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W. G. Palmer

Excerpt

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Chapter I

THE ORIGINS

1. Dalton

While science is pursuing a steady onward movement, it is convenient from time to time to cast a glance back on the route already traversed, and especially to consider new conceptions which aim at discovering the general meaning of the stock of facts accumulated from day to day in our laboratories.

MENDELEEFF, Faraday Lecture of the Chemical Society,
J. Chem. Soc. 55, 634 (1889).

Had Mendeleeff been lecturing on the theory of valency he would doubtless have chosen a stronger word than 'convenient', for unless the reasons for the long delay in its discovery are properly assessed and appreciated, an essential perspective is wanting, and the dominance attained by the theory in later chemistry will hide its subtlety, and unexpectedness. It is tantalizing to speculate whether this central doctrine of modern chemistry would have emerged much earlier, if Dalton had been more sensitive to the chemical aspects of the atomic theory, Avogadro's principle been more generally accepted at the date of its first proposal, and atomic weights fixed by Berzelius in place of Gerhardt and Cannizzaro. An affirmative answer is improbable, for the hesitation of the earlier generations of chemists to accept the hypotheses that to-day are seen in so clear a light was mainly due, not to any obtuseness or prejudice, but rather to the lack of a secular maturation of both thought and experiment, which, inherited in the end by their successors, enabled the latter to progress at a hitherto unparalleled rate.

That the discoverer of the law of multiple proportions should have failed to realize some of the implications of the law in regard to the subdivision and limitation of combining power is traceable in part to Dalton's preoccupation with physical matters, in particular with the serious problems of gaseous diffusion arising from the Newtonian picture of gaseous constitution still held in Dalton's time. A gas was conceived of as consisting of a sparse distribution of heavy particles kept

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separated by a relatively voluminous but tenuous envelope of 'caloric' or heat. The elastic properties of a gas were ascribed to the compressibility of the caloric envelope. On withdrawal of heat the system contracted, liquefaction and finally solidification ensuing. When Dalton and his contemporaries wrote of the size of a gaseous particle they meant the diameter including the caloric envelope. To a world regarding a kinetic theory of matter as almost axiomatic this entirely static picture seems fantastic, but when the single idea of molecular motion was unknown it gave a workable, and it may be the only possible picture. It is too seldom realized that those who laid the experimental foundations of our knowledge of gases—Priestley, Gay-Lussac, Dalton, Avogadro—all thought of a gas in some such way.

Dalton's early interest in meteorology (see footnote)* had brought him into contact with the properties of those gaseous mixtures that form the atmosphere; and he had, as is well known, sufficiently studied the solubility of gaseous mixtures to enunciate a law (1802). He saw that the fact, unknown to Newton, that the atmosphere was a mixture of gases, would demand, on the static Newtonian picture, a stratification, the denser particles accumulating in immediate contact with the earth. Such an effect would of course have results quite distinct from the well-known gradual change of density with height and pressure. In 1803 Dalton discussed such problems in a memoir entitled *Spontaneous Intercourse of Different Elastic Fluids in confined Circumstances* (in modern terms—Gaseous diffusion). He tentatively advanced the novel theory that spontaneous mixing might be due to the inequality of the 'sizes' of particles of gases differing in the chemical sense, suggesting that the smaller particles might penetrate between the larger, and, as he said, 'an intestine motion' be set up. It was obvious that if the relative weights w of different particles could be found, the (relative) number N per unit volume of gas was immediately calculable as $N = d/w$ (d = specific gravity), and then the relative diameter as $1/\sqrt[3]{N}$.

In Dalton's mind the atomic theory had at this time become the basis of his mode of thought, and he now associated with the

* *Meteorological Observations and Essays*, London, 1793.

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DALTONIAN THEORY

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general theory certain rules of chemical combination, and in so doing took an epoch-making step in the history of chemistry. His most important rules may be thus summarized: (a) if two elements A and B yield only one compound, its composition is assumed to be AB, (b) if more than one compound is known, there will be A_2B and AB_2 in addition to AB, and so on for still more complex unions. In fact he took a purely statistical view of the probability of formulae, regarding A_2B and AB_2 as equally likely. Here was certainly no inkling of the principle of valency, but it is not to be forgotten that a number of Dalton's contemporaries with livelier chemical intuition, notably Gay-Lussac, Wollaston and Davy, expressed scepticism of these arbitrary rules (see e.g. Wollaston, *Phil. Trans.* **104**, 1 (1814)). Using existing analyses mainly of compounds he regarded as of the type AB (e.g. water HO, sulphuretted hydrogen HS, carbonic oxide CO, ammonia NH, phosphoretted hydrogen PH) he prepared (1803) his first table of 'atomic weights' ($H=1$), including of course what we should now term molecular weights. Later, Dalton himself experimented on the composition of nitrous and nitric oxides, and of methane and ethylene, in order to secure an acceptable experimental basis for his rules of combination, which however he himself probably regarded as self-evident. The law of multiple proportions resulted.

