reaction of lime with water and even the formation of water from its elements.⁵³

Because of this many chemists admitted the existence of caloric which did not affect the volume of the particle, in a state of combination with the elements.⁵⁴ It was however possible to fiddle the variables to account for the anomalies to some extent, although this made a final explanation even more remote. Dalton, at least, was not deterred by such general scepticism; in 1810 he wrote "All modern experience concurs in showing that the heat of

⁴⁴*New System* I, 226.

⁴⁵*New System* I, 203.

⁴⁶L.E.Nash, *Isis* XLVII (1956).

⁴⁷*Phil. Trans.* CXVI, part 2 (1826), 179.

⁴⁸*New System* II, 310.

⁴⁹*Phil. Mag* IX (1800) 160.

⁵⁰Davy *Chem. Phil.*, 92.

⁵¹Gay-Lussac *Ann. Chim. Phys.* I (1816) 214.

⁵²*New System* I, 75.

⁵³Delaroche & Berard, *Ann. Chim.* LXXXV (1813) 174.

⁵⁴Laplace, *Connaissance des Temps* 1825.

combustion is primarily dependent on the quantity of oxygen combining."⁵⁵ This was not a reflection of Lavoisier's view because Dalton had written earlier that combustion "...is generally accompanied by the evolution of heat in consequence of the diminished capacities of the products."⁵⁶

Dalton's view on the thermal properties of matter seem rather contradictory. He certainly believed that all forms of heat were contained, indistinguishably, in the caloric envelopes of atoms and molecules. He drew a model of three concentric cans labelled *solid*, *liquid* and *gas*, into which heat was poured. Its period of overflow from one can to the next, without any vertical rise (which was proportional to temperature), represented the latent heat.⁵⁷ The cans were cylindrical, indicating that the heat capacity of a substance was constant between changes of state.

So while Davy and others attributed the heat given out by compressing a gas to the change in its specific heat⁵⁸ Dalton was forced to confine *his* theory to within the limits made available by experimental error: he said that the heat caused by doubling the density of a gas was about 50°. This was less than a hundredth part of the whole and so did not affect the specific heat; and he continued "It seems to be merely the interstitial heat among the small globular molecules of air."⁵⁹

Dalton also claimed that the heat given out on condensing gases under pressure was no greater than that given out by compressing a permanently elastic fluid to the same volume.⁶⁰ This was consistent with his view that latent heat was merely that amount of caloric necessary to cause a sufficient increase in volume to account for the density of the vapour.

On the other hand he accounted for the cooling of the atmosphere with increasing height by supposing that the heat capacity of air increased with its rarefaction and so although the quantity of heat remained the same the temperature had to fall.⁶¹

One of the most awkward problems for the caloric theory was the generation of heat by rubbing and by striking. This was also explained by Dalton as a consequence of the condensation of volume and the resulting diminution of capacity. (Tilloch in 1800 had suggested that when the specific gravity of a body was diminished its absolute gravity must decrease, just as adding a cork to a piece of metal under water increases its weight but also its buoyancy.⁶²) Davy however dismissed such an explanation as "a very rude mechanical idea."

Dalton considered three possible distributions of heat among the particles of gases: i. Equal weights of gases might have equal quantities of heat. ii. Equal bulks of gases might have the same quantity of heat or iii. The quantity of heat belonging to the particles of gases could be the same.⁶³

⁵⁵*New System* II, 296.

⁵⁶*Ibid.* I, 75.

⁵⁷*Ibid.* 217.

⁵⁸Delaroch & Berard, *Ann. Chim.* LXXXV (1813) 161.

⁵⁹*New System* I, 73.

⁶⁰*New System* I, 149.

⁶¹*Ibid.* 125. The belief that heat capacity changed with pressure was no doubt due to the difference between the measurement of specific heat at constant pressure and at constant volume. Laplace suggested that the change of heat capacity on compression accounted for the error in the calculated value of the velocity of sound, and Poisson reversed this calculation find the change in specific heat. Gay-Lussac found the same effect in a different experiment but admitted his error after the discovery of Dulong & Petit's law. *Ann. Chim.* LXXXI (1812) 98.

⁶²*Phil Mag.* IX (1800) 163.

⁶³*New System* I, 69.

He favoured the third alternative and varied the size of the atom by varying the affinity of the element for heat – if the element had a greater affinity the caloric atmosphere contracted but there was no change of heat. The condition for thermal equilibrium between atoms was that the caloric density at their surfaces should be equal. The variation in density of the caloric was considerable as this passage shows: "We know that the particle of steam, reduced to the state of water, still retains the greater part of its heat. What a powerful resistance then ought it not to make against a compressing force?"⁶⁴

Interpretations of Gay-Lussac's law

The greatest cause of controversy over the volume relationships between gases was Gay-Lussac's law. Only Dalton refused to believe this law⁶⁵ but nearly every other chemist misinterpreted it. Dalton's calculations convinced him that the simple reacting volumes found by experiments were an approximation to the real, non-integral values. Gay-Lussac's results were not of course exactly integral and the difference between the two interpretations lay merely in the direction attributed to experimental error. Dalton thought the correct value was, for instance, oxygen : nitrogen :: 0.833 : 1. Dalton failed to convince his contemporaries and his antagonism to a law which gave support to his atomic theory shows how much he had changed his attitude since his early experiments on gases: how he had gone over to a gravimetric theory – basing his atomic weights, and from these his atomic volumes, on the combining weights of the elements. In the first volume of his *New System* he showed a faith in simple numbers approaching that of Gay-Lussac: on the combination of oxygen and hydrogen in simple volume ratio he wrote that it was most probable that there was the same number of particles in two measures of hydrogen as in one of oxygen.⁶⁶ And also: "When two atoms unite by chemical affinity to form one, one half of their heat is disengaged."⁶⁷ In his attempt to fix the relative complexity of the oxides of carbon he used gas density values to find which was the lightest and therefore simplest – a very dangerous procedure on his later theory, in which the particle sizes could differ by some 100%.

Dalton seems to have lost the sympathy of his contemporaries in his denial of Gay-Lussac's law and his views had little influence. But the evidence of this law against the idea that all gases had equal numbers of particles in equal volumes was echoed by chemists for many years and this misconception was based on Dalton's atomic theory.

Berzelius, who used Gay-Lussac's law as the most useful device for fixing atomic weights and the strongest proof of the atomic theory, had no explanation of why the expansion of the product gas occurred.

Unlike Dalton he, and nearly all other chemists, believed that the reacting volumes of gas produced also an exactly simple multiple of that of the reactants. To account for all this simplicity by theories of affinity, which showed no tendency to simplify to integral numbers, proved to be impossible.

Gay-Lussac himself had no explanation for the production of a compound gas less dense than its constituent elements. He merely pointed out that the difficulty seemed to come from the supposition that the coming together of the elementary particles should be represented in the product by the diminution of volume on reaction, which was not always true.⁶⁸

⁶⁴*New System* I, 195.

⁶⁵Unless his letter to Daubeny can be taken as a recantation: "I do not know where we are to look for the exact specific gravity of hydrogen gas, and if this be not correctly known, then all the atomic weights will be wrong and the doctrine of volumes be in jeopardy." *Atomic Theory* 479.

⁶⁶*New System* I, 171.

⁶⁷*Ibid.* 72.

⁶⁸*Mém. d'Arcueil* II, 227.

He also said that his law supported Dalton's theory.

Davy described Gay-Lussac's law but gave no explanation.⁶⁹

Daubeny observed that the condensation of hydrogen and chlorine to give the same volume of HCl indicated either the presence of H₂ and Cl₂ or that all gases did not have equal expansions with equal increments of heat.⁷⁰

In the middle of the century Gmelin wrote: "Compound bodies in the gas state are more expanded, and have fewer atoms in a given volume than simple substances ... it appears that the compound atom becomes surrounded with a larger calorific envelope." A more exact statement would doubtless have clashed with his later remark that the less complicated the combinations of elements the stronger was their attraction for heat and the greater their elasticity.⁷¹

The equal expansion of gases with temperature and pressure indicated that some fundamental similarity must obscure their chemical diversity, but few chemists thought that this similarity was obviously an identity of particle size among all gases. Very few noticed such views and most of those who did disagreed with them, or failed to understand them.

The inability of chemists to conceive that the particles of elementary gases might contain more than one atom and therefore have a specific gravity greater than that corresponding to the atomic weight was odd, but nearly universal. Certainly they believed that most reactions were additive, particularly those between elements, but double decomposition reactions were known – the law of equivalent proportions was based on the double decomposition of salt solutions.

Speculation on the relative sizes of the atoms continued for many years. Gmelin in a passage which contradicted at least one of those already given said: "It is probable that the atoms of all bodies have the same density, so that the weights of two heterogeneous atoms are in direct proportion to their volumes."⁷² This was an attractive idea as it accounted for the uniform mixing of gases of different specific gravity – the different specific gravities of gases being due to the varying particle density, not the varying density of the particles themselves. Daubeny shared this view and also Lowig.⁷³ But the unmistakable proportionality between atomic weights and gas densities made it unlikely and also it would demand closer packing of the heavier and therefore larger particles of high atomic weight, when the reverse would be expected. Gmelin overcame this difficulty by giving the same specific gravity to all particles and attributing the varying density of materials to the varying space between the particles.⁷⁴

The phenomenon of isomorphism, and simple density measurements, made it probable that the atomic volumes of elements in solid compounds varied considerably and the values obtained were used to find the atomic volume of gaseous elements and vice-versa. Germany

⁶⁹*Chemical Philosophy*, 106.

⁷⁰*Atomic theory*, 142.

⁷¹*Handbook of Chem.* 67 & 157. Even Dalton, who had set himself the slightly less intractable problem of explaining a non-integral expansion, had no explanation. *New System II*, 349.

⁷²*Handbook of Chem.* 146

⁷³*Atomic Theory* 279.

⁷⁴*Ibid.* 57. Perhaps the same idea is implied in this enigmatic passage by Daubeny: "The atomic volume of a body may be calculated by dividing its atomic wt. by its sp.gr. Thus taking hydrogen as our standard and assuming the wt. of its atom as 1 and that of oxygen as 8 it will follow that as the sp. gr. of the latter is 16 the volume of its atom as compared with hydrogen taken as unity will be $8/16 = 0.5$ or, in other words, that the volume of the hydrogen atom will be twice as great. Since however every volume of oxygen is supposed to contain 2 atoms the sp.gr. of its atoms must be calculated at half that of its volume and consequently the atomic volume will be the same as of hydrogen." *Atomic Theory* 281.

was a fecund source of articles on the atomic volumes of elements, some of an impressive complexity and obscurity of argument; many made use of simple fractional multipliers, some of which came close to three figures, to correlate theory with experience.⁷⁵

Some encouragement was given to these views by early, partial recognition of the periodic nature of atomic volume with increasing atomic weight.⁷⁶

It is unlikely however that chemists automatically assumed that since the atoms of solids obviously varied in size, those of gases did also. The great simplicity in the volume relationships of reacting gases has already been described and also how it was attributed to the fact that the nuclei were out of range of inter-atomic forces. It is interesting to notice that Avogadro, the first chemist to announce that all *gas* particles were of equal size, used the variation in the sizes of the atoms of *solids* as a measure of their chemical affinity.⁷⁷

Gas density and atomic weight

Dalton's atomic weight values were sufficiently wrong to conceal the connection between gas density and atomic weight but the close relationship between the two was soon seen.

One of the first expositions was that of Prout.⁷⁸ He pointed out, in the course of a paper celebrated for something quite different, that the gas densities of most elemental and compound gases were proportional to their atomic or molecular weights, or to simple multiples of them. This final modification – or simple multiples – was accepted for over forty years. As atomic weight values were changed to account for new compounds or new laws it turned out that most gas densities were either proportional to the atomic or molecular weight or to a half or a quarter of this weight. Compounds were described as 1,2 or 4 volume gases and if they were solid or liquid they were theoretically vaporised to the gas state.

