SCIENCE

FRIDAY, OCTOBER 27, 1911

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FARADAY LECTURE[1]

THE FUNDAMENTAL PROPERTIES OF THE ELEMENTS

WE meet to-night to honor the memory of Michael Faraday. It is fitting that we should come to this historic place; for here were his home and his laboratory, and in this room he lectured. Science is one of the great influences promoting the solidarity of mankind; it is world-embracing, and recognizes no bounds of nationality. Faraday's work especially was a message to the whole world, and has grown into a priceless heritage for all humanity. Therefore, from time to time the generous guardians of this famous lectureship have called chemists and physicists from many lands to honor his unique genius. England, Germany, France, Italy, Russia have all sent eminent representatives; and now from across the sea there comes a pilgrim who is proud indeed to bring the homage of the new world to this shrine of cherished memories. The many ties which bind together our two nations add especial pleasure to the fulfilment of the trust.

The mystery that enshrouds the ultimate nature of the physical universe has always stimulated the curiosity of thinking man. Of old, philosophers sought to solve the cosmic problem by abstract reasoning, but to-day we agree that the only hope of penetrating into the closely guarded secret lies in the precise estimation of that which is tangible and visible. Knowledge of the

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[1] Delivered before the fellows of the Chemical Society in the theater of the Royal Institution, on Wednesday, June 14, 1911. Printed in the *Journal of the Chemical Society,* Vol. 99, p. 1201, 1911. See also *Proceedings* of the Chem. Soc. Vol. 27, p. 177, 1911.

actual behavior of material and of energy provides the only safe basis for logical inference as to the real essence of things. Faraday was deeply imbued with this conviction; and it is widely recognized as the basis of all modern experimental science. The subject of my lecture to-night concerns the methods and general results of several extended series of investigations, planned with the hope of adding a little to the foundations of human knowledge by means of careful experiment.

At the outset let me remind you of an old saying of Plato's, for it sounds the keynote of the lecture: "If arithmetic, mensuration and weighing be taken away from any art, that which remains will not be much."[2] In other words, the soundness of all important conclusions of mankind depends on the definiteness of the data on which they are based.

Lord Kelvin said: "Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than looking for something new. But nearly all the grandest discoveries of science have been the rewards of accurate measurement and patient, long-continued labor in the minute sifting of numerical results."[3] The more subtle and complicated the conclusions to be drawn, the more exactly quantitative must be the knowledge of the facts.

Measurement is a means, not an end. Through measurement we obtain data full of precise significance, about which to reason; but indiscriminate measurement will lead nowhere. We must choose wisely the quantities to be measured, or else our time may be wasted.

Among all quantities worthy of exact measurement, the properties of the chemical elements are surely some of the most fundamental, because the elements are the vehicles of all the manifold phenomena within the range of our perception.

Weight is clearly one of the most significant of these properties. The eighty or more individual numbers which we call the atomic weights are perhaps the most striking of the physical records nature has given us concerning the earliest stages of the evolution of the universe. They are mute witnesses of the first beginnings of the cosmos out of the chaos, and their significance is one of the first concerns of the chemical philosopher.

Mankind is not yet in a position to predict any single atomic weight with exactness. Therefore the exact determination of atomic weights rests upon precise laboratory work; and in order to arrive at the real values of these fundamental constants, chemical methods must be improved and revised so as to free them from systematic or accidental errors.

What, now, are the most important precautions to be taken in such work? These are worthy of brief notice, because the value of the results inevitably depends upon them. Obvious although they may be, they are often disregarded.

In the first place, each portion of substance to be weighed must be free from the suspicion of containing unheeded impurities; otherwise its weight will mean little. This is an end not easily attained, for liquids often attack their containing vessels and absorb gases, crystals include and occlude solvents, precipitates carry down polluting impurities, dried substances cling to water, and solids, even at high temperatures, often fail to discharge their imprisoned contaminations.

In the next place, after an analysis has once begun, every trace of each substance

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[2] Plato, "Philebus" (trans. Jowett), 1875, Vol. IV., p. 104.

[3] Sir W. Thomson (Lord Kelvin), "Address to British Association," August, 1871, *Life*, II., 600.

to be weighed must be collected and find its way in due course to the scale-pan. The trouble here lies in the difficulty in estimating, or even detecting, minute traces of substances remaining in solution, or minute losses by vaporization at high temperatures.

In brief, "the whole truth and nothing but the truth" is the aim. The chemical side of the question is far more intricate and uncertain than the physical operation of weighing. For this reason it is neither necessary nor advisable to use extraordinarily large amounts of material; from five to twenty grams in each experiment is usually enough. The exclamation, "What wonderfully fine scales you must have to weigh atoms," indicates lack of knowledge; the real difficulties precede the introduction of the substance into the balance case.[4] Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every measurement must be assumed to contain error, until proof to the contrary can be obtained. Only by means of the utmost care, applied with ever-watchful judgment, may the unexpected snares which always lurk in complicated processes be detected and rendered powerless for evil.