Having prepared a table of relative weights, Dalton proceeded to his main object, the calculation of 'atomic sizes', and produced the table given in full below.

Table 1

Compound (modern formulae)	Specific gravity (air = 1)	Diameter	Compound (modern formulae)	Specific gravity (air = 1)	Diameter
SiF_4	—	1.15	Cl_2	—	0.981
HCl	—	1.12	NO	1.102	0.980
CO	—	0.94	SO_2	2.265	0.95
CO_2	1.500	1.00	N_2O	1.610	0.947
H_2S	1.106	1.00	NH_3	0.580	0.909
PH_3	—	1.00	C_2H_4	—	0.81
H_2	0.077	1.00	O_2	1.127	0.794
CH_4	—	1.00	N_2	0.966	0.747

Atomic weights (1810)

Hydrogen	1	Carbon	5.4
Oxygen	7	Sulphur	13
Nitrogen	5	Phosphorus	9

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During the course of this work Dalton noted but could not explain the facts that although the 'atom' of water must be heavier than that of oxygen, and that of nitric oxide nearly twice as heavy as the 'atom' of oxygen, yet steam was much lighter than oxygen and nitric oxide of about the same density. By assigning the formulae H_2O , NO and O_2 in 1811 Avogadro provided a complete explanation, which however failed to convince Dalton (see below).

In the table are recorded Dalton's atomic weights of 1810, those specific gravities that he left on record, and his final calculation of diameters, given in a lecture in 1810. For convenience and brevity the gases are listed under modern formulae. It will be seen that five different gases appear to have identical sizes, and the general variation from equality is much less than the variation of either the 'atomic weight' or the density. Yet Dalton, perhaps a little biased by his theory of diffusion, refused to see anything suggestive in this near-equality. He in fact regarded the values of the table as finally refuting the claims of Avogadro (1811) and others to interpret Gay-Lussac's law of gaseous combination (1809) as proving the equal 'sizes' of all gaseous particles, or as is now said 'equal volumes contain equal numbers of particles'. It is an interesting speculation that had Dalton been of a rather more sanguine temperament he might have given to the world not only the atomic theory, but also that generalization, now associated with the name of Avogadro, which yields in importance only to the atomic theory. At least he would have withheld that bitter opposition, which, combined with his great prestige, more than any other single influence militated for fifty years against the general acceptance of Avogadro's principle.

The following quotations illuminate Dalton's tendency to adopt a deductive attitude, and also the movement of chemical thought in his day. (*Italics have been inserted.*)

The combination of gases in equal or multiple volumes is naturally connected with this subject. Cases of this kind, or at least approximations to them, frequently occur; but no principle has been suggested to account for the phenomena; *till this is done I think we ought to investigate the facts with great care: and not suffer ourselves to be led to adopt analyses till some reason can be discovered for them.*

New System, Vol. II, 1827.

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THE DUALISTIC THEORY

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When he [Dalton] did see it [Gay-Lussac's account of his law of gaseous combination, in 1809] he set himself to show that Gay-Lussac's opinions were ill-founded. But the later researches of chemists have left no doubts about their accuracy; and if Mr Dalton still withholds his assent, he is, I believe, the only living chemist to do so.

System of Chemistry, edition of 1825 by Thomas Thomson. In the edition of 1807 Dalton encouraged Thomson to publish a preliminary summary of the atomic theory.

2. Berzelius

Dalton could have had no more wholehearted supporter of his ideas than Berzelius, who patiently devoted the early years of a long life of chemical research to discovering and perfecting methods of analysis, ultimately demonstrating beyond all doubt the validity of the law of multiple proportions. Berzelius, in his approach to the problems of chemical composition, made full use of the results of his pupil Mitscherlich in the new field of isomorphism (1819), and also of the law of atomic heats announced by Dulong and Petit in 1819. His analyses soon compelled him to modify Dalton's original rules of chemical union; thus on finding the oxygen in two oxides of iron to be in the proportion 2:3, he changed Dalton's formulae FeO and FeO₂ to FeO₂ and FeO₃; later an application of the principle of isomorphism forced a further modification to the modern formulae FeO and Fe₂O₃.

