A BRIEF HISTORY OF THE INVESTIGATION OF INTERNAL PRESSURES

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Long ago Sir Isaac Newton perceived that the forces of cohesion and chemical affinity probably obey laws different from the simple law of gravitation (1). At the time of writing the "Principia," however, his ideas on this subject were vague, as shown in the quotation:

> And now we might add something concerning a certain most subtle Spirit, which pervades and lies hid in all gross bodies; by the force and action of which Spirit, the particles of bodies mutually attract one another at near distances, and cohere, if contiguous; and electric bodies operate to greater distances, as well repelling as attracting the neighbouring corpuscles; . . . . But these are things that cannot be explain'd in few words, nor are we furnish'd with that sufficiency of experiments which is required to an accurate determination and demonstration of the laws by which this electric and elastic Spirit operates (2).

Newton evidently perceived that cohesive forces must fall off more rapidly with increasing distance than in the case of gravitation, whereas electrical attraction resembles gravitation more closely as regards its distance-effect. The disastrous fire which consumed the results of so many years of Newton's work prevents us from knowing how searchingly Newton may have discussed these matters. A hint of his line of thought, however, was published shortly before his death, indicating the important rôle which common sense played in his very penetrating ratiocination:

> The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. And for explaining how this may be, some have invented hooked Atoms, which is begging the

> Question; and others tell us that Bodies are glued together by rest, that is, by an occult Quality, or rather by nothing; and others, that they stick together by conspiring Motions, that is, by relative rest amongst themselves. I had rather infer from their Cohesion, that their Particles attract one another by some force, which in immediate Contact is exceeding strong, at small distances performs the chymical Operations above mention'd, and reaches not far from the Particles with any sensible Effect. . . . . There are therefore Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out (3).

If, as Newton inferred, "the particles of bodies stick together by very strong attractions," these attractions must cause the atoms to exert great pressure upon one another. The internal cohesive and chemical pressures (that is to say, the pressures produced by cohesion and chemical affinity, respectively) thus exerted must be an essential characteristic of each form of matter. Furthermore (although Newton did not carry his argument so far), there must be resident in the atoms some resisting pressure or pressures to balance these; for otherwise the cooler parts of the universe would shrink to a collection of widely separated mathematical points of infinite density. It is the business of this paper to discuss the history of the study of these internal pressures, which have been also variously named "molecular pressures," "normal pressures," "intrinsic pressures," "Binnendrucke," "innere Krafte," etc.

The existence of internal pressure, important though it is, seems subsequently to have been ignored for thirty years, when the concept was revived by Segner (4) in 1750 to explain capillary action, a phenomenon long before discovered, probably by Leonardo da Vinci. Lack of experimental data doubtless contributed to this neglect,—which was continued for fifty years more, since not until 1804 did the question receive further attention. At that time Thomas Young (5), in the course of his epoch-making studies on capillarity, assumed that cohesive affinity is independent of distance "throughout the minute distance to which it extends;" but that it ceases entirely at the distance of 1×10^{-7}

mm. His argument is somewhat obscure, but he saw that one must assume a "repulsive" or distending tendency to withstand cohesion, and ascribed all the intimate variations of the effect to this latter tendency, which he assumed to diminish progressively with increasing distance. The nature of the "repulsive" force was not defined; as will be seen, it was often afterwards assumed to be purely thermal.

Laplace (6) in his almost synchronous comprehensive mathematical investigation of surface tension, also based his theory upon powerful cohesive forces. Nevertheless, as Lord Rayleigh pointed out,

> In Laplace's theory . . . . no mention is made of repulsive forces, and it would appear at first as if the attractive forces were left to perform the impossible feat of balancing themselves. But in this theory there is introduced a pressure which is really the representative of the repulsive forces (7).

Laplace, perhaps quite independently, cast many of Young's ideas into mathematical form. He was probably the first to suggest that the work done by cohesive pressure should be considered as an integral involving some function of the changing attractive force.

After Laplace no other important addition to our knowledge of internal pressures seems to have been made before the contributions of Athanase Dupré in 1864. He was probably the first to point out that the expression $T\alpha/\beta$ (in which T is the absolute temperature, α the cubic coefficient of expansion and β that of compression) is a significant one (8) but he seems to have thought that this thermal pressure $T\alpha/\beta$ practically equals the total internal pressure. Dupré further saw clearly that cohesive pressure might account for heat of evaporation;—indeed there is no other reasonable explanation for this latter phenomenon. In attempting to compute thus the value of the internal pressure, he drew, however, an erroneous conclusion, namely, that the internal pressure multiplied by the atomic volume is equal to the heat rendered "latent" (9). Expressed mathematically, this gives $\Pi = \frac{L}{V_A}$, in which Π is the cohesive internal pressure, L the atomic heat of evaporation and V_A the atomic volume. The result is the same as it would be if the attracting pressure remained constant over a volume equal to the atomic volume and then suddenly ceased, although he reached the conclusion in different ways. As will be seen, his values were probably of the right order of magnitude, but the fundamental assumptions involved in his integration are questionable.

Hirn (10), whose thoughtful excursions into thermodynamics were often suggestive, was perhaps the first to consider (in 1865) the effect of cohesive pressure upon the gas-law; he introduced into the latter an additional pressure to account for the abnormally great contraction of imperfect gases on moderate compression, but made no attempt to relate this pressure mathematically to the cohesion of liquids.