Gay-Lussac found the hypothetical gas density of combustible elements by finding the ratio by weight of oxygen to combustible and, knowing that either 1 or 1.5 or 2 volumes of oxygen were needed for every volume of combustible gas he chose a volume ratio from these alternatives and from it found the theoretical gas density of the solid element.⁷⁹ Prout, with his more general theory of the relation between gas density and atomic weight, merely vaporised his elements on paper without reacting them with oxygen. Avogadro and Ampère did the same, and Persoz drew analogies from these values, themselves based on analogy; and all chemists accepted this process until Dumas measured the gas density of sulphur, phosphorus and arsenic, whose atomic weights had to be multiplied by 8, 6 or 4 to be proportional to the vapour density.⁸⁰

These arguments were of course circular: both the vapour density and the atomic weights of solids were calculated by analogy to related compounds and the triumphant acclamation of the accordance between theory and experiment⁸¹ shows how the theories of gases and the atomic theory had become confused.

Berzelius deduced from Gay-Lussac's law that equal volumes of elemental gases probably contained the same number of atoms, and therefore that the gas densities of such elements were proportional to their atomic weights. The same could not be true of compounds.

⁷⁵Otto, *Graham's Chem. repts.* 60.

⁷⁶Gaudin *Bibliothèque universelle de Genève* LII (1833), 131.

⁷⁷*Ann. Chim. Phys* XIV (1845) 330.

⁷⁸*Ann. Phil.* VI (1815) 321, VII (1816) 111.

⁷⁹*Mém. d'Arcueil* II (1809) 229.

⁸⁰*Ann. Chim. Phys.* XLIX (1832) 219, L (1832) 170.

⁸¹Dumas, *Ann.Chim.Phys* XXXIII (1826) 353.

Berzelius' system of atomic weights fell into difficulties because it demanded that some elements always combine two atoms at a time, which contradicted the principle of the indivisibility of the atom. His theory of volumes was destroyed when Dumas and Mitscherlich⁸² measured the vapour densities of mercury, phosphorus and sulphur and found them several times greater than the value corresponding to the atomic weights. Berzelius then confined his theory to the permanent gases.

Since he was doubtful of the elemental nature of nitrogen and for a considerable time doubtful of the simplicity of chlorine he was left with only the components of water as the basis of his theory.⁸³ In 1847 he admitted the existence of an allotropic gaseous modification of oxygen, ozone.⁸⁴ (Dumas who believed that nitrogen and chlorine were elements wrote in 1826 that there were only 4 elements whose density had been directly determined.)⁸⁵

The failure of the atomic theory to give certain values for the atomic weight led chemists to adopt the law of equivalents as based on fact rather than hypothesis and the theory of volumes was likewise dropped in favour of a notation which described only the reacting volumes of gases without giving them any atomic structure.

The doctrine of equivalents, which was that the combining weights of substances, found by analysis, should merely be listed, without theorising on the value of their component elements, was only based on fact when used with acid – base reactions; compounds such as CS₂ demanded a hypothetical extension of it. In much the same way the notation by reacting volumes hypothetically applied to solids.

The contrast between the equivalent volume system and the atomic weight system of chemical description is well shown by Avogadro's interpretation of Gay-Lussac's law. He merely stated that since gases combined in simple ratios these combining volumes, whose weights could be derived from gas density measurements, would be the best measurement of the combining quantities of the elements and their compounds. He also derived from Gay-Lussac's law the hypothesis known by his name but *he did not use it to find the atomic weights*; he considered it too hypothetical.

The doctrine of equivalents will be described in a later chapter because Avogadro's hypothesis, which will be described next, was, from its birth, capable of reconciling all the different methods of describing the quantitative relationships of chemical reactions.

Avogadro's hypothesis

Avogadro's hypothesis, and the similar theories of Ampère, Dumas and Gaudin, were the only ones which accepted the implications of the identical rates of expansion with heat and pressure of all gases. It accounted for the smaller densities of many compound gases, compared with those of their elements, by the lightness of their particles and not by their greater sparseness in space.

Avogadro's theory was that the particles or molecules of the elements were not single atoms but groups of atoms, which could split into two or more parts either immediately before or after chemical reaction.⁸⁶ These particles were equally numerous in all gases under the same conditions. Avogadro's account of the reaction of oxygen with hydrogen was that two molecules of hydrogen united with one of oxygen. The product then divided into

⁸²Ibid. LV (1833) 5.

⁸³Journal de Physique LXXIII (1811) 283; Ann. Chim (1812) 288.

⁸⁴Letters of Berzelius and Schonbeim.

⁸⁵Ann. Chim. Phys. XXXIII (1826) 339.

⁸⁶Journal de physique LXXIII (1811) 60.

two molecules of water. This meant that the oxygen molecule must have contained at least two atoms; the hydrogen molecule need not. The reaction of hydrogen and chlorine however demanded the division of the molecules of both the elements, because one molecule of each gave two of hydrogen chloride. Hydrogen, oxygen and chlorine gases had molecules which contained *at least* two atoms, and certainly an even number.

Avogadro set out to explain Gay-Lussac's law but he brought in as evidence the physical properties of gases. This evidence was somewhat weakened by his adherence to the caloric theory and his attempts to find quantitative values for the caloric content of particles.

Avogadro was very late in accepting Dulong and Petit's law.⁸⁷ and he preferred his idea to Dalton's as better according with the law of volumes: Dalton's version, taken together with Dulong & Petit's law seems the more plausible and Gay-Lussac's law is the only strong evidence against it: why should the volume ratio of equivalent gases have been so very nearly integral?

Perhaps this was why Avogadro, unlike Ampère, laid very little stress on the physical properties of gases as support for his hypothesis.

Even in 1824 he was considering the affinity of different substances for heat and the connection between refractive index and attraction for caloric.⁸⁸ He decided that the specific heat of gases was very probably proportional to the square root of the affinity of the molecule for caloric. By this time Dulong & Petit's law was generally accepted; but Avogadro built up his theory: the most oxygenic bodies were those with the least affinity for caloric, and caloric was itself the oxygenic substance par excellence.

Later on Avogadro accepted Dulong & Petit's law in a modified form which prevented him from fixing the relationship between molecule and atom to complete his theory. He also became more sceptical about the nature of caloric.

Avogadro supported his hypothesis on two arguments: firstly the fact that in the atomic theory's explanation of many gas reactions the particle density of the product was half that of the reactants when, according to all gas theories, there were no forces available to cause this expansion (gas particles were supposed to be separated beyond the influence of atomic and molecular forces). Secondly he had the philosophical idea that all gas particles should be of an equal order of complexity. Since a compound molecule must contain at least two atoms, the molecule of an element should also contain more than one atom.

The first argument was either accepted or ignored – no-one had any but the vaguest reply. The second was unsupported by any other evidence and contradicted the widely held views that combination was strongest between the most dissimilar elements, and that all reactions were additive.

A corollary to the second argument was that the large molecule formed by the union of two elemental molecules would split into two because of its excessive weight, which might otherwise be too great for it to remain in the gaseous state. Avogadro laid great stress on this. It, at least, received some support from those who believed in the weakness of unions between identical atoms: compounds with an excessive number of atoms of the same element were considered unstable.⁸⁹

⁸⁷*Annales de Chimie* X (1819) 405. Dulong & Petit's law: the atomic heat of the atoms of all elements is the same. The specific heat of an element divided by its atomic weight is a constant number whose value of course depends on the standard chosen for atomic weight numbers.

⁸⁸*Mem. di Torino* XXVIII (1824) 27.

⁸⁹Dumas, quoted by Brodie *Phil. Trans.* CXL (1850) 773.

One might have hoped that all this would have led to a combination of the "Equal order of complexity" rule with the "No more of one element per molecule than is absolutely necessary" rule, which would have united the molecular theory of Avogadro with the atomic theory. For instance: one volume of oxygen and two volumes of hydrogen make two volumes of water, therefore each oxygen molecule must split into two to form two molecules of water; therefore the oxygen molecule must contain two atoms and the hydrogen one atom *but* in the reaction of hydrogen and chlorine one molecule of hydrogen makes two of hydrogen chloride, so hydrogen gas must be di-atomic. By continuing this process through all the gas reactions and, by using the gas density where reactions are not available, one would find the maximum complexity *necessary* to account for the reactions of all the gaseous elements, or elements with gaseous compounds. This would correspond with the definition of the atom as the unit of chemical combination; but it was not done until 1858 when Cannizzaro published his atomic weight system. In the years between 1811 and 1858 little progress was made.

Physical and chemical atoms

In 1811 Avogadro's claim for his hypothesis was that it gave the relative masses of molecules of gases and the relative numbers of such molecules in compounds. He avoided the use of the word *atom* in his paper, using instead *molecule*, qualified by various adjectives to indicate the various particles. Also he used as a standard the *molecule* of hydrogen, not the atom, which would correspond to 1/2 on his system. This is only a formal division of the atom, of course, but it does seem to indicate that he was not much concerned with the weight of atoms. Avogadro went on to discuss Dalton's version of the constitution of water, using the word *molecule* even when describing the ideas of Dalton, who was quite unaware of the concept as applied to elements. After this he said that Dalton's result was correct from a combination of two errors, that of the mass of the oxygen molecule and that of ignoring the division.

The extent to which elementary molecules divided on reaction was difficult to gauge because very few suitable reactions were known. Avogadro favoured a division into four in the case of N_3O_5 , which was formed from one volume of oxygen and three of nitric oxide, which corresponded to three volumes of nitrogen and five of oxygen. The nitric oxide, itself the product of division of nitrogen and oxygen molecules, reacted with oxygen to give a product which split again, so that the original molecules were split into two twice. The vapour density of the product was unknown at the time but in a later memoir he said that Gay-Lussac had confirmed this idea.⁹⁰

Avogadro attributed a division of the elements molecule into eight in some cases, a much greater division than was necessary to account for Gay-Lussac's law. One reason was his apparent desire to extend his theory to solids, which made him postulate a division or combination of the molecule on physical change of state as well as on chemical change. The solidity of carbon worried him: if one supposed that carbon dioxide was formed by a division of the carbon molecule into two like the gaseous elements it would have a lighter molecule than the gases oxygen and nitrogen. Avogadro overcame this by supposing that the solid carbon molecules divided into four or even eight parts when they formed carbon dioxide. He also attributed solidity to other properties of carbon not yet discovered.

Avogadro had another reason for distrusting the idea that solid molecules were of the same complexity as gas molecules: this was caused by his modification of Dulong & Petit's law.

⁹⁰*Journal de Physique* LXXVII (1814) 133.

By 1824 he had accepted this law and in 1833 he applied it to gases in a modified form.⁹¹ Accepting the equality of the specific heats of simple gases under the same conditions he extended the law to compound gases: "The specific heat of compound gases, for equal volumes, is expressed by the square root of the number, whole or fractional, of volumes of simple gas which form one volume of compound gas." (taking as the unit one volume of elemental gas). For instance: 1 volume of hydrogen and 1/2 volume of oxygen give one volume of water so its specific heat relative to hydrogen or oxygen was $\sqrt{1.5} = 1.225$.

By chance the atomic heat of carbon is about half that of most elements at room temperature. Carbon is now considered an anomalous substance in this respect but Avogadro took it as his standard and halved the coefficient of Dulong & Petit's law, which had the effect of halving all atomic weights relative to carbon. Because of the difficulty of comparing the specific heats of gases and solids, sulphur rather than oxygen was used as the basis of comparison for Dulong & Petit's law. The specific heat of gas and solid could be related, however, by calculation and with Avogadro's coefficient the hypothetical specific heat of solid oxygen was the same as that of gaseous oxygen whereas the use of Dulong & Petit's coefficient gave a specific heat double that of the gas. This argument convinced Avogadro of the correctness of his modification and he applied his new coefficient to water. From the specific heat of steam, 1.225 derived above, Avogadro obtained that of ice by an appropriate conversion factor to allow for the change of unit; it came to 0.4084. But the specific heat of ice was known to be over 0.7.