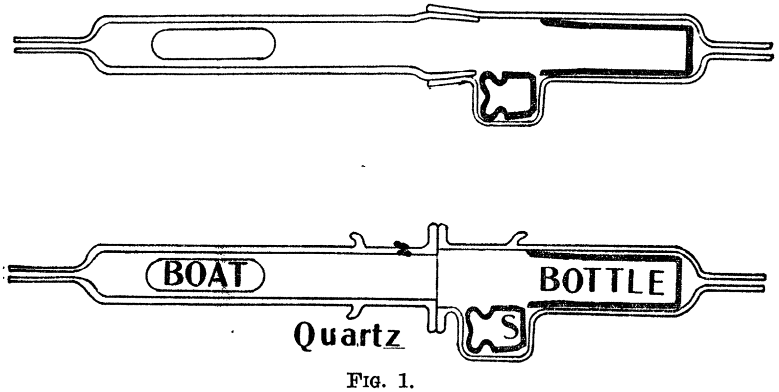

Fig. 1.

Among all the possibilities of error, the unsuspected presence of water is perhaps the most frequent and most insidious. Hence I shall show you a device for overcoming this potent source of confusion, a device which has played a great rôle in the recent researches concerning atomic weights at Harvard, and is in large measure responsible for such value as the results may possess. The instrument[5] enables one to dry, enclose and weigh an anhydrous substance in such a manner as to preclude the admission of a trace of water from the atmosphere; it might well find applications in every quantitative laboratory. The simple device consists of a quartz ignition tube fitted to a soft-glass tube which has a projection or pocket in one side (Fig. 1). A weighing-bottle is placed at the end of the latter tube, and its stopper in the pocket. The boat containing the substance to be dried is heated in the quartz tube, surrounded by an atmosphere consisting of any desired mixture of

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[4] Richards, "Methods Used in Precise Chemical Investigation," published by the Carnegie Institution of Washington, 1910, No. 125, p. 97.

[5] Richards, *Zeitsch. anorg. Chem.*, 1895, 8, p. 267; also Richards and Parker, *ibid.*, 1897, 13, p. 86. One form of apparatus shown in this diagram is slightly different from the original arrangement, although the main idea is the same. The flat ground joint between quartz and glass allows for their different coefficients of expansion, and makes a quartz tube interchangeable with any other, in case of breakage.

gases. These gases are displaced, after partial cooling, first by nitrogen, and then by pure dry air, and the boat is pushed past the stopper into the weighing-bottle, the stopper being then forced into place, and the substance thus shut up in an entirely dry atmosphere. The weighing-bottle may now be removed, placed in an ordinary desiccator and weighed at leisure. The substance is really dry, and its weight has definite significance.

Mention may be made also of another instrument, which likewise has greatly facilitated the recent work at Harvard, namely, the "nephelometer."[6] With the nephelometer, minute traces of suspended precipitate may be approximately determined from the brightness of the light they reflect. The construction is very simple. Two test-tubes, near together and slightly inclined toward one another, are arranged so as to be partly shielded from a bright source of light by sliding screens. The tubes are observed from above through two thin prisms, which bring their images together and produce an appearance resembling that in the familiar half-shadow polarimeter. The unknown quantity of dissolved substance is precipitated as a faint opalescence in one tube by means of suitable reagents; and a known amount, treated in exactly the same way, is prepared in the other. Each precipitate reflects the light; the tubes appear faintly luminous. If the tubes show like tints to the eye when the screens are similarly placed, the precipitates may be presumed to be equal in amount. In case of inequality of appearance, the changed positions of the screens necessary to produce equality of tint give a fairly accurate guide as to the relative quantities of precipitate in the two tubes. Traces of substance, which are too attenuated to be caught on any ordinary filter, may thus be estimated.

The two errors obviated by these simple devices—namely, the presence of residual water and the loss of traces of precipitate, respectively—have perhaps ruined more previous investigations than any other two causes, unless the inclusion of foreign substances by precipitates may be ranked as an equal vitiating effect. But these are merely details; the scope and method of the recent work on this subject at Harvard (in the course of which thirty atomic weights have been redetermined) may be seen in their full bearing only in the original papers.[7]

That the atomic weights may be connected by precise mathematical equations seems highly probable; but although many interesting attempts have been made to solve the problem,[8] the exact nature of such relationships has not yet been discovered. No attempt which takes liberties with the more certain of the observed values is worthy of much respect. It seems to me that the discovery of the ultimate generalization is not likely to occur until many atomic weights have been determined with the greatest accuracy. No trouble being too great to attain this end, the Harvard work will be continued indefinitely, and attempts will be made to improve its quality, for the discovery of an exact

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[6] Richards, *Zeitsch. anorg. Chem.*, 1895, 8, p. 269; Richards and Wells, *Amer. Chem. J.*, 1904, 31, p. 235; Richards, *ibid.*, 1906, 35, p. 510.

[7] An important part in these researches has been taken by G. P. Baxter, and many able students also have assisted the author in the work. A complete bibliography is given in *Publ. Carnegie Inst. of Washington*, 1910, No. 125, p. 91. Most of the papers are reprinted in full in a volume entitled, "Experimentelle Untersuchungen über Atomgewichte," by the author and his collaborators (Hamburg, 1909). The Carnegie Institution of Washington has generously subsidized the work in recent years.

[8] See especially Rydberg, *Zeitsch. anorg. Chem.*, 1897, 14, p. 66.

mathematical relationship between atomic weights would afford us an immeasurably precious insight into the ultimate nature of things.