During the first decade of the last century, it had been established that by electrolysis the results of chemical combination can often be disunited. As examples we may cite the electrolysis of water (without addition of acid or alkali) by Nicholson and Carlisle in 1800; the decomposition of salts into acid and base by Berzelius and Hisinger in 1803; and, most famous of all, the isolation of metals from the caustic alkalis in 1807 by Davy using the electrolysis of fused alkali, electrolysis of saturated solutions having failed to produce the metal. The notion that 'chemical action is reversed electrolysis', to be so insisted upon in later years by the late Professor Armstrong, was already present in many minds, but it was especially Berzelius who devised a working electrochemical theory of chemical union (1812–1819). Elementary atoms were supposed to possess

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(unspecified) quantities of both positive and negative electricity, but usually not in equal amounts; in electronegative, i.e. anode-seeking elements, the negative predominated, and conversely for cathode-seeking or electropositive elements. The supporters of this theory never made clear how it could be compatible with the electroneutrality of matter in its normal state. Both kinds of electricity seemed to be needed in each atom. First, in order to take account of the formation of more than one compound between atoms A and B; it appeared necessary, for example, to explain the two chlorides taken to be CuCl and CuCl_2 by assuming that copper could adopt two electropositive states, in which the balance between the two kinds of electricity was different. Secondly, to explain how, for example, sulphur could be negative in CaS and positive in SO_2 . Chemical combination was simply regarded as the partial mutual saturation of the residual charges on the combining elements, which were necessarily of electropositive and electronegative character respectively. The idea of a *saturation* (Berzelius used the term 'neutralization') rather than of mere electrostatic attraction was demanded even to ensure a constant composition for a given chemical individual; and in this we may see, with some risk of committing an anachronism, the first germ of a theory of valency.

The *partial* nature of the saturation was essential to the theory. In bases (basic oxides), such as sodium, calcium and copper oxides, the original positive electrification of the metal predominated; in acids (acid anhydrides) the negative character of oxygen had the upper hand. Hence the possibility of salt formation; and, if the electrification were not then finally neutralized, double-salt formation could follow. All chemical compounds were regarded as at least formally dissociable into two oppositely charged parts, an attitude summarized in the description 'dualistic'. The theory afforded a classification of acids and bases—bases such as the oxides of sodium and calcium which, owing to the high net positive charge on the metal, still retained much positive charge were classed as 'strong'; acids were 'strong' if the negative charge was marked. Since the negative charge on the acids was ascribed to oxygen, acids with a high proportion of oxygen were strong. It is noteworthy that,

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with the modern meaning of strength, such a classification is still in the main valid—as examples, we may take sulphurous and sulphuric, nitrous and nitric, hypochlorous and perchloric. The most stable compounds were naturally those formed from two ‘strong’ components: stability and charge were interrelated.

This first electrochemical theory of combination is typical of a class of hypotheses, that by their very elasticity excite scepticism; they seem to explain everything but predict nothing. Whether the second, modern, electrochemical theory is also in this class may be a matter for argument, but at least it may be urged that it rests on a far more quantitative basis than the first. It was upon a quantitative question that the theory of Berzelius came finally to grief. In 1834 Faraday announced his laws of electrolysis, which show that the same amount of electricity is needed to release an atom of copper from its sulphate as to liberate two atoms of hydrogen from a molecule of water; atomic charge and stability—or as we now might say, affinity—are not related. Other contemporaneous developments damaging to the theory were the discovery, associated with the name of Dumas, that the electronegative atom chlorine could replace the electropositive hydrogen in organic compounds without fundamental change of properties, and the growing acceptance of the polyatomicity of elementary molecules such as those of the common elements (p. 12). Had the theory of substitution been seen against a more general background than that of the compounds of carbon, less weight would have attached to it, for PH_3 and PCl_3 are certainly bodies of very distinct properties. Although the theory had to be abandoned, the ideas on which it was based became a permanent acquisition to chemistry. It raised for the first time the *nature* of chemical union, and rightly ascribed it to electrical action; it postulated rightly, although in an entirely speculative way, the presence of both kinds of electricity in atoms, and it assumed that mere electrostatic attraction between the combining units is insufficient to explain the facts of combination.

The difficulty about elementary molecules, such as H_2 and Cl_2 , was of course that no polar mechanism could be assumed to act between identical atoms. In this matter Berzelius allowed

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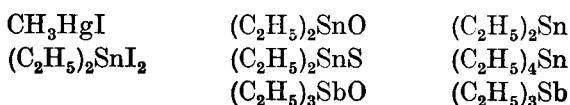
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himself to take a grossly illogical position; he accepted Avogadro's doctrine for compounds, but rejected it for elements. We must, however, not allow longstanding familiarity with the 'doubled' formula to blind ourselves to the fact that a real explanation of the union of like atoms was first forthcoming from the work of Heitler and London in 1927, which was based on the modern subject of quantum mechanics. A point of similarity in the scientific attitude of Dalton and Berzelius may be detected, in that both men refused to accept apparently well-founded experimental facts because these facts appeared to controvert preconceived theories. Before real progress could be achieved in understanding the nature of chemical union, the most difficult step had to be taken—the disentanglement of the *existence* of what we should now call a bond, from the *strength* of the bond. In the series HCl, HBr, HI it is assumed that in all cases a single bond unites the elements, but, as we now well recognize, the bond *strength* decreases regularly in the series, in a non-integral manner. The distinction here being drawn, in effect between valency and affinity, is entirely unexpected and at first sight unpalatable. We should rather have expected the very reactive chlorine to unite with more atoms of hydrogen than the less reactive iodine. That the difficulty was long felt is shown by the fact that A. W. Hofmann, in his *Einleitung in die moderne Chemie*, edition of 1877, after a carefully worded warning (on p. 183) against confusing 'intensity of chemical avidity' with 'quantivalence', proceeds to use words and phrases such as 'Bindekraft' and 'Kraft des Sauerstoffatoms' (on p. 269), and thus seems himself, at least to a literal reader, to confuse 'bond force' with bond. The first to draw public attention to the need for distinction was Frankland, whose ideas form part of the subject-matter of the following section.