He measured the specific heat of phosphorus and applied to it his version of Dulong & Petit's law. He found that the value of atomic weight it gave was one quarter of that used by Berzelius, so that phosphorus pentoxide would be P_8O_5 . The vapour density of phosphorus corresponds to twice the atom of Berzelius and therefore to eight times that of Avogadro; so phosphorus gas was P_8 .

In the same way iodine, bromine and chlorine were found to be tetratomic in the gaseous state – a complexity unnecessary to account for any of their chemical reactions.

It does seem that Avogadro failed to unite the physical and the chemical atom through a combination of two errors: that of halving the coefficient of Dulong & Petit's law through taking carbon as a standard when in reality it is an anomalous substance with an atomic heat quite accidentally half of the normal value, and that of deciding that the specific heat of a compound gas would be the square root of the total volume of its constituent gases.

These are the most obvious reasons why Avogadro did not take the smallest bits of molecules necessary to account for the volume changes of chemical reactions as the true atoms of the elements. He believed that further division of the molecule occurred during changes of state. Gaudin and Cannizzaro did not accept this modification of Dulong & Petit's law and so neither could have made the same mistake.

Avogadro's claims for the ability of his hypothesis to give any accurate idea of the atomicity of molecules were even more modest than the previous pages indicate. The system of chemical equivalent quantities which he advocated did not depend at all on his hypothesis of the splitting of the molecules during reaction. He merely pointed out that the equivalent volumes would be the least arbitrary and hypothetical measure of the quantities of reacting substances. "It is only the volumes of gaseous substances, or those represented as such, and the corresponding weights, which are fixed and natural units on which one can base in all its simplicity the system of definite proportions: if these volumes do not represent

⁹¹*Ann. Chim. Phys* LV (1833) 80.

the molecules themselves they at least deserve to replace them in the present state of our knowledge to serve as a base for the application of theory."⁹²

He launched into theory, in fact, in the very next paragraph by pointing out that to generalise this system one must find out by experiment or conjecture the gas density which different substances would have if they were gases. (Since most gas reactions demanded the splitting of element molecules into two parts Avogadro used this generalisation on solid elements which gave gaseous compounds: phosphorus and arsenic were at first given molecular weights according with this hypothesis.)

This is probably why no-one took much notice of his system, which was as hypothetical as the system of equivalents by weight and much farther from the recognition of the weight of the atoms of matter.

In 1821 Avogadro reviewed his system and the attitude to it of other chemists.⁹³ He repeated that the volume relationships of chemical substances were the best measure of their chemically equivalent quantities, and of his suggestion that equal volumes of gases contained equal numbers of particles he said that it was certainly the simplest way of explaining the relationship between molecular weight and gas density and he could not imagine that any other explanation was possible. But all this came from "considering the thing from a theoretical point of view which interests particularly the physicist." Later he wrote "whether these ... molecules remain whole, or divide in combination is interesting in itself but is not relevant to the simple theory of definite proportions."

He dismissed the attempts of chemists to find atomic weights, defined as the smallest weight attributable to an element in any of its compounds, because this least number was only founded on the combinations already known and the probable modifications which would be made necessary by future discoveries would confuse such a system.

His contemporaries took this failure to define atomic weights as a sign of the uselessness of his theory and they ignored the work of Avogadro.

Ampère's hypothesis

Most of the chemists who accepted, or independently invented Avogadro's hypothesis also failed to fix the atomicity of gas particles. Ampère attempted it but the exuberance of his imagination does not seem to have aroused the enthusiasm of his contemporaries. Dumas approached the problem with such caution that he hesitated to fix the complexity of a particle within a range of thousands of atoms, but Gaudin and Cannizzaro succeeded.

Ampère's theory seems to have been the best publicised version of Avogadro's hypothesis; it was certainly the most bizarre. It was also the least likely to gain acceptance of Avogadro's hypothesis because this was only an incidental part of his theory of gases. His theory was concerned with the geometrical form of the gas particles and their reactions were only used to help in this attempt. No grand system of chemical generalisation comparable to that of Avogadro was put forward and Ampère's use of crystallographic data and also his introductory remarks on the reason for his theory show the physical rather than chemical nature of his speculations. "The consequences of the theory of universal attraction considered as the cause of cohesion and the ease with which light penetrates transparent bodies has led physicists to suppose that the last molecules [atoms] of bodies were held by attractive and repulsive forces that were their own properties, at distances infinitely great compared with the dimensions of these molecules."⁹⁴

⁹²*J. de Phys.* LXXVIII (1814) 131.

⁹³*Memorie dell'Accademia delle scienze di Torino* XXVI (1821) 1–162.

⁹⁴*Ann. Chim.* XC (1814) 44.

On this view the volume of a solid must consist mainly of the space *inside* each particle rather than the caloric outside it. Ampère seems to have used a combination of both, certainly in gases and probably in solids also, according to his theory of gas conduction.⁹⁵

If they were to include space his particles had to contain at least four molecules (probably equivalent to modern atoms but Ampère appeared to change his views later) so that the simplest particles of any substance, element or compound, would be polyhedra, with a molecule (atom) at each summit, which would stack together to give the bulk of the solid material.

"The equal physical behaviour of all gases indicates that the number of particles is proportional to the volume of gas."⁹⁶ After this Ampère acknowledged Avogadro's paper in a footnote: "Since the writing of my memoir I have learned that M. Avogadro has made this last idea the basis of a work on the proportions of the elements in chemical compounds." He justified the hypothesis by its success: although the theoretical reasons were no more than hypotheses the consequences of accepting it accorded so well with experimental results that it acquired a degree of probability "which physicists call certitude."

It appeared later that Ampère's intention was almost the reverse of Avogadro's, although he said that the theory was formulated to explain Gay-Lussac's law. To find the nature of the polyhedron of a compound or element he used two methods: one was to take the crystal shape of the solid as an enlargement of the particle design, which would give indications, but only indications of the shape of the particle. Then Ampère wrote: "There is another way of finding these forms [of particles], that is to determine, by the ratio of the components of a substance the number of molecules [atoms] which are found in each particle of the substance. To do this I have started from the assumption that when bodies pass into the gaseous state their particles will be separated from each other by the expansive force of caloric."⁹⁷

Here Ampère has used the atomic theory to find the constitution of gas particles in the same sort of way as Dalton, and has quite reversed the procedure of Berzelius and Avogadro. Ampère also found the composition of solids by seeing how they fitted into their gaseous compounds to form polyhedra.⁹⁸

Ampère's memoir was devoted mainly to the geometrical form of the elements and their compounds. He started by taking the various crystal forms recognised by mineralogists – the tetrahedron, parallelepiped, hexahedral prism and dodecahedral rhomboid and casting the smallest particles of all gases into one of these forms.

Apart from the methods already given for finding the shapes of the particles Ampère used one other – the enthusiasm with which different gases combined. His theory of reaction was that the two reacting particles interpenetrated until their centres of gravity coincided and if all the molecules (atoms) of both parties could, in this condition, place themselves at the summits of *one* regular polyhedron reaction would occur and a new polyhedron, or two new polyhedra, formed by its splitting into fragments, would be formed. For instance: two regular tetrahedra could be intermingled to form a cube which could then split into two tetrahedra, each containing two molecules from each reactant.

⁹⁵*Bibl. Univ. de Genève* XLIX (1832) 225.

⁹⁶*Ann. Chim* XC (1814) 47.

⁹⁷*Ibid.* 45.

⁹⁸*Ibid.* 72.

Some regular figures could not inter-penetrate and form a regular polyhedron from their combined molecules. In such a case no reaction would occur. The same considerations applied to the solution of gases in water.

Ampère was however a skillful mathematician and his list of regular polyhedra extended at least to the eptacontahedron made from two octahedra and eight tetrahedra, with 44 apices, 4 hexagonal faces, 2 square and 64 triangular faces.⁹⁹ One feels that Ampère was well able to deal with any new reactions which might at first contradict his theory.

Such complexity was not however required of the gases known at that time – most elemental and many compound gases had particles in the form of a regular tetrahedron with a molecule at each apex but chlorine, to conform with its reactions had to be a parallelepiped with eight molecules at its corners. So for Ampère hydrogen chloride was H_2Cl_4 and water H_4O_2 .

Geometrical theories

This is a convenient place to review the influence of geometrical theories on chemistry.

Mitscherlich's law of isomorphism, that compounds of similar composition have a similar crystal form, was used in the determination of atomic weights by analogy. Its reliability was however clouded by the dimorphism of many crystalline solids and the fact that two atoms could sometimes replace one in the crystal without any change in form (though this of course could be an illusion of the atomic system). Dimorphism was an argument in favour of the spherical nature of atoms: one could imagine spheres packing together in a number of crystal forms but cubes must make a cubic or hexagonal crystal.¹⁰⁰ The general ignorance of the nature of the affinity between elements or of the cohesive forces between particles of the same element led to mechanical explanations of both.

Berzelius used the shape of a molecule as an indication of its constitution – 1:1 combination of elements was less favourable to crystal formation of the product than 1:2 combination which was less linear and more amenable to crystal packing. One notices here an echo of Berthollet's theory of affinity – compounds were only formed in definite proportions when conditions for the separation of the product were favourable.¹⁰¹

In spite of the general belief that atoms and even molecules were spherical, a strong angular tradition of molecular structure is clearly felt through the chemistry of this period.

Davy believed that spherical atoms formed polyhedral molecules,¹⁰² Avogadro described Ampère's theory as a happy application of the forms of crystals, and he himself explained the involatility of carbon, silicon and aluminium as due to the length of their molecules: the centres might repel one another to a great distance but the ends would still be close enough to give the appearance of solidity (presumably he meant that the ends of the molecules stuck out of the spheres of caloric centred on their middles even when the caloric spheres were very large). But chlorine and mercury, though heavy, he thought to be spherical and easily vaporised.¹⁰³

Gaudin had a geometrical criterion for reaction more like that of Berzelius than that of Ampère. "Substances are oxides (bases) or acids because the number and mutual effect of their atoms does not allow them to arrange themselves symmetrically, and if certain oxide hydrates cannot dissolve in certain acids it is because the result of their combination would be a yet more imperfect molecule, a monstrous molecule in fact, which because of

⁹⁹Ibid. 71.

¹⁰⁰Daubeny *Atomic Theory* 2nd edition ch VI.

¹⁰¹Ibid. 117.

¹⁰²*Elements of Chem. Phil.* 115.

¹⁰³*Mem. di Torino* XXVI (1821); *J. de Phys.* LXXVIII (1814) 135.

its lack of symmetry would no sooner be formed than it would break up under the slightest pressure."¹⁰⁴

Gaudin mentioned the grouping of atoms in regular polyhedra only as a subject for future study.

His theory of the lack of direct correspondence between the molecular weight and the volatility of a substance was not however geometrical – it was based on a rudimentary periodic system in which volatile elements recurred at intervals.

Dumas thought it extremely reasonable that the shape of the molecule governed the equilibrium of solids.¹⁰⁵

Dumas' use of the hypothesis

In 1826 Dumas stated that he had made a series of experiments to find the atomic weights of many substances by means of their gas density. "To do this only one hypothesis is needed (Avogadro's) and all physicists are agreed on this."¹⁰⁶ At this time he made great claims for this procedure although he realised that it gave no certain value for the number of atoms in a gas particle. He considered it the only way in which one could arrive at the real composition of substances and the only one which would reveal the molecular arrangement of bodies at the moment of reaction, and the general properties of the molecules themselves. But he hesitated to reach definite conclusions on the interpretation of the laws of Gay-Lussac and Dulong & Petit until the gas density of phosphorus, arsenic, selenium and potassium had been measured.