But weight is only one of the fundamental properties of an element. Volume is almost, if not quite, as important in its own way, although far more variable and confusing. All gases, indeed, approach closely to a simple relationship of volumes, defined by the law of Gay Lussac and the rule of Avogadro, and well known to you all. In the liquid and solid state, however, great irregularities are manifest, and very little system as regards volume is generally recognized.

About twelve years ago, the study of such small irregularities as exist among gases led me to the suspicion of a possible cause for the greater irregularities in liquids and solids.[9] On applying van der Waals's well-known equation to several gases, in some tentative and unpublished computations, it seemed clear that the quantity *b* is not really a constant quantity, but is subject to change under the influence of both pressure and temperature. This conclusion has also been reached independently by van der Waals himself.[10] But if the quantity *b* (supposed to be dependent upon the space actually occupied by the molecules) is changeable, are not the molecules themselves compressible?[11]

The next step in the train of thought is perhaps equally obvious. If changes in the bulk of molecules are to be inferred even from gases, may not the expansion and contraction of solids and liquids afford a much better clue to the relative expansion and contraction of these molecules?

Most physical chemists refer all changes in volume to changes in the extent of the *empty space* between the molecules. But are there, after all, any such empty spaces in solids and liquids? Solids do not behave as if the atoms were far apart within them; porosity is often conspicuous by its absence. Take, for instance, the case of glass; the careful experiments of Landolt on the conservation of weight[12] show that glass is highly impermeable to oxygen, nitrogen and water for long periods. Such porosity as occurs in rigid, compact solids usually permits the passage only of substances which enter into the chemical structure of the solids themselves. Thus, nitrogen can not free itself from imprisonment within hot cupric oxide, although oxygen can escape;[13] again, water can not evaporate into even the driest of atmospheres from accidental incarceration in crystals lacking water of crystallization.[14] Palladium, on occluding hydrogen, is obliged to expand its bulk in order to make room for even this small addition to its substance. The behavior of platinum, nickel and iron is probably analogous, although less marked.[15] Fused quartz, impermeable when cold, allows of the passage of helium and hydrogen at high temperatures;[16] but most other gases seem to be refused admission, and

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[9] Richards, "The Significance of Changing Atomic Volume," *Proc. Amer. Acad.*, 1901, 37, p. 1; 1902, 37, p. 300; 1902, 38, p. 293; 1904, 39, p. 581; *Zeitsch. physikal. Chem.*, 1902, 40, pp. 169, 597; 1903, 42, p. 129; 1904, 49, p. 15.

[10] Van der Waals, *Zeitsch. physikal. Chem.*, 1903, 28, p. 257. His earlier publication on this topic (*Proc. R. Akad. Wetensch. Amsterdam*, 1898, 29, p. 138) was unknown to me at that time. See also Lewis, *Proc. Amer. Acad.*, 1899, 35, p. 21.

[11] Van der Waals speaks cautiously, but with some conviction, as to the probable compressibility of the molecules on p. 283 of the paper cited above.

[12] H. Landolt, "Ueber die Erhaltung der Masse bei chem. Umwandlungen," *Abhandlung der königl. preuss. Akad. der Wissenschaften*, 1910.

[13] Richards, *Zeitsch. anorg. Chem.*, 1892, 1, p. 196; *Proc. Amer. Acad.*, 1893, 28, p. 200.

[14] Baker and Adlam, *J. Chem. Soc. Trans.*, 1911, 99, p. 507.

[15] Richards and Behr, *Publ. Carnegie Inst.*, 1906, No. 61.

[16] Jacquerod and Perrot, *Compt. rend.*, 1907, 144, p. 135.

very many solid substances appear to act as effective barriers to the passage of even hydrogen and helium, especially when cold. In these cases, as in so many others, the so-called "sphere of influence" of the atom is the actual boundary by which we know the atom and measure its behavior.[17] Why not call this the actual bulk of the atom?

From another point of view, the ordinary conception of a solid has always seemed to me little short of an absurdity. A gas may very properly be imagined with moving particles far apart, but what could give the rigidity of steel to such an unstable structure? The most reasonable conclusion, from all the evidence taken together, seems to be that the interstices between atoms in solids and liquids must usually be small even in proportion to the size of the atoms themselves, if, indeed, there are any interstices at all.

Very direct and convincing evidence of another sort is at hand. The idea that atoms may be compressible receives striking confirmation from a recent interesting investigation of Grüneisen[18] concerning the small effect of low temperatures on the compressibility of metals. The average compressibility of aluminium, iron, copper, silver and platinum falls off only seven per cent. between the temperature of the room and that of liquid air. Extrapolation of the curves indicates that at the absolute zero very little further diminution should occur. As far as we can guess, therefore, the hard metals are almost as compressible at the absolute zero as at room temperatures. But at the absolute zero all heat-vibration is supposed to stop; hence this remaining compressibility must needs be ascribed to the atoms themselves.

If the atoms are compressible, all mathematical reasoning which assumes them to be incompressible rests upon a false basis. The kinetic theory of *gases* remains unmolested by these considerations, except as they indicate the changeability of b in the equation of van der Waals, but the new views affect seriously the application of this equation to solids and liquids.