3. Frankland and Kekulé

In the *Phil. Trans.* of 1852, at p. 440, at the close of a paper describing the preparation and properties of novel organo-metallic compounds including (in modern formulae):



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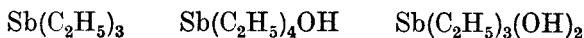
THE DISCOVERY OF VALENCY

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Frankland writes as follows: 'When the formulae of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction; the compounds of nitrogen, phosphorus, antimony and arsenic especially exhibit the tendency of these elements to form compounds containing 3 or 5 equivalents of other elements, and it is in these proportions that their affinities are best satisfied; thus in the ternary group we have NO_3 , NH_3 , NS_3 , PO_3 , PH_3 , PCl_3 , SbO_3 , SbH_3 , SbCl_3 , AsO_3 , AsH_3 , AsCl_3 , etc., and in the five-atom group NO_5 , NH_4O , NH_4I , PO_5 , PH_4I , etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident from the examples just given that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms.'

(The formulae are expressed in Gmelin's equivalent notation $\text{O} = 8$, $\text{H} = 1$.)

Referring to the series of antimony compounds, which may be expressed in modern formulae as follows:



Frankland says:* 'Stibethine furnishes us, therefore, with a remarkable example of the operation of the law of symmetrical combination above alluded to, and shows that the formation of a five-atom group from one containing three atoms, can be effected by the assimilation of two atoms, either of the same, or of opposite electrochemical character: this remarkable circumstance suggests the following question—is this behaviour common also to the corresponding compounds of arsenic, phosphorus and nitrogen; and can the position of each of the five atoms with which these elements respectively combine be occupied indifferently by an electronegative or an electro-positive element?' We discern in the first of these excerpts the first clear conception of valency; and in the second, some final hesitation to contravene the surviving dualistic hypothesis. It was particularly propitious that the idea of valency should have

* *Loc. cit.* p. 422.

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been first promulgated in connection with *metallic* compounds, for although the increasing recognition of the value of vapour and gaseous densities in fixing molecular weights and thence molecular formulae had been very generally applied to *volatile* compounds, metallic compounds, of which few are volatile, were still largely regarded as amenable to Dalton's arbitrary rules; in particular it had been customary to ascribe metallic oxides to the binary type MO (NaO, CaO, CuO, SbO, FeO, etc.), any appearance of specific valency being thus hopelessly obscured.

On reading Frankland's communication impartially a doubt must arise whether he realized the far-reaching importance of his conceptions, and his aloofness from controversies and participation in later developments does not lessen that doubt. In this he differed from Kekulé, who in his *Lehrbuch der org. Chemie*, p. 115 (1861), gave a clear discussion of valency, with special reference to the valency of carbon, without however in any way acknowledging a debt to Frankland. Whatever the true circumstances may be, Kekulé certainly soon became the dominating figure in the rapid expansion of the new ideas. With characteristic energy (and no little dogmatism) Kekulé proceeded to reorganize the already large bulk of knowledge in organic chemistry. In this direction he could successfully assume that in nearly all organic compounds hydrogen, oxygen, nitrogen and carbon had the constant valencies 1, 2, 3 and 4 respectively. He explained chain formation in the following words: '...the carbon atoms are themselves linked together, whereby a part of the affinity of the one carbon atom is necessarily tied by an equally large part of the affinity of the other',* and showed that $2n + 2$ is the saturation capacity of C_n . The possibility that the valency of carbon was less than 4 in unsaturated compounds was held by most of Kekulé's contemporaries (e.g. Wurtz, Kolbe, Erlenmeyer, Gerhardt, Williamson, and Couper).† The following extract from Williamson's *Chemistry for Students*, edition 1868, p. 126, indicates his cautious attitude:

'When carbon is burnt to form carbon monoxide each molecule of the oxide contains one quadrivalent atom of carbon

* *Ann. Chem.* **106**, 154 (1858).

† For Couper's views see *Compt. rend.* **46**, 1157 (1858).