When this had been done he became noticeably more cautious. His attitude reflected that of many chemists of his age and so it will be described.¹⁰⁷

"One may suggest...that in gases the molecular groups or the atomic groups are of equal number in equal volume, this will satisfy everyone, but it will be no use to anyone at present. It is after all only a hypothesis...and we have not done much on this subject."

For this hypothesis to be useful one had to consider the physical and the chemical atom as identical but they were evidently not the same because ammonia and phosphine were analogous compounds but the gas density of phosphine was twice as great as that calculated on this basis (it corresponded to P_2H_6). Also oxygen and sulphur were very similar but the vapour density of sulphur was three times the expected value. Evidently the particles of different gases contained different numbers of chemical atoms.

Dumas did not however believe that molecules split up or aggregated on change of state, like Avogadro, because he thought that such a process would affect the chemical properties of the substance just as C_4H_4 (methylene) differed chemically from C_8H_8 (olefiant gas).¹⁰⁸

The problem could not be solved by using Dulong & Petit's law because this also applied to a physical property of the substance and did not necessarily indicate the size of the chemical unit of the element and also there seemed to be some exceptions: cobalt had only 2/3 of that specific heat value which would make it of similar atomic weight to the analogous elements iron and nickel. Dumas believed that the particles of bodies which had the same heat capacity were the true atoms – the indivisible atoms of the elements, but that the chemical atoms might sometimes be equal to these and at other times multiples of the true atom. He gave

¹⁰⁴*Bibl. Univ.* LII (1833) 131.

¹⁰⁵*Leçons sur la Philosophie Chimique* 293.

¹⁰⁶*Ann. Chim. Phys.* XXXIII (1826) 337.

¹⁰⁷*Phil. Chim.* 267–286.

¹⁰⁸*Ibid.* 307. Dumas' carbon atom was only half the modern one.

an extravagant example: if the chemical atoms of sulphur, copper and zinc each contained 1000 true atoms while tellurium had 2000 and carbon 250, then according to an atomic weight system based on the majority of the elements the chemical atom of tellurium would be double that of the true atom, and that of carbon 1/4 of the true weight. These large numbers may be due less to Dumas' caution than to his belief in a form of Prout's hypothesis¹⁰⁹ – that all the elements were made from small basic atoms which aggregated in different numbers to form the chemical element:¹¹⁰ another reason in favour of differentiating between chemical and physical atoms.

It seemed in fact that neither the specific heat nor the gas densities of the elements bore any constant ratio to their chemical combining units, so the atomic theory, whether true or false, was useless.

Dumas seems to have taken the most rational view of the problem and given the most lucid explanation of the inter-relation of the various methods used to find atomic weights. His reasoning was clear and his caution justified but Gaudin with a more naive attitude got a more accurate result.¹¹¹

"To find [the true atomic weights] here is how I proceed: I give first a definition of the words atom and molecule [this was an innovation] and simplify the language of chemistry, then by means of Gay-Lussac's law [here Gaudin states *Avogadro's hypothesis*]... I show that the molecules of the gases hydrogen, nitrogen and oxygen, and the vapours of chlorine and iodine are all biatomic." This, he said, made sense of all the contractions of volume which took place on combination and he went on to give the correct atomicity of HCl, HI, H₂O, NH₃ and many gaseous oxides. He also derived the correct atomicity of mercury vapour, silicon tetrachloride and the chlorides of titanium, tin and boron; and he claimed that all the results, for both elements and compounds, agreed with Dulong & Petit's law.

This exposition was intended to be part of a complete paper, with experimental results, but the latter did not arrive and after keeping it for two years the editor of the *Bibliothèque Universelle* decided to publish this preliminary note. It seems to have attracted little more notice in print than it did in the editor's drawer.

In 1858 Cannizzaro extended Gaudin's simplification of the molecular theory into a general synthesis of the atomic and molecular theories.¹¹² He considered whether to adopt the cautious attitude of Dumas and Avogadro and express the composition of compound molecules in terms of the molecules of their components, but he decided that the use of atomic weights was justified.

Cannizzaro's original contribution to the gas theory started by Avogadro was that the gas densities of the *compounds* of an element rather than those of the elements themselves were the ones that should be studied. From a large number of analyses of, say, gaseous hydrogen compounds the smallest weight of hydrogen present in any of the substances would be the atomic weight. The assumption was that for every element at least one compound was known whose molecule contained only one of its atoms. The values obtained by Cannizzaro were only justified by the fact that all the known compounds of the elements had molecules which contained either the atomic weight given by him or an integral multiple of it.

¹⁰⁹*Ann. Phil.* VI (1815) 321.

¹¹⁰*Leçons sur la phil. chim.* 278.

¹¹¹*Bibl. Univ.* LII (1833) 131.

¹¹²'Sketch of a course of chemical philosophy' (transl.) *Alembic club reprint*, no. 18.

Three other chemists, Prout,¹¹³ Krönig and Clausius also accepted Avogadro's hypothesis in 1834, 1855 and 1857 respectively.

This chapter has described the ideas of those who accepted the hypothesis of Avogadro and the theory of gases based on it. And it has shown one reason for its neglect – its initial uselessness because of its inability to fix the atomicity of gas particles, which was largely caused by Avogadro's belief in the infallibility of Dulong & Petit's law, which is, at normal temperatures, not universally obeyed by the elements.

There were other reasons for its neglect. The next chapter deals with the electrical theories current at the time, and with the theories of acids.

Electrical theories of affinity and theories of the nature of acids

Berzelius defined electropositive substances as those which gathered round the positive electrode during electrolysis and electronegative substances those which appeared at the other pole. This division was not absolute but relative, sulphur for instance was electronegative¹¹⁴ to gold but electropositive to oxygen. All the elements could be arranged in a series of steadily decreasing electronegativity and increasing electropositivity.¹¹⁵

This electrolytic phenomenon was then applied to chemical combination under all circumstances: when two substances of opposite electrical nature combined the two electricities were discharged and caused a rise in temperature (Berzelius did not attempt to find the exact relationship between electricity and the light and heat of reaction).

Later, this theory was refined¹¹⁶ and a model for the reaction between atoms taken from a combination of two phenomena: the generation of electric poles of opposite sign on heating a crystal of tourmaline and the belief that an electrolytic circuit interrupted by the aura of a hydrogen flame would only pass the positive electric fluid and the phosphorus flame only the negative electricity.

These characteristics were then applied to the atoms themselves. Each atom had opposite electric charges on opposite sides, only one of which could be removed by reaction. Two reacting atoms would align themselves with opposite charges adjacent, one pair would annihilate each other to provide the heat and light and expansion of reaction and the other pair would remain to provide its bondage.

This later theory presented no obvious objections to the union of similar atoms but Berzelius himself did not at first allow this. He attributed loose combination of similar elements to "affinity", not electricity. Later his system of chemical atomic weights forced him to acknowledge that some elements always reacted in units of pairs of atoms.¹¹⁷

The explanation Berzelius gave of the combination of elements of similar electrical properties was that the *absolute* amounts of electricity at the poles of the atoms were as important as the ratio of positive to negative electricity. For example: oxygen reacted more readily with sulphur than with gold. This was because gold, although it had a more positive than negative electricity had nevertheless less positive electricity than sulphur (which, of course, had much more negative electricity than positive). Oxygen however had very little positive

¹¹³Prout, the only chemist of the trio, also differentiated between chemical and physical atoms: *Bridgewater treatise* no 8 (1834) 62, 123. Daubeny, *Miscellanies* II 123.

¹¹⁴From here on, read electropositive for electronegative and vice-versa: Berzelius terminology was the reverse of that used today.

¹¹⁵*Journ. de Phys.* LXXIII (1811) 257.

¹¹⁶Dumas, *Leçons sur la Phil. Chim.* 415.

¹¹⁷Berzelius' atom pairs arose like this: all strong bases were MO. So: $MO + H_2Cl_2 = MCl_2 + H_2O$. He believed water to be H_2O because of his theory of volumes.

and about as much negative electricity as sulphur had positive so these last two quantities conveniently annihilated each other and the reaction was successful, and quite hot.¹¹⁸

Berzelius contemporaries were no doubt cautious about such a very speculative hypothesis and its importance in forming the chemical theories of the age has possibly been confused with the general belief that most reactions were additive, which of course Berzelius, and such an electrical theory supported.

This was Gaudin's criticism of Berzelius: "A famous chemist who, to extend to all bodies a law on the salts, which he thinks he has discovered...has considerably obscured the composition of molecules and delayed for ten years, by the authority of his name and his genius, the opinion of the academic world."¹¹⁹

Other reasons for supposing that the influence of his *electrical* theory, rather than his belief in the additiveness of reaction, has been exaggerated are that Avogadro himself not only had a similar theory but claimed precedence over Berzelius. Ampère also had a theory which, though similar in some ways, differed sufficiently to be prophetically accurate. And Brodie's variation on Berzelius theory, although incorrect, provided positive support for Avogadro's hypothesis.

Avogadro believed that there was only one electric fluid, which was found in varying quantities and held with varying affinities on one hemisphere only of the surface of the atom.¹²⁰ When the electrically charged hemispheres of two atoms came together the electricity redistributed itself according to the relative affinities of the two atoms and the total quantity available. Avogadro considered the electrical fluid independent of, or at least not yet proved identical with, caloric.

In 1813 Avogadro claimed some share in Berzelius' electrochemical theory. He also had devised an electrochemical series of steadily changing polarity, but it was noticeably less dogmatic and therefore both more accommodating and less attractive.¹²¹

Ampère's theory was that the atmosphere of the atomic nucleus consisted of concentric spheres of oppositely charged electric fluids which behaved on reaction in much the same way as Berzelius' electric poles or modern ionic salts.¹²²

Brodie's theory applied the dipolar system of Berzelius to *pairs* of atoms rather than single ones. This dipolar state was induced rather than inherent. Brodie gave the formation of sulphur trioxide by the lead chamber process as an example: The positively charged nitrogen dioxide and the negative sulphur dioxide polarised an oxygen molecule sandwiched between them:



Just as polarisation only occurred at the moment of chemical change so the pairing of elemental atoms might be very temporary: "At the moment of chemical change the same chemical relation exists between the particles of which certain elements consist, as between the particles of compound substances under similar circumstances."¹²³

Brodie did not in fact regard double decomposition, as expressed in chemical formulae, as absolutely necessary; it might occur at the instant of reaction by temporary liaisons between the components of the system.

¹¹⁸Gmelin, *Handbook* 155.

¹¹⁹*Bibl. Univ.* LII (1833) 132.

¹²⁰*Journal de Physique* LXV (1807) 136.

¹²¹*Ann. Chim.* LXXXVIII (1813) 286.

¹²²Dumas, *Leçons sur la Phil.Chim.* 414.

¹²³*Phil.Trans.*CXL (1850) 764.

He did obviously favour double decomposition. He gave the same argument as Avogadro, and later Gerhardt, about the unreasonableness of considering the elements to be a race of single atoms while all other substances were at least twice as complicated. He also pointed out that in the decomposition of nitrogen chloride into its elements heat, generally considered the symptom of chemical combination, was generated in a reaction widely held to be a decomposition. A hint, based on similar reasoning, that the formation of water involved the decomposition of its elements is found even in 1801.¹²⁴

Another argument used by Brodie was that the elements chlorine and nitrogen were far more permanent than their compound and so the reactivity of their atoms must have been satisfied by a close tie with another atom, which could only be another atom of the same element. Schonbeim pointed out that combined oxygen was often more reactive than the free element.¹²⁵

The significance of the electrical system in the history of Avogadro's hypothesis seems to be that except for the last one described they supported the idea that nearly all reactions involved nothing but the addition of elements to one another and the coming together of two compounds to form one. This idea preceded the electrical theories; it was clearly the basis of Dalton's atomic system.¹²⁶

Double-decomposition

The double decomposition of salts had been demonstrated by Richter in 1792 but the reactions between acids and bases were considered to be additive even in the middle of the nineteenth century.