Let us proceed to trace a few of the outcomes of our hypothesis. If atoms may really be packed closely together, the volumes of solids and liquids should afford valuable knowledge concerning the relative spaces occupied by the atoms themselves under varying conditions. The densities of solids and liquids then assume a significance far more interesting to the chemical philosopher than before, because they have a more definite connection with the fundamental nature of things.

An apparent objection at once suggests itself; if the particles in condensed material are really touching one another, how can we account for heat within the material? Would such closely packed atoms be able to vibrate?

The theory of compressible atoms supplies as one of its own corollaries the immediate answer to this question. If atoms are compressible throughout their whole substance, they may contract and expand, or vibrate within themselves, even when their surfaces are prevented from moving by being closely packed together. It is thus possible to conceive of a vibrational effect, even in contiguous atoms, provided we can conceive of these atoms as being elastic

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[17] Since these ideas were first advanced, Barlow and Pope have brought forward much interesting evidence concerning the significance of the volumes of solids and liquids, which supports the idea that the atoms are closely in contact with one another (*Trans.*, 1906, 89, p. 1675; 1907, 91, p. 1150; 1908, 93, p. 1528; 1910, 97, p. 2308).

[18] E. Grüneisen, *Ann. Physik*, 1910 (IV.), 33, p. 1239. The *relative* values for the compressibilities recorded in this investigation are doubtless trustworthy, although the absolute magnitudes are somewhat uncertain because they depend on the rather inadequate theory of elasticity.

throughout all their substance. Agitation sufficient to produce even the Brownian movement might easily exist in such a system.

Clearly there is nothing impossible or obviously contradictory to experimental knowledge in the notion that atoms are compressible; indeed, the old idea of small, hard particles far apart is really more arbitrary and hypothetical than the new conception. The obvious simplicity of the latter is rather in its favor than otherwise, as in Dalton's atomic theory. In general, the more simply an hypothesis interprets the phenomena of nature, the more useful the hypothesis is likely to be, provided, of course, that the interpretation is adequate. The modern philosophy of pragmatism is a good guide in such matters; a theory not obviously illogical should be judged by its usefulness. Let us then test the new hypothesis by applying it to other aspects of physical chemistry.

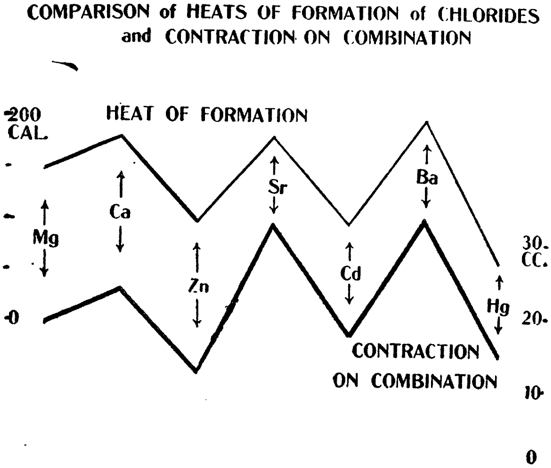
COMPARISON of HEATS OF FORMATION of CHLORIDES and CONTRACTION ON COMBINATION

FIG. 2.

If pressure produces a change in the sizes of the atoms and molecules themselves, may not the actual volumes of liquids and solids be used as a guide to the unknown internal pressures within them? Cannot we thus discover whether or not chemical affinity exerts pressure in its action? To follow this clue, the simplest possible case was chosen at first, namely, the comparison of the contractions taking place on combining several elements in succession with a single very compressible one. The changes of volume occurring during the formation of oxides were first computed; later, chlorides and bromides were studied. According to the theory of compressible atoms, we should expect to find greater contraction in cases of greater affinity. The diagram (Fig. 2), which depicts typical data concerning certain nearly related chlorides, strongly supports this inference.[19] One of these lines shows the total change of volume which occurs when a gram-molecule of chlorine combines with the equivalent weight of metal; the other gives the heat evolved during combination. The lines show distinct parallelism; that is to say, reactions evolving much heat manifest great contraction. In cases of this kind the heat of reaction is usually not very different from the change of free-energy, therefore we may infer that greater *affinity* is associated with greater contraction; and it is but a small leap in the dark to guess that the change of volume is *caused* by the pressure of affinity. Since chemical attraction holds two elements firmly together, why should it not exert pressure? And if it exerts pressure, why should not the volume of the system be diminished by this pressure?

This interpretation is not wholly new. Faraday's great teacher, Davy,[20] pointed out for the first time a similar fact; namely,

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[19] Richards, *Proc. Amer. Acad.*, 1902, 37, p. 399; also especially *J. Amer. Chem. Soc.*, 1909, 31, p. 188.

[20] Humphry Davy, "Collected Works," 1840, 5, p. 133 (foot-note).

that the contraction which takes place on forming the oxide of potassium is greater than the contraction which takes place on forming several other oxides, and he ascribed this effect to the well-known differences of affinity in these cases; but he did not carry the idea further. Long afterwards, Braun,[21] Mueller-Erzbach,[22] Hagemann[23] and Traube[24] independently and apparently without knowledge of each other's work, called attention to other cases of similar relationships.

