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978-0-521-14814-6 - A History of the Concept of Valency to 1930

W. G. Palmer

Excerpt

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INTRODUCTION

We have a universally acknowledged system of constitutional formulae based on valency, which we define as the habit in regard to combination exhibited by elementary atoms, without necessarily forming any hypothesis on the nature of affinity.

SIR WILLIAM TILDEN, Cannizzaro Memorial Lecture
of the Chemical Society, 1912

Today more than one hundred chemical elements are recognized, and it is known that almost all of them form compounds, or fluorides, of the general chemical formula AF_n , with the element fluorine (symbol F). The known formulae of these compounds provide, however, no examples of the type A_mF in which the number m is greater than unity. The number n derived from the formulae AF_n therefore affords a genuine measure of the extent to which the total combining power of the element A is subdivided, since the combining power of fluorine is evidently indivisible: and it defines the *valency* of the element A towards fluorine.

Although it might well be expected on general grounds that each element would maintain a fixed but specific valency in all its compounds, only some thirty elements have this property. The valencies of those elements, carbon, nitrogen, oxygen, and hydrogen, with the multifarious combinations of which organic chemistry is primarily concerned, are invariable (C, IV; N, III; O, II; H, I) and consequently organic chemists, by devising consistent structural formulae based on these fixed valencies, achieved spectacular advances. It is among the metallic elements that the most numerous examples of varying valency are to be found: it was fortunate that Frankland (in 1852) based the earliest explicit formulation of the concept of valency upon his studies of (organo-) metallic compounds, and indicated from the first the possibility of variable valency. Many chemists, and especially Kekulé, who welcomed and exploited the concept with great acumen and enthusiasm, found it repugnant to

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follow Frankland's lead, and thereby entailed continued confusion and uncertainty in the field of inorganic chemistry. Indeed it was only in the present century when the then well-established principle of atomic valency became the main incentive towards a general theory of chemical combination (in which the principle became merged) that such difficulties were finally resolved.

The concluding clause of the excerpt from Tilden's lecture must almost certainly be the last public example of the over-complacency or even pride of the chemists of the later nineteenth century in the empiricism of their science, in which they differed widely from the contemporary physicists. The chemical attitude was no doubt engendered and fostered by the supreme successes of organic chemistry, resting only on the empirical principles of valency. Less than a year after the delivery of Tilden's lecture Bohr was to give his first exposition of the 'Rutherford-Bohr' model of the atom, to be followed in 1916 by the tentative but extremely significant speculations of G. N. Lewis on the nature of chemical union and the explanation of valency. The modern historian of chemistry must therefore regard the doctrine of valency as destined from the first to be subsumed in a general principle of chemical union. It is for this reason not irrelevant to review briefly the ideas on chemical combination which had gained wide acceptance before the rise of a clear conception of valency, and which were undoubtedly in the minds of those, including Frankland, who promulgated and first exploited its usefulness.

Scarcely any chemist at the present day speaks of Radicals or of Types: and yet the type-theory, like its forerunner, the dualistic view, had its good points. It would, I think, be wise, not wholly to lose sight of these several theories, which, after all, are based upon a considerable number of facts.*

* Kekulé, 'On some points of chemical philosophy', *The Laboratory*, 1 (1867), 303.

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DALTON AND WOLLASTON

Early notions of chemical combination

Chemical analysis or synthesis can go no further than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.

JOHN DALTON, *A New System of Chemical Philosophy*, vol. 1, part 1 (1808), p. 212.*

John Dalton (1766-1844)

John Dalton was born in 1766 at Eaglesfield, near Cockermouth in Cumberland, into a family of small proprietors. His paternal grandfather had joined the Society of Friends and his grandson was undoubtedly much influenced in his habits and character by the continuance of his parents in that body. He attended the village school, but only during the winter months, and in later life testified to the salutary effect of the outdoor exertions, willingly entered upon with his school mates during the months of summer, in fortifying the robust health he enjoyed all his life. Such was his progress, especially in 'ciphering', that at the age of twelve he took part in the teaching, and a year or two later enabled his former master to retire.

A cousin, George Bewley, kept a school in Kendal, where Dalton's elder brother Jonathan had already become an assistant, when John at the age of fifteen joined him. In 1785

* Cited hereafter as *New System*.