The trouble started with Lavoisier who believed that oxygen combined with bodies to give acids and with metals to give bases. In 1800 Henry said that the theory of the formation of acids was one of the most important parts of the new system of chemistry, but no start could be made until the composition of hydrochloric acid was known.¹²⁷ He was over optimistic. The evidence for the presence of oxygen in this acid has been given in the first chapter but by 1809 Davy's analysis, that it was a compound of hydrogen and an element, chlorine, was widely accepted. Nevertheless the indispensability of the hydrogen in all acids was not. The title of acid was invariably given to what would now be called the acid anhydride. In solid state reactions the union of the oxide of a non-metal and that of a metal to give a salt could sometimes occur and in gas reactions the oxides were usually damp enough to ensure reaction, so the water was considered to be merely a catalyst.

One might expect that the salts of ammonia, which are formed by addition, would have given a clue to the structure of acids but the methods of analysis neglected the water in the compound, which was presumably listed, if at all, as water of crystallisation.

Berthollet analysed ammonium bicarbonate as containing by weight 73.34 parts of carbon dioxide and 26.66 parts of ammonia. The correct ratio is $\text{CO}_2:\text{NH}_3:: 69:26.6$ so allowing for experimental error these must have been the only components attributed to ammonium bicarbonate: $(\text{NH}_4)\text{HCO}_3$. It was known that water was necessary for its formation.¹²⁸

¹²⁴J. Astley, *Nicholson's V* (1801) 27.

¹²⁵*Letters of Berzelius and Schonbeim* 107.

¹²⁶*New System* I 222.

¹²⁷*Phil. Trans.* XC (1800) 188.

¹²⁸Gay-Lussac, *Mèm. d'Arcueil* II 212.

The case of ammonium chloride was more difficult because the hydrogen of the acid did appear in the analysis, so it was necessary for Gay-Lussac to allow a quarter of its weight of water in the hydrochloric acid gas to accord with the composition of the salt by weight.¹²⁹

Evidently the analysis of salts gave no hint of the nature of acids but one bit of evidence for the presence of combined water in acids was overlooked: the unusual solubility of the acidic oxides in water and the heat generated by their solution; even Dalton recognised that these gases reacted with water and that some were not removed from solution even by a vacuum.¹³⁰

Davy's theory of acids

Davy's theory of acids gave them the formulae used today but it was criticised strongly.

Berzelius admitted that Davy could not be proved wrong, there was no doubt that sulphuric acid always contained a certain amount of water, and he said that water could combine with acidic oxides in two ways, as a base and as water of crystallisation. Berzelius' objection was rooted in the established oxygen theory of acids *and* bases:¹³¹ anhydrous metal chlorides on Davy's system would contain no oxygen and would not therefore be salts.¹³²

Dumas objected that Davy's theory demanded the existence of an unidentified compound with an extra oxygen atom for each acidic oxide: SO_4 as well as SO_3 , which was unnecessarily hypothetical. This objection was not even as philosophically sound as it might appear as it was based on an additive view of reaction, which was not that of Davy. According to Davy it was not SO_4 which existed as a new unverifiable compound but H_2SO_4 which was the product of an additive reaction, which of course was exactly comparable to the reaction: $\text{PbO} + \text{SO}_3 = \text{PbO}.\text{SO}_3$ (= PbSO_4 , which Dumas would accept).¹³³

Another argument used by Dumas was the ease with which the three phosphoric acids could be interconverted by drying or wetting; this indicated the presence of water in loose combination.

Laurent used the *salts* of phosphoric acids to support the opposite view. The elimination of water caused for him a complete alteration in the properties of the salts of these acids; but even more persuasively he listed the acids, according to Davy's theory, in increasing basicity with increasing oxygen content: PH_3O_2 , PH_3O_3 , PH_3O_4 .¹³⁴ He also said that scarcely one salt in a thousand was made from the oxides but rather from the hydrated oxides, and that the formula $\text{CuO}.\text{SO}_3$, for instance, did not account as well as that of Davy for the replacement of copper by iron. Laurent also denied that the production of alkali and acid at the electrodes of an electrolytic cell provided any evidence for dualism: the splitting of potassium sulphate gave not KO and SO_3 but KOH and H_2SO_4 . Finally Kopp found that specific volume calculations supported Davy's formulation of salts.¹³⁵

These are some of the arguments used over the nature of acid-base reactions. Their direct relevance to the attitude of chemists to Avogadro's hypothesis and the existence of poly-atomic particles of the elements is doubtful, particularly as Dumas held apparently opposing views on both, but the generalised theory of double decomposition, which owed something to Davy's theory, had the effect of supporting a belief in the poly-atomicity of elemental molecules without admitting complete acceptance of Avogadro's hypothesis.

¹²⁹ see page 6.

¹³⁰ *New System* I 197, 202.

¹³¹ This was his objection to the elemental nature of nitrogen, in ammonia.

¹³² *Ann. Chim.* LXXXI (1812) 283.

¹³³ *Leçons sur la Phil. Chim.* 339.

¹³⁴ *Méthode de Chimie* 40.

¹³⁵ *Ann. Chim. Phys.* IV (1842) 462.

Gerhardt's system of chemistry was based on the belief that nearly all reactions were double decompositions and that all reactions could be written in the form of a double decomposition. The purpose of this was to clarify the inter-relationships of different reactions, not to be dogmatic about their mechanisms. It was, in fact, a rather unrealistic system: "Since double decomposition is the most frequent form of reaction in chemistry, perhaps even the universal form of all chemical change, it is reasonable to use it as a basis for our rationalised formulae."¹³⁶

Gerhardt wrote the reaction between hydrogen and chlorine $\text{Cl.Cl} + \text{H.H} = \text{ClH} + \text{ClH}$, achieving the result of Avogadro's hypothesis by a much more questionable method. The evidence for this reaction was the simultaneous formation of chloride and hypochlorite from chlorine and calcium oxide – doubtful reasoning since nitrogen dioxide NO_2 gives a mixture of nitric acid and nitric oxide.¹³⁷

Gerhardt's insistence on double decomposition as the only reaction mechanism forced him to make metal molecules diatomic: the reaction $\text{Zn.Zn} + \text{HCl} = \text{ZnH} + \text{Cl.Zn}$ was followed immediately by $\text{Zn.H} + \text{ClH} = \text{H.H} + \text{Cl.Zn}$. Gerhardt realised that this two stage reaction might be regarded as a device to bolster his universal system and reassured himself with the fact that copper hydride was known and was decomposed in this way, although copper did not react with hydrochloric acid.

Gerhardt's system sometimes *prevented* him from arriving at the results of Avogadro's hypothesis: he said that the oxygen molecule was composed of more than two atoms. This was suggested by the oxidation of potassium sulphide: $\text{SK} + \text{O}_3\text{O} = \text{SO}_3 + \text{K}_2\text{O}$. The two product molecules remained more or less united, written according to the standard notation of salts, as the addition product. This reaction is very thinly disguised as a double decomposition.

Equivalent weights and equivalent volumes

Gerhardt's addiction to double decomposition is unexpected in an age sceptical of all theory and devoted to the collection and arrangement of data soundly based on experimental results.

The experimental results used in the classification of reactions and compounds were the reacting weights and the reacting gas volumes, taken with reference to some element or compound of standard weight and volume. The result of such a system, the system of equivalents, did not support Avogadro's hypothesis because the varying valency of the elements masked the relationship between gas density and atomic weight; and many chemists were trying to do without molecules anyway.

Giving hydrogen a reacting weight of 1 and a volume of 2 one finds the equivalent weight of oxygen 8 and its equivalent volume 1. But oxygen is 16 times as heavy as hydrogen. This problem has been mentioned before in connection with Gay-Lussac's law but now the determination to avoid explanations in molecular and atomic terms made it yet more intractable.

The change in attitude was shown in the work of Persoz,¹³⁸ whose system was similar to Berzelius' and even had echoes of his electrical theory.

Persoz mentioned but misinterpreted Ampère's hypothesis (this failure of communication will be discussed later) and seemed to accept Berzelius' theory of volumes (that equal vol-

¹³⁶*Traité de Chimie* IV 576.

¹³⁷*Traité de Chimie* IV 570.

¹³⁸*Intro. à l'étude de la chimie moléculaire* 38.

umes of elemental gases contained equal numbers of atoms) but he distrusted it and questioned its usefulness since there weren't many gases anyway. In spite of this lack of gases he based his theory on the gaseous volumes of substances but made no assumptions about the number of particles in these volumes. He rejected the atomic theory as unusable and considered that this purely experimental use of reacting volumes would show up several unforeseen relationships.

His philosophy is interesting because it is transitional between the concrete models of those scientists who believed the atomic theory and those who refused to believe any theory and used the equivalent weight system. "This principle [the atomic theory] seems to be inadmissible because it is insufficient to explain the most fundamental physical and chemical properties of substances."¹³⁹

Persoz did however use a form of atomic notation as a subsidiary method of classification: Molecular composition of sulphur trioxide: 2 volumes SO₂. 1 vol. oxygen.
Atomic composition: 1 atom sulphur. 3 atoms oxygen.

It is necessary to digress here and consider in more detail the use and derivation of equivalent weights and volumes.

The equivalent volume did not always conform with the equivalent weight. The equivalent weight of nitrogen in ammonia was 2/3 of its atomic weight. The gas reaction was given as 1 volume nitrogen + 3 volumes of hydrogen but the equivalent volume of nitrogen was not 2/3 but 2, presumably because in the formation of nitrous oxide 1 volume of nitrogen reacted with 1/2 volume of oxygen.

Dumas gave:

H₂Cl₂ & N₂H₆ as representing 4 vols and 1 equiv.¹⁴⁰

H₂S & SO₃ as representing 2 vols. and 1 equiv.

As₂O₅ as representing 1 vol. and 1 equiv.

He also showed how compounds of the same empirical formula could have the same composition, the same vapour density but different equivalent volumes; the compounds were probably alcohol and dimethyl ether:

"C₂H₆O corresponds to two volumes of both compounds, but consider their formation. Alcohol is made from 1 equiv. of olefiant gas and two equivs. of water but methylene hydrate is made from 1 equiv. methylene and 1 equiv. water. Evidently the equivalent volumes are different.

C₄H₈ + H₄O₂ = C₄H₁₂O₂ 1 equiv. alcohol.

C₂H₄ + H₂O = C₂H₆O 1 equiv. methylene hydrate."¹⁴¹

The anomalies of the equivalent weight system lay not only in the varying basicity of compounds and the varying valency of elements but in the impossibility of direct comparison of many compounds with the standards on which the system was based. The only direct indication of equivalent weights was the change in the colour of the indicator during an acid base reaction and indicators did not always mark the completion of an acid-base reaction. Also the basicity of acids was, on the equivalent system, a mere convention.

The equivalent of a metal was that quantity which, as a base, contained a unit amount of oxygen; clearly iron, with two oxides, had two equivalents and so when it reacted with some other element there was no way of telling which equivalent was in use. So when the

¹³⁹*Ann. Chim. Phys* LX (1835) 117.

¹⁴⁰*Leçons sur la Phil. Chim.* 311.

¹⁴¹*Ibid.* 311. I have modernised Dumas' formulae by doubling the atomic weight which he gave to carbon.

system of equivalents was extended beyond acid–base reactions it rested on assumptions of the same sort as those used in the atomic theory which it was designed to replace but unlike the atomic weight system it gave no guarantee that the sum of the equivalents of two elements was the equivalent of their compound.