All of these researches have produced so little effect on the literature of the subject[25] that they were entirely overlooked during the earlier part of the present investigation. The oversight mattered little, however, because the whole subject needed a fresh attack. Essential factors in the situation had not been noticed by any of these earlier investigators. Affinities, indeed, had been considered, but the nature of the substances on which the affinities act had been overlooked. Evidently the change of volume in any case must depend not only on the intensity of the pressure exerted by the affinity, but also, among other things, on the compressibility of the substances concerned. The greater the compressibility, the greater should be the change of volume caused by a given pressure of affinity. Before any definite conclusion can be drawn, the differences in compressibility must be taken into account.

These thoughts led to the measuring of the compressibilities of a large number of elements and simple compounds. The previously employed methods for solids and liquids being unsatisfactory, a new and highly satisfactory method was devised for the work done at Harvard. Pure mercury is compressed in a suitable tube, measuring both pressure and change of volume, and then most of the mercury is displaced by the substance to be studied, again noting the relationship of pressure to volume. The difference between the compressibility of mercury and that of the substance is then easily calculated. Obviously, in such a method as this, the compressibility of the apparatus itself is eliminated. The relation of volume to pressure is easily determined by causing the mercury meniscus to make electrical contact with a very fine platinum point in a tube of narrow diameter, adding weighed globules of mercury, and noting the corresponding pressures.[26] Time forbids the description of the details of the procedure.

The compressibilities of thirty-five elements and many simple compounds were studied by this method with sufficient care to leave no doubt as to their relative values. It became at once manifest that the formation of a compound of a compressible element was attended with greater decrease of volume than the formation of a similar compound of a less compressible element, other things being equal.[27] This is just what the theory leads us to expect, and is a fact inexplicable by any other hypothesis as yet known to me.

Another essential aspect of the theory of compressible atoms is that which concerns

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[21] V. Braun, see Johnson, *J. Chem. Soc. Trans.*, 1877, 31, p. 252.

[22] Mueller-Erzbach, *Ber.*, 1881, 14, pp. 217, 2043.

[23] Hagemann (private publication, Friedländer, Berlin, 1900).

[24] Traube, "Ueber den Raum der Atome," Ahrens's *Sammlung der chem. und chem.-techn. Vorträge*, IV., p. 256.

[25] See, for example, Ostwald's *Grundriss der allgemeinen Chemie*, 1899, p. 185.

[26] Richards, in collaboration with Stull, Bonnet, Brink, Mathews, Jones, Speyers, *Publ. Carnegie Inst. of Washington*, Nos. 7 and 76; *J. Amer. Chem. Soc.*, 1904, 26, p. 399; 1909, 31, p. 154; *Zeitsch. physikal. Chem.*, 1904, 49, p. 1; 1907, 61, p. 77.

[27] Richards, *Proc. Amer. Acad.*, 1904, 39, p. 581.

cohesion.[28] If the pressure of chemical affinity causes atomic compression, may not the pressure of cohesive affinity also have the same effect? Traube suggested this possibility, but looked at the whole question from a different point of view.[29] The affinity which prevents solids and liquids from vaporizing is generally admitted to produce great internal pressure; must it not tend to compress the molecules into smaller space? Molecules with high cohesive affinity (those of substances hard to volatilize) should be much compressed and possess small volume, whereas molecules with a slight cohesive affinity should be more bulky. Moreover, those molecules already much compressed by their own self-affinity would naturally be but little affected by additional pressure. Thus, as regards two substances otherwise similar, the less volatile one would be less compressible, denser and possess greater surface tension.[30] These outcomes of the theory agree with the facts in eighty per cent. of the cases thus far studied; for example, *o*-xylene is denser, less volatile, less compressible and possesses a greater surface tension than either *m*-xylene or *p*-xylene.[31] Differences of structure and differences of chemical nature sometimes conceal these relations; the parallelism appears most strikingly among isomeric compounds. In brief, the bulk of evidence strongly indicates that cohesiveness as well as chemical affinity exerts pressure in its action, and hence that each plays a part in determining the volumes occupied by molecules.

Thus the computation of the space occupied by either a solid or a liquid becomes a very complex matter. Not only must the various chemical affinities at work be taken into account, but also the cohesive attraction of both factors and products, and the compressibilities over a very wide range of all the substances concerned. Discoverable parallelism in volume changes is to be expected only when one alone of these forces is the chief variable.

The exact mathematical working out of the consequences is very far in the distance, if, indeed, it can ever be attained. This fact does not, however, militate in the least against the plausibility of the idea. Although mankind has not yet been able to devise a method of mathematical analysis which will solve at one stroke the gravitational relations of three bodies, nature is not on that account prevented from causing three or more bodies to act on one another with the force of gravity, or astronomers from calculating as nearly as may be the consequences by a process of approximation.

Carried through to its logical conclusion, the idea that atoms are compressible gives one quite a new conception of the molecular

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[28] *Ibid.*

[29] See especially Traube, *Ann. Physik.*, 1897, (III.), 61, p. 383; 1901, (IV.), 5, p. 548; 1902, 8, p. 267; 1907, 22, p. 519; *Zeitsch. physikal. Chem.*, 1910, 68, p. 289; also Walden, *Zeitsch. physikal. Chem.*, 1909, 66, p. 385. Their interpretation depends largely on the application of van der Waals's equation and the complicating assumption of a *co-volume;* however, Walden's very recent paper presents a number of interesting and important relations concerning internal pressure, which seem to demand the assumption of atomic compressibility for their explanation.