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Bewley resigned the school to the brothers Dalton. It was during his twelve years at Kendal that Dalton found in John Gough (also a member of the Society of Friends) a scientific preceptor of whom he afterwards wrote ‘For about eight years we were intimately acquainted. Mr. Gough was as much gratified with imparting his stores of science as I was in receiving them. . . . It was he who first set the example of keeping a meteorological journal.’*

Gough, who lost his sight in infancy, also prepared Whewell for his entry at Cambridge in 1812, and stirred him to write ‘a blind man, but very eminent in classics, mathematics, botany, and chemistry’: and Wordsworth acknowledged that the remarkable portrait in Book VII (ll. 482–515) of *The Excursion* was drawn from Gough. It was undoubtedly through Gough that Dalton was introduced to the writings of Newton, from which he formed his conviction of the atomic nature of matter. Dalton is said to have taken during his life upwards of 40,000 meteorological observations, the last on the day he died. He himself constructed the barometers and thermometers necessary for the purpose, and it may be remembered that it was an essentially meteorological problem that led to his first published table of atomic weights (p. 87).

With an intention, it may be thought, to clarify and consolidate his own knowledge in imparting it to others, in October 1787 Dalton circulated in Kendal a notice: ‘Twelve Lectures on Natural Philosophy to be read at the school (if a sufficient number of subscribers are procured) by John Dalton.’ The syllabus contained sections on ‘Mechanics, Optics, Pneumatics, Astronomy, and the Use of the Globes’ and concluded with ‘*Ex rerum causis supremam noscere causam*’. It was again Gough who in 1793 launched Dalton into wider fame, by recommending him as a teacher of mathematics in the New College of Manchester, which had arisen out of the Warrington Academy, where Priestley had taught. The teaching at Manchester was evidently more catholic than its description suggests for Dalton used Lavoisier’s new *Elements of Chemistry* in his work. Although

* Preface, *Meteorological Observations and Essays*, 2nd edition (London, 1834).

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making his first visit to so large a town Dalton was soon recognized by being elected to membership of the Literary and Philosophical Society in 1794, and a month after his election read his first communication to the society (on his colour-blindness). He became Secretary in 1800 and was President of the Society from 1817 until his death in 1844. One of his early Memoirs which recorded his experiments leading to the observation that 'elastic fluids are equally expanded by heat', was published six months before Gay-Lussac's similar observations. Dalton had in early life developed a habit of extreme diligence in all forms of intellectual activity, and replied to an inquiry, that he had never found the time to marry.

We must see him (Dalton) as a man having limited assistance from the knowledge of others, ignorant of many of the elegant and easy methods of procuring knowledge and illustrating facts which have become the common inheritance of universities, and accustomed to the society of few only who had similar studies. . . . Davy and Dumas add poetry and eloquence to sterling scientific vigour, whilst in Dalton we find only strength and rude simplicity.*

During the early nineteenth century the term 'gas' was used more specifically than today: for example, nitrous gas (nitric oxide), olefiant gas (ethylene). When it was desired to focus attention on the gaseous state in general the term 'elastic fluid' was commonly preferred. In this state the minute units of matter were thought to be embedded in a voluminous and 'globular' envelope of 'caloric' or heat. The elastic properties were ascribed to the compressibility of this envelope, and Boyle's law was explained by supposing that through its agency the chemical units repelled each other inversely as the distance between them.

When any body exists in the elastic state, its ultimate particles are separated from each other to a much greater distance than in any other state; each particle occupies the centre of a comparatively large sphere, and supports its dignity by keeping all the rest, which by their gravity, or otherwise, are disposed to encroach up to it, at a respectful distance.†

* From 'Memoir of Dr Dalton', by Dr Angus Smith, Secretary of the Manchester Literary and Philosophical Society, 1856.

† Dalton, *New System*, vol. 1, part 1, p. 211.

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On withdrawal of heat the gaseous system contracted, liquefaction and finally solidification ensuing. To a world accepting a kinetic theory of matter as almost axiomatic such an entirely static concept may seem incredible, but before the general recognition of 'heat as a mode of motion' (under the lead of Clausius and Clerk Maxwell from 1857) it gave a workable, and it may be the only possible model.

Respecting the nature of the principle (heat) there is diversity of sentiment: some supposing it a *substance*, others a *quality* or property of substance. Boerhaave, followed by most moderns, is of the former opinion; Newton with some others, are of the latter: these conceive heat to consist in an internal vibratory motion of the particles of bodies.*

The problem of the spontaneous interdiffusion of gases presented very serious difficulties, and Dalton, especially in his role as a meteorologist concerned with the atmospheric gaseous mixture, gave much attention to it. His discovery of the law now universally accepted as 'Dalton's law of partial pressures', which asserted that from a mixture of 'elastic fluids' each constituent dissolves in a liquid as though the others were absent, led him to the belief that in such a mixture only the *like* 'particles' repel each other: for in the process of solution like particles appear to suffer no constraint (or pressure) from the admixed unlike particles.