As a result of this uncertainty Laurent preferred a system of *proportional numbers* which was an arbitrary system of combining weights, numerically identical with the equivalents, based on vague analogies of the sort formerly used to work out the atomic system but which, unlike the latter, did not claim to represent the weight of the atom.¹⁴²

The reacting volumes of gases were compared in the same way and suffered similar difficulties to the equivalent weight system.

To return to Persoz:

The equivalent weight system had shown that the equivalent weight of any base always contained the same weight of oxygen but the volume system alone showed any connection between acidity and oxygen. Acidity depended on the presence of 1 volume of oxygen in the compound. Compounds containing 2 or 4 volumes of oxygen were never acidic.

2 volumes of carbon monoxide + 1 volume of oxygen gave the acid anhydride CO_2 .

2 vols. MnO_2 + 1 vol. oxygen gave manganic oxide

and 2 volumes of hydrogen with one of oxygen gave the weakly acidic (or basic) water.

Persoz used volume composition to draw analogies between different compounds: water = 2 of hydrogen + 1 of oxygen; hydrogen sulphide = 2 hydrogen + 1 sulphur.

Here he drew analogies between the volumes of elements whose relative volumes had been found by analogies – he was evidently unaware of the true vapour density of sulphur (cf. p 14).

Hydrogen peroxide and hydrogen disulphide were analogous and composed of 2 volumes of each element.

In the same way the hydrogen halides had analogous compositions, as they did also on the equivalent system, and the hydrides of carbon, boron and silicon contained 8 volumes of hydrogen to two volumes of the other element.

The contrast between the first two groups and the last showed how the capacity (meaning roughly valency), and therefore the combining volume, changed according to whether the element played the electropositive or the negative role. In another context Persoz commented on the fact that the product of gas reactions was equal in volume to that of its negative constituent.¹⁴³

Simplification of volumes by Gerhardt and Laurent

The division of gases into volume types was widely practised about the middle of the century. Kopp said that the volumes containing the atomic weights (meaning also the molecular weight) of all substances were 1, 2 or 4 times one standard volume.¹⁴⁴ Gmelin described one atom, two atom and up to six atom gases (indicating by this the number of particles in equal volumes of the gas) and allowed the possibility of 1/3, 1/2 and 1/4 atom gases.¹⁴⁵

The original cause of the unnecessarily large formulae which were responsible for the "4 volume gases" was that Berzelius described all metal oxides as MO so that hydrochloric

¹⁴²*Méthode de Chimie* 1.

¹⁴³*Chimie Moléculaire* 832.

¹⁴⁴*Comptes Rendus* XLIV (1857) 1347.

¹⁴⁵*Handbook* 53.

acid had to be H_2Cl_2 (p. 24) from which ammonia had to be N_2H_6 to give the correct empirical formula for ammonium chloride. Nitric acid was MN_2O_6 , because of the dualistic system, according to which the salt was made by the addition reaction $\text{N}_2\text{O}_5 + \text{MO}$. Gerhardt and Laurent halved the atomic weight of the metals and at the same time pointed out the absurdity of supposing that the compound had any structural similarity to the reactants and that hardly one salt in a thousand was made by the union of oxides and that many reactions replaced the metal of the salt, not the metal oxide.¹⁴⁶

This was how some formulae came to be twice as big as they should have been; their volumes were four times as great they should have been because that of oxygen, the standard, was only half its correct value, and *this* was because it was given an atomic weight of 8 instead of 16.

Gerhardt and Laurent both reduced the volumes containing the molecular weight of all substances to one of two: 1 or 2, and then to one only, whereby they attained the same result as Gaudin.

Gerhardt cautiously introduced the final simplification in the last volume of his *Traité de Chimie*, but he forecast it in the first volume by pointing out that in the commonly accepted formulae he used, in which volatile compounds were represented by 4 volumes of vapour, the atoms of carbon, oxygen and sulphur were always present in even number, so their equivalents could be multiplied by two.¹⁴⁷

By doubling the equivalents of these elements he was effectively using atomic weights, the smallest weight of an element present in any of its compounds.

Gerhardt's approach to Avogadro's hypothesis is less simply explained than the reasoning of Avogadro and Ampère. His doctrine of double decomposition led him to double-up the atoms of the elemental gases, but this, unlike Avogadro's hypothesis, would not lead him to the correct molecular weights of gases like sulphur and phosphorus vapours; beside he got the wrong answer for oxygen. He came nearer to the physical truth in naming a number of *types* of compound in which substitution of one element or radical for another would produce all the compounds known to chemistry.¹⁴⁸

The first of these types was water $\text{O}\left\{\begin{smallmatrix} H \\ H \end{smallmatrix}\right.$ in which one or both of the hydrogen atoms could be replaced by other radicals: $\text{O}\left\{\begin{smallmatrix} C_2H_5 \\ H \end{smallmatrix}\right.$ alcohol and $\text{O}\left\{\begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}\right.$ ether.

All three compounds occupied the same volume. Gerhardt's reason for making water H_2O was that as well as conforming with the volume relationship of the elements of water it accorded with the fact that many elements formed two oxides – one by replacing both the hydrogen atoms of water and the other, the hydroxide, by replacing only half the hydrogen.

The same effect was shown in Gerhardt's second choice of volume type: if the oxygen of water were replaced by chlorine the product would be H_2Cl_2 and it would occupy twice the volume of the water it was derived from, but only a single chloride was known for most elements and no metal hydrogen chlorides existed so the formula could be halved to HCl which had the same volume as water. Similar reasoning surrounded the other two volume types of Gerhardt: NH_3 and HH .¹⁴⁹

One notices that the emphasis had shifted from the phenomena described by Gay-Lussac's law to the generalised reactions of chemistry as supports for Avogadro's hypothesis.

¹⁴⁶*Méthode de chimie* 23.

¹⁴⁷*Traité de Chimie* I, 74.

¹⁴⁸*Ibid.* IV, 582.

¹⁴⁹*Ibid.* 595.

Gerhardt gave some physical evidence to support the theoretical neatness of his system. The formula weights corresponded with the vapour densities and with the progression of the boiling points. The formulae gave the correct values for the numbers of replaceable hydrogen atoms of acids and therefore the number of acid salts that could exist (as shown earlier this was not conclusive evidence). He also used the argument that the particles of both elements and compounds should be of the same order of complexity.

Gerhardt justified his doubling of the formulae of the elements in the free state by analogy with organic radicals. "I am generalising a principle which I first announced at the time of the discovery of the so-called radicals of the alcohols by Mr. Frankland. These, which have the formulae CH_3 , methyl, C_2H_5 , ethyl...must be doubled to represent the molecule of the substances...the study of their vapour density has led me to this opinion...and it is confirmed by the existence of mixed radicals." for example $\text{CH}_3.\text{C}_2\text{H}_5$.¹⁵⁰

Laurent¹⁵¹ had similar ideas to those of Gerhardt. He listed the compounds of chemistry in four groups of which only the first, with formulae equivalent to 4 volumes and the second, with formulae corresponding to 2 volumes, were important. He then showed that the second group with the simpler formulae contained dibasic acids whereas the first group did not, and that the vapour density of the first group was less than that of the second for comparable formula weight. Gerhardt also showed that in reaction the compounds of the first group always gave double molecules of water and carbon dioxide, H_4O_2 & C_2O_4 .¹⁵²

Obviously the formulae of the first group should be halved to bring all formulae to correspond to 2 volumes of vapour.

In this way Laurent, agreeing with Gerhardt, reduced all the formulae to accord with their vapour density; but then he modified Gerhardt's system in a way which made the oxygen atom identical with its gas molecule.

Laurent described the reaction of potassium with chlorine: $\text{ClCl} + \text{KK} = \text{ClK} + \text{ClK}$. The molecules of both elements split up and the atoms were not stable until they had paired. But the formation of carbon suboxide was different: $(\text{CC}) + (\text{CC}) + (\text{OO}) = (\text{CC})\text{O} + (\text{CC})\text{O}$. Here each oxygen atom had not paired but had taken a whole molecule of carbon to give a triatomic molecule. Laurent separated the elements into those which always formed even-atom molecules and those which did not.

Among the latter were oxygen, sulphur and carbon. In the system modified in this way 1 volume of oxygen contained 1 molecule, which was equal to 1 atom; and 1 volume of hydrogen also contained 1 molecule, which was made up of 2 atoms.

The consequence of this reasoning was that Laurent could generalise his own misinterpretation of the theory of Ampère correctly while giving a wrong atomicity to the individual gas particles; a paradox which neatly points the difference between the attitudes which led the later and the earlier chemists independently to Avogadro's hypothesis: "One can generalise the idea of Ampère in which all the elemental gases contain the same number of atoms in the same volume [this was *not* Ampère's idea]. One can say that all substances, simple and compound, contain the same number of molecules in the same volume."¹⁵³

¹⁵⁰*Traité de Chimie* IV 596.

¹⁵¹*Méthode de Chimie* 57 – 82.

¹⁵²*Traité de Chimie* IV 598.

¹⁵³*Méthode de Chimie* 85.

Publicity and terminology of Avogadro's hypothesis

The last passage shows how Ampère's hypothesis was misunderstood by chemists, and also shows how much more well known it was than the work of Avogadro. Until the time of Cannizzaro the name of Ampère is, of the two, far more frequently found in the literature of the subject. Ironically Avogadro devoted many years to working out the consequences of his hypothesis while Ampère merely gave a summary of a more detailed paper which never appeared. This, and the ignorance and lack of comprehension accorded to this theory by scientists, points to a failure in its communication rather than a disbelief in its validity. There is little evidence that it was attacked by those who understood it.

It must be admitted that the language used by its founders seems to have prejudiced English chemists against reading of the hypothesis; and the various terms used to describe the various particles showed no consistency whatever.

Avogadro's imperfect French was further obscured by his addiction to subordinate clauses – some of his sentences were over 300 words long; and Ampère's bizarre crystallographic ideas tested the clarity of *his* prose to the full.

The nomenclature of the fundamental particles was interesting, and confusing. The majority of chemists used *atom* indiscriminately for the smallest particle of both element and compound. In contrast both Avogadro and Ampère used, at the beginning, only the word *molécule*, modified by various adjectives by the former, to describe the smallest particles of matter. Later they both came to use atoms, Avogadro in his later researches on the systematic ordering of combining quantities and Ampère in a curious paper in which he appears to have modified his own earlier ideas. It may be however that the loose use of the word *atom* for both molecule and atom was increasing generally as belief in the physical particle to which it was first applied declined: "In order to avoid all hypothesis I shall not attach to the term *atom* any other sense than that which is included by the term proportional number. I apply the word *molécules* or *atoms* to the equivalents or atoms of compound bodies."¹⁵⁴ Faraday, who was also sceptical about the atomic theory wrote: "An atom of hydrate of potassa contains four elementary atoms."¹⁵⁵

In his earlier papers Avogadro used *molécule élémentaire* to signify atom, *molécule constituante* for molecules of elements and *molécule intégrante*, *molécule composée* or just *molécule* for the molecules of both compounds and elements. In a footnote on the work of Davy he wrote: "the molecule of most substances or as he [Davy] expresses it, the smallest proportion in which bodies combine." A definition usually applied to the word atom. He also referred to Dalton's supposition that hydrogen and oxygen combined "molecule to molecule".¹⁵⁶

In 1821 Avogadro added *molécule partielle* and *molécule simple* to his list of fundamental particles; they corresponded to the modern atom but the former reflected his caution over assigning any absolute indivisibility to such a particle. *Molécules* had meanwhile become *molécules totales*. But Avogadro now introduced the word *atome* when quoting the work of other chemists, together with *molécule indivisible*.¹⁵⁷ In this paper there also occurred a *molécule intégrante primitive*, which indicated that compound molecules as well as elemental molecules were divisible. This was the mistake which was described on page 18. But the most significant use of *atoms* in this paper was in his discussion of Dulong & Petit's

¹⁵⁴A. Laurent, *Méthode de Chimie* 57.