[30] Richards and Mathews, *Zeitsch. physikal. Chem.*, 1908, 61, p. 449.

[31] With the help of C. L. Speyers I have determined these constants with great care. The substances were unusually pure, the *p*-xylene freezing at 13.2°. The details will be published as soon as possible. The results are recorded in the following table:

	Boiling Point	Density, 20°/4°	Surface Tension mg./mm.;20°	Compressibility 10^6 at 20°
o-Xylene	144.0°	0.8811	3.09	60.0
m-Xylene	139.0	0.8658	2.96	63.5
p-Xylene	136.2	0.8611	2.92	66.2

mechanics of the universe. The influence of atomic compressibilities may be perceived everywhere, and in most cases each fact seems to fit easily and without constraint into its place in the hypothesis. Even apparent exceptions, such as the abnormal bulk of ice, may be ascribed in a reasonable fashion to superposed effects. A detailed discussion of many applications of the theory is impossible here, but a few may be suggested, in order to make clearer its possibilities.

The satisfying of each valence of an atom would cause a depression on the atomic surface, owing to the pressure exerted by the affinity in that spot. The stronger the affinity, the greater should be this distortion. Evidently this conception gives a new picture of the asymmetric carbon atom, which, combined with four other different atoms, would have upon its surface depressions of four unequal magnitudes, and be twisted into an unsymmetrical tetrahedron. The combining atoms would be held on the *faces* of the tetrahedron thus formed, instead of impossibly perching upon the several peaks. According to this hypothesis, the carbon atom need not be imagined as a tetrahedron in the first place; it would assume the tetrahedral shape when combined with the other four atoms. One can easily imagine that the development of each new valence would change the affinities previously exercised, somewhat as a second depression in the side of a rubber ball will modify a forcibly caused dimple in some other part. Thus a part of the effect which each new atom has on the affinities of the other atoms already present may be explained.

Many other physico-chemical phenomena assume a new aspect when viewed from the standpoint of this idea. New notions of the mechanism of the critical phenomena, surface tension, ductility, malleability, tenacity and coefficient of expansion are gained. The peculiar relations of material and light, such as magnetic rotation, fluorescence, partial absorption, and so forth, may be referred to the modified vibrations of distorted atoms. The deviations from the exact fulfilment of many older generalizations concerning volume (such as the equation of van der Waals already cited, the comparative volumes of aqueous solutions, especially of electrolytically dissociated substances,[32] and the variations in the crystal forms of isomorphous substances) are seen to be a foregone conclusion. Moreover, the theory, although not necessarily dependent on the modern belief that atoms are built up of numbers of much smaller corpuscles, is consistent with that belief, for would not such an entity be compressible?

The more closely the actual data are studied, the more plausible the hypothesis of compressible atoms appears. Ten years' experience with its interpretations leads me to feel that the idea is highly suggestive and helpful in stimulating new search after truth and in correlating and codifying diverse facts. By such fruit are hypotheses justified.

The relation between heat of reaction and change of volume stimulates interest in chemical thermodynamics and curiosity as to the mechanism of the output of energy during chemical change. A search for accurate data wherewith to reason about this question soon revealed the uncertain nature of many of the figures. Here, in the domain of thermochemistry, as in those of atomic weights and compressibilities, new methods were needed in order to attain precise results. Accord-

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[32] Baxter has very recently discussed this matter from the point of view of the theory of compressible atoms (*J. Amer. Chem. Soc.*, 1911, 33, p. 922).

ingly, a device was adopted which at one stroke annihilates the pernicious "cooling correction"—the worst foe to accuracy—by merely causing the temperature of the jacket around the calorimeter to change in temperature at the same rate as the calorimeter itself. There are several ways in which this may be accomplished; among these ways the following was chosen as the best method for a chemical laboratory. The calorimeter, enclosed in a slightly larger water-tight vessel, with tubes above—a kind of submarine—is immersed under the surface of dilute crude alkali in a pail. Thermometers inside and out enable one to adjust the temperatures at the same point. The reaction is then started in the calorimeter, and at the same moment and at a corresponding rate acid is dropped into the dilute alkali in the pail, so that the two temperatures inside and out keep pace with one another. Thus there is no loss of heat from the inside vessel; the thermochemical reaction is strictly adiabatic. This method has already been used at Harvard with very encouraging outcome in determining a wide variety of thermochemical data, heats of combustion of hydrocarbons, of solutions of metals in acids and of neutralization, specific heats of solutions, and also of the elements at very low temperatures, and finally latent heats of evaporation.[33] It has proved itself especially valuable in the study of slow reactions, where the cooling correction may become a large portion of the total result. The effort is being made to apply to this experimentation concerning chemical energetics the same degree of care which has recently been attempted in the revision of the atomic weights, and although on account of the greater complexity of the problem the percentage accuracy thus far reached has not equalled that in the case of atomic weights, one can not help thinking that the proportional gain over previous investigations is perhaps as great in this case as in the other.