Thus for Dalton the physical properties of gases were related to a natural repulsion between like particles. It appeared to follow that *attractive* force was to be expected only between unlike particles and this Dalton identified with chemical affinity, leading to 'chemical synthesis'. Herein lay a main cause of his antagonism to Avogadro's thesis, which required *like* particles to exhibit attraction and chemical union (to give 'elementary molecules'); and also the central theme to be embodied somewhat later by Berzelius in his dualistic theory. The (compound) atoms resulting from 'synthesis' were classified as follows:

If there are two bodies *A* and *B*, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple: namely,

* Dalton, *Meteorological Observations and Essays*, 2nd edition (1834), p. 17.

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- 1 atom of A + 1 atom of B = 1 atom of C , *binary*,
 1 atom of A + 2 atoms of B = 1 atom of D , *ternary*,
 2 atoms of A + 1 atom of B = 1 atom of E , *ternary*,
 1 atom of A + 3 atoms of B = 1 atom of F , *quaternary*,
 3 atoms of A + 1 atom of B = 1 atom of G , *quaternary*, etc. etc.*

Dalton's profession as a schoolmaster was probably not unrelated to the somewhat abrupt style in which he was apt to publish his chemical principles, with little discussion and as almost self-evident. He could, however, be stirred by criticism to a more lively and persuasive vein. Such an occasion occurred in 1811 when, in a letter to *Nicholson's Journal*,[†] one of the principal scientific journals of the day and a forerunner of the 'Philosophical Magazine', Dr John Bostock, a practising chemist of some distinction, challenged Dalton's rules of chemical combination as arbitrary. These rules, published in the *New System*,[‡] were as follows:

1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.

2nd. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.

3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.

4th. When four combinations are observed, we should expect one *binary*, two *ternary* and one *quaternary*, etc.

5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.

6th. A *ternary* compound should be specifically heavier than the mixture of a *binary* and a simple, which would, if combined, constitute it.

7th. The above rules and observations apply, when two compound bodies are combined.

The following passages are extracted from Dalton's long and reasoned reply to Bostock, in *Nicholson's Journal*.[§]

I proceed now to point out the mechanical consistency of the 1st rule, which Dr Bostock has quoted, p. 283, namely, that 'when only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary'; and if this be established, the other three he quotes may be considered as corollaries from it.

* *New System*, vol. 1, part 1, p. 213.

† Vol. 28, p. 280. The editor and proprietor, Wm. Nicholson, F.R.S., was, with Carlisle, the first to electrolyse water.

‡ Vol. 1, part 1, p. 214.

§ Vol. 29, p. 145 (1811).

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Let us suppose a mixture, for instance, of hydrogenous and oxygenous gas, in such sort, that there are the same number of atoms of each gas; now as the gasses are uniformly diffused, each atom of hydrogen must have one of oxygen more immediately in its vicinity. The atoms of hydrogen are all repulsive to each other; so are those of oxygen; the atoms of hydrogen are all equally attractive of those of oxygen, and the attraction increases in some unknown ratio as the distance diminishes. Heat, or some other power prevents the union of the two elements, till by an electric spark, or some other stimulus, the equilibrium is disturbed, when the power of affinity is enabled to overcome the obstacles to its efficiency, and a chemical union of the elementary particles of hydrogen and oxygen ensues.

In the next paragraph Dalton contrasts the case that each hydrogen atom combines with its neighbouring oxygen ('and no part of either elementary gas is left uncombined') with the supposition that an oxygen atom 'should leap over the more proximate atoms of hydrogen to another at a greater distance, and consequently less attractive'.

The 2d, 3d, and 4th rules are necessarily consequent to the 1st. When an element *A* has an affinity for another *B*, I see no mechanical reason why it should not take as many atoms of *B* as are presented to it and can possibly come into contact with it (which may probably be 12 in general), *except so far as the repulsion of the atoms of B among themselves are more than a match for the attraction of an atom of A*. Now this repulsion begins with 2 atoms of *B* to one of *A*, in which case the 2 atoms of *B* are diametrically opposed; it increases with 3 atoms of *B* to one of *A*, in which case the atoms of *B* are only 120° asunder; with 4 atoms of *B* it is still greater as the distance is then only 90°; and so on in proportion to the number of atoms.^{1*}

¹ [Footnote] I find from the principles of statics, that, upon the supposition of spherical atoms of equal size, and that the law of repulsion after chemical union is the same as before, namely, reciprocally as the central distance, the repulsion of any one atom of *B* upon another of *B*, to separate it from *A*, is a constant quantity, on whatever point of the surface of *A* it may be placed; so that when there are three atoms of *B* the 3d atom is repelled twice as much by the other two as it would be by a single atom placed diametrically opposite. When there are 4 atoms, then the 4th is three times as much repelled, &c.