¹⁵⁵*Phil. Mag.* XXIV (1844) 139.

¹⁵⁶*J. de Phys* LXXVIII (1814) 131.

¹⁵⁷*Mem. di Torino* XXVI (1821) 1.

law – he considered that it would be very useful in deciding between the various multiples of a number for the weight of a *molécule*.¹⁵⁸

Avogadro used *atoms* freely in his memoir of 1833 in which he was concerned with modifying Dulong & Petit's law, and he used it to mean molecule. *Atome composé* was the molecule of a compound and *atome simple* not an atom but the molecule of an element. He also used just *atome* to indicate a molecule of a compound or an element. Later he used *atome simple et indivisible* and *atome partiel* in the sense of atom. Although Avogadro had completely reversed his terminology the caution which seems to have decided the use of *molécules* exclusively in his earlier papers was still applied to the use of *atome* in his later papers, where it was only a relative, not an absolutely indivisible measure of the element: "There is no evidence that the density [of sulphur vapour] represents the atom of sulphur of a constitution analogous to that of an atom of oxygen gas."¹⁵⁹

In 1834 Avogadro introduced the *veritable atome*, attained by the misuse of Dulong & Petit's law.¹⁶⁰ But he retained the *atome simple partiel* in his more hypothetical passages. By the end of the paper¹⁶¹ he was using *atome* and *atome vrai* as the absolute, indivisible atom and *atome gazeux* as the molecule. But by this time the complexity of the *atome vrai* exceeded that of the atom which took part in chemical combination, which, no doubt, lay somewhere between *atome gazeux* and *atome vrai*.

By 1845 however he had rationalised his nomenclature and used *atomes* and *molécules integrantes* in the same paper; but some ambiguity remained in that his chemical *atomes* could divide to form *molécules integrantes* as well as unite to form them.¹⁶²

Ampère's hypothesis revisited

The case of Ampère was different – his terminology was always precise but his ideas seem to have changed. In his memoir of 1814 the particles of gases consisted of molecules placed at the apices of some regular polyhedron and there was no hint of any further division of the molecules. On reaction the particles broke up and the molecules rearranged themselves.¹⁶³

In 1832 and in 1835 Ampère published two papers¹⁶⁴, identical but for the fact that the first was written in the third person and the second in the first. In these Ampère divided the molecules into atoms and said that equal volumes of gases contained equal numbers of molecules; an equality formerly assigned to particles, which the new theory retained.

Furthermore Ampère claimed that these distinctions had been established for a long time: "This division of molecules by chemical forces is the result of a principle shown by M. Ampère in a memoir printed in 1814 in the *Annales des Mines*, namely, that in equal volumes of any gas or vapour...there is the same number of molecules." There are two interesting points about this passage – one is that it is not true and the other is that Ampère quoted not the earliest publication of his work, that in the *Annales de Chimie* of 1814, but its reprint in a more obscure journal of which he gave the wrong date (it should have been 1815).

In the early memoir the *particles* were equidistant in all gases and all gases did *not* contain the same number of molecules in the same volume. As for the chemical difference, compare these two passages on the formation of water:

¹⁵⁸Ibid. 41.

¹⁵⁹*Ann. Chim.Phys.* LV (1833) 80.

¹⁶⁰Ibid. LVII (1834) 113.

¹⁶¹Ibid. 123.

¹⁶²Ibid. XIV (1845) 330.

¹⁶³*Ann. Chim.* XC (1814) 47.

¹⁶⁴*Bibl. Univ.* XLIX (1832) 226. *Ann. Chim.Phys.* LVIII (1835) 432.

"Water vapour contains...1 volume of hydrogen and 1/2 volume of oxygen, one of its particles will be composed of a whole particle of hydrogen and half a particle of oxygen."¹⁶⁵

"The particles are composed of molecules...he [Ampère] calls molecules a group of atoms... In the explosion of 1 volume of oxygen and 2 volumes of hydrogen...each molecule of oxygen is divided into two, and the atoms of each half join with atoms of a molecule of hydrogen to form a molecule of water."¹⁶⁶

The change in his theory seems to have been caused by the demands of physics rather than those of chemistry – Ampère attributed to molecular vibrations the phenomenon of sound and to atomic vibration light and heat.¹⁶⁷

The interpretation of Ampère's ideas by other chemists varied. "The word molecule was used in the sense of atom by Ampère."¹⁶⁸ "Ampère had arrived at the idea that in every chemical substance there were...three forms of matter – the indivisible atom, the molecule,... and the particle."¹⁶⁹ Laurent's misunderstanding of Ampère's hypothesis has been given on page 32. Gaudin promised to give a rigid definition of atom and molecule but attributed Ampère's or Avogadro's hypothesis to M. Gay-Lussac.¹⁷⁰ Persoz described Gay-Lussac's theory correctly but confused Ampère's theory with the theory of volumes of Berzelius.¹⁷¹

It seems that Ampère's theory of gases was much better known than Avogadro's. It is ironical to find Avogadro saying "This principle is today sufficiently generally admitted either explicitly or implicitly by physicists and chemists."¹⁷² The principle, in so far as it was admitted at all, was that of Ampère. In 1826 Dumas wrote that all physicists agreed in supposing that in gases under the same conditions the molecules were in equal numbers in the same volume.¹⁷³

English chemists knew of Avogadro's hypothesis, if at all, through the work of the English chemist Prout and through Dumas. Whatever the source it was not well understood. Whewell raised the etymological objection that in the formation of hydrogen chloride the volume expansion could only be reconciled with Avogadro's hypothesis by dividing into two each of the compound particles, each constituted of an atom of chlorine and an atom of hydrogen – which contradicted the indivisibility of the atom.¹⁷⁴

Here is an extract from an extremely disdainful book review in the *Philosophical Magazine*:¹⁷⁵ "The selection of hydrogen for this purpose [the standard of combining weights] had nothing whatever to do with its lightness, for that circumstance does not in the slightest degree affect the question; if it did then nitrogen should be represented by a lower number than oxygen instead of a higher one, in the proportion of 14 to 8; the reason for selecting hydrogen is the smallness of its combining weight."¹⁷⁶ The combining weight system accepted in England was that of equivalents.

Gmelin was even more obtuse: "If it [Avogadro's hypothesis] be admitted...then it will follow that all gases must contain equal numbers of atoms in equal volumes. But that such a

¹⁶⁵*J. des Mines* XXXVII (1815) 9.

¹⁶⁶*Bibl. Univ.* XLIX (1832) 225.

¹⁶⁷*Ibid.* 227.

¹⁶⁸Tilden, *J.C.S.* CI (1912) 1682 footnote.

¹⁶⁹Brodie, *Phil. Trans.* CXL (1850) 760.

¹⁷⁰*Bibl. Univ.* LII (1833) 131.

¹⁷¹*Intro. à la Chim. Mol.* 38

¹⁷²*Ann. Chim. Phys.* XIV (1845) 330.

¹⁷³*Ibid.* XXXIII (1826) 337.

¹⁷⁴*Philosophy of the Inductive Sciences* (1847) 424.

¹⁷⁵XXIV (1844) 298.

¹⁷⁶Odling (translator) Laurent, *Chem. Method*, London (1855) v.

supposition is by no means necessary is seen at once from this – that with respect to compound gases the law in question is sometimes true, sometimes false."¹⁷⁷ and he described the formation of hydrogen chloride and showed how the hydrogen chloride molecules could only be half as numerous, in the same volume, as the reactant molecules. This argument was of course frequently used in earlier years.

It is difficult to find evidence of the ignorance of Avogadro's hypothesis except in its neglect, and in occasional outbursts of exasperation: "Mr. Griffins at least (an English chemist) has failed to understand what I mean by splitting atoms."¹⁷⁸

Atomic theory: the change from belief to scepticism

The chapters on Laurent, Gerhardt and Persoz have shown how theories of gases came to be derived not by direct speculation but through the demand for a simpler chemical notation. On the microscopic nature of gases these chemists showed no opinions, although they used the physical evidence of vapour density and the progression of boiling points in analogous compounds, and the polybasicity of acids. There is in their abstract theories nothing comparable with the polyhedra of Ampère, the long interlocking molecules of the carbon of Avogadro or the miniature lead shot tumbling slowly among the bouncing spheres of Dalton's gases. They were not struggling with the phenomena of nature but with the entirely artificial confusions of the competing systems of chemical nomenclature, devised to avoid the need for hypothesis altogether. How did the belief in the ability of theories to give an insight into physical reality decline from the concrete models of Dalton and Ampère to the abstractions of Faraday, Liebig, Ostwald and Divers?

Dalton's arguments in favour of the existence of atoms were probably the law of multiple proportions, the independence of mixed gases, the ratios in which gases dissolved in water, the independence of vapour pressure from external gas pressure and the existence of three states of matter, gas, solid and liquid, accessible to most materials.¹⁷⁹ Later on, the discovery of isomers supported the existence of atoms¹⁸⁰ and some less convincing arguments were derived from crystal forms.

The general line of argument against the atomic theory was that it might be true but that it was certainly useless because an unambiguous list of atomic weights was unattainable. It was dangerous to clutter up chemistry with unnecessary hypotheses whose mere existence might, with the passing of time, give them bogus authority.¹⁸¹

The concrete arguments against the theory belonged, characteristically, to the early period of the theory itself and later both the theory and its opponents became more vague and cautious.

The evidence for the reality of atoms was provided by those who most mistrusted their use, Wollaston and Faraday, and the first battle was fought in the true Daltonian manner in the upper reaches of the earth's atmosphere.

Wollaston argued that if matter were continuous there would be no limit to the earth's atmosphere, it would just fade away; but if there were atoms in the atmosphere there would come a point where they would be so far apart that their mutual repulsion would be equalled by the force of gravity. Above this point no atom would be in equilibrium.¹⁸²

¹⁷⁷ *Handbook*.

¹⁷⁸ Dumas, *Leçons sur la Phil. Chim.* 264.

¹⁷⁹ *New System* I, 141.

¹⁸⁰ Daubeny, *Atomic Theory* 120.

¹⁸¹ Faraday, *Phil. Mag.* XXIV (1844) 136.

¹⁸² *Phil. Trans.* CXII (1822) 89.

The refraction of light from the stars by the atmosphere confirmed its finite nature but not the validity of the argument. Whewell pointed out that apart from the general ignorance of the behaviour of very rarefied gases, the need for compression and the compressing weight vanished together at the surface of the atmosphere so that their balance was unpredictable.¹⁸³ Dumas also mentioned that the behaviour of very rarefied gases could not be predicted, nor even their state – the extremity of the atmosphere might be liquid or solid. He also used an argument similar to Wollaston's but surprisingly geocentric: if the atmosphere were to extend to infinity it would also concentrate round the other bodies of the solar system, but it didn't because the transit of the planets was undistorted by any atmospheric refraction.¹⁸⁴

Faraday attempted a direct experiment to reproduce the conditions of the upper atmosphere at the surface of the earth. He cooled rather involatile liquids in an evacuated box to see if the vapour pressure of the liquid diminished steadily or suddenly dropped to zero. He found that below a certain temperature a gold leaf suspended above mercury did not tarnish, however long the experiment continued, and he concluded that there was a limit to evaporation. However after describing other experiments of a similar nature he wrote: "I refrain from extending these views as might easily be done, to the atomic theory, being rather desirous that they should first obtain the sanction or correction of scientific men."¹⁸⁵ Faraday later described the atomic theory as "at best but an assumption."¹⁸⁶

Wollaston was another opponent of the use of the atomic theory who provided strong evidence in favour of its truth.¹⁸⁷ This was his discovery of acid salts such as NaHSO_4 . If, as Wollaston believed, these were true compounds and not molecular complexes ($\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4$) they supported the atomic theory and showed the inadequacy of the system of equivalents, on which the existence of such salts could be abolished by a simple change of number. This was the argument used by Laurent to halve the molecular formulae of many compounds. Both Laurent and Gerhardt admitted the possibility of molecular compounds and all three chemists were cautious in their belief.