In thermochemical reasoning particularly, accurate data possess a significance wholly denied to cruder results. The relations between the heat of formation of organic substances, if determined accurately enough, may be hoped to throw light on organic structure and the nature of valence. Approximate values are of no use at all for such a purpose. Enough has been done already to suggest relations of a highly interesting sort between heats of combustion, heats of evaporation, compressibility and many other properties; and to add support to the theory of compressible atoms.[34] Moreover, taken in connection with more precise knowledge of the free energy of chemical changes, the new results will permit the evaluation of bound energy, and give results which may decide whether or not bound energy is really a simple function of change of heat capacity, as has been more than once intimated.[35] There is time now only to suggest possibilities, each of which would take hours to elucidate.

How can we collate all the varying properties so as to show their many-sided relationships? How can we piece together the scattered evidence so as to synthesize an adequate conception of the ultimate nature

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[33] Richards, in collaboration with Henderson, Forbes, Frevert, Mathews, Rowe, Jesse, Burgess and Jackson, *Proc. Amer. Acad.*, 1905, 41, p. 3; 1907, 42, p. 573; 1908, 43, p. 475; 1911, 46, p. 363; *J. Amer. Chem. Soc.*, 1909, 31, p. 1275; 1910, 32, pp. 268, 432, 1176; *Zeitsch. physikal. Chem.*, 1905, 52, p. 551; 1907, 59, p. 531; 1909, 70, p. 414.

[34] Richards, *Proc. Amer. Acad.*, 1908, 39, p. 581; also *Zeitsch. physikal. Chem.*, 1904, 49, p. 15.

[35] Helmholtz, Lewis, van't Hoff, Nernst and Haber, as well as the author and many others, have contributed to this discussion. An interesting résumé, with references to many of the original papers, will be found in Haber's "Thermodynamics of Technical Gas Reactions" (translated by Lamb), London and New York, 1908.

of things? These questions may never be adequately answered, but science must ceaselessly endeavor to solve the problem which they present.

A first step is clearly to find the way in which each property varies in relation to every other. With this in mind, let us appeal to the irregular system of the periodic classification, which formed the subject of the Faraday lecture by Mendeléeff twenty-two years ago. This mysterious index of uncharted tendencies must hide within itself guiding ideas capable of pointing us onward.

Clearly each property must receive, not merely qualitative, but strictly quantitative treatment. With this in mind, let us compare our various facts by plotting atomic weight in one direction, and all the other properties in another. Then by noting the parallelism or anti-parallelism of the wavy lines, many relationships may be traced. The device is not new. Carnelley compared Lothar Meyer's atomic volume curve with that of melting points, and other similar data have been plotted; but the method has not been used to its full extent.

Let us then turn to the diagram (Fig. 3) in which the variations in a number of properties are plotted with relation to the atomic weights. Prominent among the lines is the atomic-volume curve just mentioned. Below it is plotted the almost parallel line depicting the compressibilities of the solid elements as determined at Harvard; these are immediately seen to be, like the atomic volumes, periodic functions of the atomic weights. The parallelism can not but suggest that atomic volume and compressibility are fundamentally connected; and, indeed, the theory of compressible atoms gives a plausible explanation of the connection. We should expect the large atomic volumes to be more com-

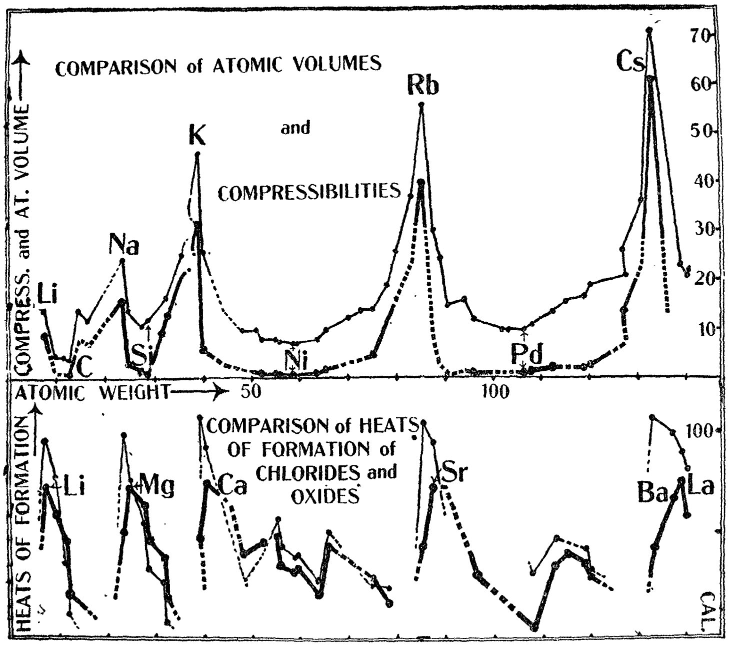

Fig. 3.

pressible, because we might infer from their bulk that they are not under as great pressures as the small volumes, and material under slight pressure is likely to be easily compressible. Moreover, the bulky and easily compressible elements are in most cases more easily melted and volatilized than those possessing small volume and slight compressibility. This is just what we might expect; all these properties combine to indicate that the bulky elements have less cohesion than the compact ones.

Next, another set of waves may be considered, representing properties not often depicted in this way. These are the heats of formation of sundry similar compounds, also plotted with relation to the atomic weights. In the third curve are given the heats of combination of chlorine with other elements, and below it a heavy line depicting the heats of the combination of oxygen with these elements, both sets of quantities being expressed in terms of gram-equivalents.