It is evident then from these positions, that, as far as powers of attraction and repulsion are concerned, (and we know of no other in chemistry) *binary* compounds must first be formed in the ordinary course of things, then *ternary*, and so on, till the repulsion of the atoms of *B* (or *A* whichever happens to be on the surface of the other), refuse to admit any more.

I must object to such loose quotations as the following; namely that I have assumed, 'that when only one compound of two elementary bodies can be obtained, it must be binary'; my language is, 'it must be *presumed to be a binary one unless some cause appear to the contrary*'.†

* Vol. 29, p. 147 (1811).

† *Ibid.* p. 149.

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[Dalton then quotes from his *New System*] ‘As only *one* compound of oxygen and hydrogen is certainly known,’ and ‘only one compound of hydrogen and azote has yet been discovered’.

The 5th rule is that a binary compound should always be specifically heavier than the mere mixture of its two ingredients. The principle on which this rule is founded is recognized by chemists as *general*, if not *universal*; namely, that condensation of volume is a necessary consequence of the expulsion of heat by the exertion of affinity. Thus steam is specifically heavier than a mixture of 2 parts hydrogen and 1 oxygen; ammoniacal gas is in like manner heavier than 21 azote with 72 hydrogen.*

It is remarkable that Dalton should nowhere else in his writings refer to a ‘principle recognized as general, if not universal’, nor does he appear to have expected a significant relation between the magnitude of the ‘expulsion of heat’ and the strength of the affinity exerted. By the time of Dalton’s death in 1844 trustworthy data in thermochemistry were being actively accumulated, and about twenty years later the two principal pioneers in this field, Thomsen (in Copenhagen) and M. P. E. Berthelot (in Paris) put forward the theorem that the heat of chemical reaction directly measured the chemical affinity of the reactants, a principle afterwards shown to be an over-simplification. As will be seen in the next chapter speculations upon the possible source of the heat released in chemical action formed one of the bases of Berzelius’ dualistic theory.

During the year 1808 one of Dalton’s most eminent English contemporaries, Wm. Hyde Wollaston (1766–1828), had published a memoir entitled ‘On super-acid and sub-acid salts’†, in which, from accurate and ingeniously contrived experiments, he demonstrated that in the ‘sulphates of potash’ and the ‘carbonates of potash and soda’ the ratios of equivalents of base to acid are exactly 1 : 1 and 1 : 2 respectively. The same relation was found between the ‘neutral oxalate’ and the ‘binoxalate’ of potash ($K_2C_2O_4$ and KHC_2O_4 in modern formulae), but when one equivalent of potash and three equivalents of oxalic acid were brought together the result was a mixture in equal proportions of two salts, the one the ‘binoxalate’ with proportions

* *Ibid.* p. 148.† *Phil. Trans.* 98, 96 (1808).

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1:2 and the other a new salt, termed 'quadroxalate', in proportions 1:4.

To account for this want of disposition to unite in the proportion of three to one by Mr Dalton's theory, I apprehend he might consider the neutral salt as consisting of

2 particles potash with 1 acid

The binoxalate

as 1 and 1, or 2 with 2,

The quadroxalate

as 1 and 2, or 2 with 4,

in which cases the ratios which I have observed of the acids to each other in these salts would respectively obtain.

But an explanation, which admits the supposition of a double share of potash in the neutral salt, is not altogether satisfactory; and I am inclined to think, that when our views are sufficiently extended, to enable us to reason with precision concerning the proportions of elementary atoms, we shall find the arithmetical relation alone will not be sufficient to explain their mutual action, and that we shall be obliged to acquire a geometrical conception of their relative arrangement in all three dimensions of solid extension.

For instance, if we suppose the limit to the approach of particles to be the same in all directions, and hence their virtual extent to be spherical (which is the most simple hypothesis); in this case when different sorts combine singly there is but one mode of union. If they unite in the proportion of two to one, the two particles will naturally arrange themselves at opposite poles of that to which they unite. If there be three, they might be arranged with regularity, at the angles of an equilateral triangle in a great circle surrounding the single spherule; but in this arrangement, for want of similar matter at the poles of this circle, the equilibrium would be unstable and would be liable to be deranged by the slightest force of adjacent combinations; but when the number of one set of particles exceeds in the proportion of four to one, then, a stable equilibrium may take place, if the four particles are situated at the angles of the four equilateral triangles composing a regular tetrahedron.

It is perhaps too much to hope, that the geometrical arrangement of primary particles will ever be perfectly known; since even admitting that a very small number of these atoms combining together would have a tendency to arrange themselves in the manner I have imagined; yet, until it is ascertained how small a proportion the primary particles themselves bear to the interval between them, it may be supposed that surrounding combinations, although themselves analogous, might disturb that arrangement, and in that case, the effect of such interference must also be taken into account, before any theory of chemical combination can be rendered complete.