"Formulae can only represent simple relationships or reactions but not the molecular arrangement."¹⁸⁸

"In order to avoid all hypothesis I shall not attach to the term atom any other sense than that which is included by the term proportional number."¹⁸⁹

Wollaston thought that the criteria for fixing the number of various atoms in a compound were too hypothetical but realised that equivalents would not be a sufficient substitute since the geometry of molecules would become important in the future.

As with Avogadro's hypothesis the ambiguity rather than the error of the atomic theory was the subject of attack. Laurent said that the physical methods for finding atomic weight: vapour density, atomic heat and isomorphism gave contradictory results.¹⁹⁰ The distinction between physical and chemical atoms, made by Avogadro and Dumas, made the possibility of finding the true atomic weight even more remote. Dumas claimed that neither the reactions of chemistry nor the phenomena observable in outer space proved the existence of atoms, and that even if they did exist the equivalents and what were called atoms were merely molecular groups. "If I had the power I would efface the word *atom* from sci-

¹⁸³ *Phil. Ind. Sciences* I, 437.

¹⁸⁴ *Leçons sur la Phil. Chim.* 237.

¹⁸⁵ *Phil. Trans.* CXVI (1826) iii, 492.

¹⁸⁶ *Phil. Mag.* XXIV (1844) 136.

¹⁸⁷ *Phil. Trans.* CIV (1814) 7.

¹⁸⁸ Gerhardt, *Traité de Chimie* IV 564.

¹⁸⁹ Laurent, *Méthode de Chimie* 57.

¹⁹⁰ *Ibid.*

ence.¹⁹¹ Persoz, on the other hand, objected to its failure to account for why two quantities should be equivalent, rather than its ambiguity.¹⁹²

Faraday's objection to the atomic theory was more concerned with its physical than its chemical aspects – whether matter was continuous or discontinuous. His argument was that if space were an insulator all bodies should be non-conductors and if space should conduct electricity all bodies would be conductors. The modification he used to overcome this was that atoms filled all space and interpenetrated rather than juxtaposed to form compounds; their atmospheres (lines of force) extended to the limits of the universe to overcome the anomaly of force acting at a distance.¹⁹³ Daubeny disagreed. He thought that conduction depended on the nature of the particle, not on the nature of space.¹⁹⁴ Faraday's theory did however allow the increased rate of reaction on heating (and therefore expanding) gases, which was a great embarrassment to the caloric theory.

Long after Avogadro's hypothesis had been accepted as a method of fixing atomic weights the physical basis of it, and of the atomic theory, was disputed.¹⁹⁵

Caloric

Chemists were mostly as sceptical as they were ignorant about the nature of caloric, or the force or the fluid which expanded gases into any space made available to them. Whewell thought the theories of heat insufficiently complete for them to be mixed up with the more quantitative ideas of chemistry.¹⁹⁶ Nevertheless atoms were often kept apart by caloric well into the middle years of the century. Persoz preferred the caloric theory to the vibratory one as giving a better explanation of the chemical effect of heat.¹⁹⁷ Daubeny also used caloric¹⁹⁸ and the diehard traditionalist Gmelin seemed confident of its status as an imponderable fluid.¹⁹⁹ Avogadro still used caloric, with caution, in 1845.

Some chemists however held kinetic theories of heat – Cavendish, Davy, and among those who supported Avogadro's hypothesis, Ampère and Gaudin.²⁰⁰

Finally here is the attitude of Cannizzaro who first gave a complete *chemical* description of the nature of gases. "We must hasten to remark that these figures [graphic representations of molecules] are nothing but artifices of the mind intended to represent to the sight that which in reality we perceive only through the veil of transformations." And of Avogadro's hypothesis: "It must indeed be either the actual truth or the image of that truth seen through media interposed between our intelligence and reality."²⁰¹

Summary and Conclusion

1. Nearly all the gas theories were static. The ability to mix demanded that all gas species should differ in some way. This was one of the reasons why chemists concentrated on the chemical rather than the physical nature of gases and derived the weights of gas particles not from their density but from their chemical combining weights.

¹⁹¹ *Leçons sur la Phil. Chim.* 242 & 290.

¹⁹² *Ann. Chim. Phys.* LX (1835) 120.

¹⁹³ *Phil. Mag.* XXIV (1844) 137.

¹⁹⁴ *Atomic Theory* 47.

¹⁹⁵ *Divers, B.A.* (1902) 568.

¹⁹⁶ *Phil. Ind. Sciences* I, 420.

¹⁹⁷ *Chim. Mol.* 218.

¹⁹⁸ *Atomic Theory* 164.

¹⁹⁹ *Handbook* 7, 111.

²⁰⁰ Ampère, *Bibl. Univ.* XLIX (1832) 228.

²⁰¹ Faraday lecture, *J.C.S.* X (1872) 948, 964.

2. All forms of heat were contained in the homogeneous caloric envelope of the atom. It was difficult to reconcile the volume and the heat content of the particles and there was sufficient vagueness in the methods to accommodate any antagonistic evidence and any useful new theory, so the direct influence of this problem was small.
3. Because of 1 and 2 above, and for other reasons, Dalton gave a different size to the particles of each gas species. He was able, in consequence, to give only a single atom to the the gas particles of the elements without contradicting vapour density measurements. This last mistake had some influence on Berzelius as he repeated it in his theory of volumes.
4. The general belief in the additive nature of chemical reaction supported this.
5. So also did the electrical theories of affinity developed after the discovery of electrolysis, which suggested that combination between similar atoms would be weak.
6. Gay-Lussac's law contradicted, successfully, Dalton's theory of gases and suggested to Berzelius an identity in size of the gas particles of elements and a different size for those of compounds.
7. Gay-Lussac's law suggested to Avogadro that the combining volumes of gases, and the volumes of solids extrapolated to this state, would be a convenient measure of their chemical combining quantities.
8. Gay-Lussac's law suggested to Avogadro the uniformity in size of *all* gas particles and consequently the divisibility of elemental gas particles. But this was mere speculation.
9. Ampère reached the same conclusion, mainly from physical reasoning. His gas particles contained discrete atoms of the elements smaller than those which took part in chemical reaction and so there arose the division between chemical and physical atoms.
10. Avogadro's gas particles were likewise more complicated than the reactions of chemistry demanded because of his wrong modification of Dulong & Petit's law, due to the experimental difficulty of finding the specific heat of a substance in more than one of its physical states (see also 11 below) and to his incorrect extension of the law to compounds, and also because of his inability to account in any other way for the solidity of light elements like carbon.
11. Dumas supported and developed the division between the chemical and the physical atom, mainly because he believed that the latter was measured by Dulong & Petit's law, whose anomalies were mistaken for simple fractional multiples through the magnitude of experimental error; and also because chemical analogies were not reflected in volumetric ones with compounds such as NH_3 , P_2H_6 , O_2 and S_8 .
12. The fall of Berzelius' theory of volumes and the ambiguity of the methods of defining atomic weights made chemists fall back on the system of description by equivalent weights and equivalent volumes which, though intended to dispense with hypotheses, were largely based on them.
13. Davy's theory of acids encouraged the admission of double-decomposition as a chemical process.
14. Gerhardt and Laurent extended double-decomposition to all chemical reactions. They arrived at some of the results of Avogadro's hypothesis but their different mistakes over the atomicity of oxygen betray the dogmatism of their reasoning.
15. Gaudin used Avogadro's hypothesis to derive the correct formulae of many substances; his only mistake was to underestimate the importance of his work.

16. Cannizzaro used Avogadro's hypothesis to remove both the ambiguity and the distrust of the atomic system.

Influences rather than events may have helped the neglect and ignorance of Avogadro's hypothesis, namely:

Avogadro's failure to see the chemical usefulness of his hypothesis.

The scepticism accorded to physical theories after the failure of the atomic theory.

Avogadro's imperfect mastery of French.

Avogadro's confused terminology.

Ampère's equally confusing modification to *his* theory.

And in support of the hypothesis:

The likelihood that the particles of both elements and compounds were of the same order of complexity.

The physical similarity of gases.

Most of the histories of the confusion of atomic weight measurements in the first half of the nineteenth century have concentrated on showing the origin of the inconsistencies which led to the multiplicity of formulae for the same substance and a corresponding multiplicity of atomic weights. From this point of view the failure of chemists to use Avogadro's hypothesis is inexplicable; the position now held by this hypothesis among the fundamental rules of chemistry is due to its use in the unambiguous fixing of atomic weights by Cannizzaro.

In this thesis I have attempted to show that the whole attitude of scientists to their work prevented them from taking this essentially modern view of the hypothesis. It is evident that not only Avogadro's hypothesis but even Dalton's atomic theory were physical theories whose applications to the investigation of the chemical composition of substances were not predominant in the minds of their inventors. Dalton was trying to find the nature of the atmosphere, Avogadro based his system of chemistry on a law from which he derived his hypothesis as something that would interest the physicist, and Ampère was a physicist, one of whose rare excursions into chemistry was the use of Avogadro's hypothesis to find the shape of the particles of matter. Dumas said that the hypothesis was generally admitted by physicists and went on to demonstrate that it was useless to chemists.

This is why I have, in the earlier chapters, described in some detail the caloric and electrical theories of gases. I have tried to show in a narrative account of the physical theories of gases that the earlier ideas which seem to us absurdly naive, were more productive than the rationalism of Dumas and the double-decomposition dogma of Gerhardt and Laurent. Gerhardt's reason for making oxygen gas particles O_4 and Laurent's reason for making them O_1 were scarcely more persuasive than Ampère's tetrahedra of oxygen atoms, and no more accurate.

The progress of chemistry in this epoch served only to confuse it. After the early years of speculation the later chemists were more concerned with classification. They used gases without bothering, or feeling able, to describe their nature; the atomicity of the gas particle became more important than its shape. Then the separation of the units of chemical and physical change persuaded chemists that a knowledge of the true atom, the smallest particle of an element, was unattainable, and they lost faith in all theories. The compromise which they devised – the equivalent weight system – is a cautionary tale in the perils of timidity.

Even if the inventors of the theories were not concerned with applying them to atomic weight determination there was no reason why others should not. Gaudin and Cannizzaro did use Avogadro's hypothesis, Berzelius used an incomplete version of it and all three, of course, used the atomic theory; but on the whole the gap between physics and chemistry, exemplified in the retirement of chemists to the equivalent system, widened throughout the period. Even in the gas theory of Laplace the greater freedom of speculation indulged in by the physicist is evident and the atomic theory of Faraday and the memoirs of Ampère show that this tradition was maintained.

On the other hand the necessity for accounting for physical phenomena encumbered the theories in their chemical applications – chemists found it impossible to amalgamate the physical and the chemical characteristics of caloric – elasticity and heat of reaction. In this case the chemical effect won and Dalton's theory of gases attests the danger of applying chemical quantities to physical phenomena. With Avogadro's hypothesis however the *physical* law of Dulong & Petit was used in error and the damage was as great – the chemical atom was divided into physical atoms.

The obstacles to the application of Avogadro's hypothesis to chemical combining weights were considerable and its neglect here is understandable, but it is surprising that chemists should have been divided so sharply into the few who believed that everyone was familiar with it and the many who had never hear of it or had not comprehended it. This does seem inexplicable. Perhaps since there was no sense of its importance chemists did not bother to become familiar with the hypothesis and the last chapters are given to the baffling twists of terminology which may have added confusion to the growing scepticism over physical theories, which questioned even the reality of such particles.

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