These two run partly parallel with one another; but a deviation in the parallelism appears, which is full of suggestiveness. The peaks of the curves representing oxides shift distinctly to the right of the curve representing chlorides as the atomic weight increases. Lithium marks a maximum with both curves, but the oxygen curve lags greatly at the succeeding peaks, having its maximum with lanthanum at the atomic weight 139,[36] and shifting over as far as lead above 200. This simple fact standing alone would perhaps mean but little, but other similar facts seem to point in the same direction. For example, the property of electro-positiveness, exhibited by the alkali metals, instead of reappearing in copper, has been carried over with diminished intensity to zinc; and finally, among the higher atomic weights the cusp has deserted mercury (the analogue of zinc) and gone as far afield as thallium. Clearly the rate of progression which determines electro-positiveness has a longer "wave-length" than that which determines valence, if we may describe the periodicity of these zigzag curves as waves. Again, the tendency towards low melting point unquestionably likewise progresses with a longer "wave-length" than most of the other properties. In the first complete period, nitrogen, oxygen, fluorine and neon all have very low melting points. At each recurrence of these groups with higher atomic weights the melting point rises, whereas with each recurrence of the immediately following alkali metals the melting point falls. By the time antimony is reached, this analogue of nitrogen has a melting point as high as 900° absolute, whereas the next alkali metal has the lowest melting point of all these metals. Clearly the property of melting has shifted toward the right. Other examples of a similar kind have been pointed out by others,

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[36] The essential data for discovering this generalization, namely, the heats of oxidation of the metals having great affinity for oxygen, are as follows: lithium, 72; sodium, 50; magnesium, 72; potassium, 43; calcium, 76; rubidium, 42; strontium, 71; cæsium, 41; barium, 67, and lanthanum, 74. These values correspond with gram-equivalents, that is, combination with eight grams of oxygen, and are expressed in kilogram-calories. The typical oxide is always meant. The figures rest chiefly upon the recent work of Rengade, de Forcrand and Guntz. References to most of the papers are to be found in Abegg's "Handbuch der anorganischen Chemie." The work of Guntz is published in *Compt. rend.*, 1903, 136, p. 1071; 1905, 140, p. 863; *Bull. Soc. chim.*, 1906, (III.), 35, p. 503. The work on lanthanum was done by Matignon, *Ann. Chim. Phys.*, 1906, (VIII.), 8, p. 426. The heat of oxidation of beryllium is not accurately known, but since the oxide may be decomposed by magnesium at high temperatures, the value is very probably less than 70 calories per gram-equivalent.

for example, the well-known displacement from strict periodicity of argon, cobalt and tellurium all point to an unequal rate of progression in isolated cases. Thus, this phenomenon seems to be a general one; the various properties of material seem to oscillate with varying rhythms as the atomic weights increase. The variation is so great that one may almost suspect not only varying rhythms but also rhythms represented by different types of mathematical functions.

These facts suggest a possible reason for the great irregularity of the last part of the periodic table. May it not be that the nature of the elements is determined by several fundamental tendencies which may be compared to the Mendelian characters of the modern theory of heredity? If these characters recur at different intervals as the atomic weight increases, a given rhythm occurring at first would necessarily be obliterated toward the end of the system. To change the analogy and borrow a term from the nomenclature of light, we may say that the tendencies which produce the curves in this diagram, might first reinforce and afterwards interfere with one another, because they possess different wave-lengths. At first, overlapping might accentuate one set of properties; later the changing relation might annihilate this set of properties and cause another. Thus, all the varieties of material may be functions of some few fundamental characteristics which progress at different rates as the atomic weights increase.

Any attempt to discover the nature of these fundamental tendencies must be of a highly speculative character. In our ignorance we can not distinguish between cause and effect. The well-known definite relations of the spectrum lines suggest that at least one of the essential requirements for the existence of an atom may be susceptibility to certain definite harmonic vibrations; those compressible atoms capable of vibrating in certain rhythms may be permanent, whilst other aggregations may be unstable. The gap in the periodic system where *eka*iodine *eka*cæsium should be, and the amazing instability of the elements immediately following, supports the notion.

But here we have a cosmic puzzle for future solution. To-day we lack adequate data, we are blocked at every turn by our ignorance; therefore, the immediate problem is to discover and test each step as carefully as possible. When the facts have been ascertained, man will have a solid basis upon which to build his future superstructure of theoretical interpretation.

The quest is not dictated by mere curiosity alone. All organic life is actuated by chemical energy, and exists in a mechanism and environment composed of chemical substances; and the effort to understand these essential conditions of human existence constitutes one of the most important objects of human endeavor. Superficial observation of the complex phenomena of life can do but little; as Faraday well knew, patient study of the fundamental laws of the physical universe alone can help to unravel the interwoven threads. Health, well-being and a profound philosophic outlook are alike dependent upon the result. No one can predict how far we shall be enabled by means of our limited intelligence to penetrate into the mysteries of a universe immeasurably vast and wonderful; nevertheless, each step in advance is certain to bring new blessing to humanity and new inspiration to greater endeavor.

THEODORE WILLIAM RICHARDS
HARVARD UNIVERSITY

SCIENCE AND LITERATURE

SPEECH was given to man to conceal his thoughts, according to some eighteenth-cen-