The next important contribution to the subject of internal pressure was the well-known equation of J. D. van der Waals (11):

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

(1873) in which the idea of Hirn was amplified by making the assumption that the cohesive pressure varies inversely as the square of the volume. The basis upon which this assumption was made is somewhat obscure (12); perhaps it was partly pragmatic. Moreover, not only the basis, but also the later interpretation of the assumption is clouded. Although the square of the volume means ordinarily the sixth power of the distance, W. C. McC. Lewis has concluded that the attraction between the molecules varies inversely as the *fourth power* (13); whereas Mie (46) and Grüneisen (47) have concluded that the *cube* of the distance is involved. The relation is not necessarily the same when the molecules are very close together as when they are widely scattered. An adequate review of all the comments upon the questions raised by this classic equation would require a volume in itself.

The equation of van der Waals was undoubtedly a highly important step forward, but it cannot, for many reasons (including the assumption just mentioned) be considered as exact.

That it represents qualitatively the main influences at work, there can be little doubt. On the other hand, the assumption that a is unchanging with temperature is questionable; and so is the assumption that the change of a with volume is simply exponential. With regard to b the situation is even less promising. Under very great pressures b is certainly not constant, and probably also it varies with temperature (14). These considerations were at least partially recognized by van der Waals (15). Moreover, inferences drawn from the very extended gaseous state are not suitably applicable (in an unmodified form) to condensed phases without further evidence. Hence van der Waals's equation, useful as it is, must be looked upon merely as an approximation. The many later modifications of this equation are not sufficiently illuminating in relation to the internal pressures of solids and liquids to deserve mention here. That of Keyes seems to be by far the best for gases (16).

The next important contribution was that by Maxwell (17), in connection with the theory of capillarity. He perceived with Laplace that if cohesive attraction diminishes with distance, the work done by this attraction should be represented by an integral to which he gave the form

$$\int_{f}^{\infty} \phi f\,df$$

but not knowing the rate of decrease with distance, he was unable to give his equation definiteness. His integral equation, like Laplace's, involved forces, not pressures, since f signifies distance.

Not long afterwards various other authors offered assumptions concerning the rate of decrease of cohesive force with distance. Pilling (18) advocated the inverse sixth power, and seven years afterwards Eddy (in 1883) (19) contented himself with a vaguer assumption,—that "some power of the distance" is concerned. In 1884 Harold Whiting (20) published his thesis upon a new theory of cohesion and maintained that the true function is the fourth power of the distance. He admitted that this was an assumption. Pearson (21), in 1888, brought forward an elaborate hydrodynamic atomic theory indicating that the exponent of the distance-effect might be variable, according to circumstances, but never more than the fifth power. Five years later Richarz (22) attempted to prove by general theorems of mechanics that some of the propositions involved in the foregoing researches do not afford sufficient stability and must therefore be rejected. The experiments of Plateau, Quincke, Sohncke, Drude, Kelvin, Boltzmann (23) and others were designed to show the range of potent action, or the size of the molecules, rather than the rate of decrease of the diminished effect at a distance. Most of these investigators and, indeed, most later ones, have confined their attention to cohesion, and have left chemical affinity entirely out of consideration. The distending potential of atoms was usually neglected. Moreover, (as has been seen) often there was a tendency to deal with a force acting through a distance rather than with a pressure acting through a volume. Even in the case of capillarity, however, the well-known equation of Laplace, ($P = K + H(1/R_1 + 1/R_2)/2$), shows that the surface-tension effect is merely a small difference between two great internal pressures, P and K, and that pressures therefore should enter into the integral equation (24a). The advantage of employing pressures instead of forces in the analysis is obvious in the work of Dupré, Hirn, and van der Waals.

The valuable and comprehensive work of Amagat on the physical effects of external pressure was rather experimental than theoretical, and concerned gases rather than liquids. Nevertheless, some of his data concerning the behavior of gases under very high pressures are pertinent (24b).

About forty years ago there was a marked reversion to the ideas of Dupré, already explained. Prominent among the theorists who embraced something like this point of view was Stefan (25) who advocated (among other doubtful hypotheses) an expression for the relation of latent heat to internal pressure essentially similar to Dupré's, except that the heat of evaporation was halved—because on an exposed plane surface a molecule may be supposed to be under the influence of half as many molecules as in the interior of the liquid. He seems to have left out of account the fact that when one molecule evaporates another must rise to the surface to take its place (or, in other words, that the total shift is from complete immersion to vapor). Stefan's logic was accepted by many followers, including Ostwald and Walden, who made it the basis of a calculation of heats of evaporation (26). Harkins and Roberts have pointed out, on the basis of experimental results, that Stefan's principle is inconsistent with the change of surface tension with temperature (27). Rather recently Davies (28), and also W. C. McC. Lewis (29), used another expression, $\Pi = RT/(V - 0.27V_c)$, in which V_c is the critical volume. These investigations (to quote two examples) give values for the internal pressure of ether ranging from 1000 to 2000 atmospheres, and for that of benzene ranging from 1400 to 3000 atmospheres (75b).

A better theoretical method of attacking the problem had nevertheless been proposed (in 1888) only two years after Stefan's publication. G. Bakker felt, with Laplace and Maxwell, that an integral expression is necessary to represent the work involved, but suggested that this integral should involve the pressure-volume relation as the best indication of the work developed by cohesive attraction during change of volume (30). Thus he combined good points in the thought of Laplace and Dupré, although in many other respects his treatment was incomplete. He decided, like van der Waals, that the exponent of the volume to be used is 2, which leads to precisely Dupré's expression, although obtained in a more logical manner. In this way (as Traube and van Laar did also at a later date), he calculated heats of evaporation. None of these theorists considered the distending potential (except as indicated by the "constant" quantity b of Dupré, Hirn, Budde, and van der Waals) or the subsidiary thermal effects. Nine years after Bakker's contribution, Milner (31) proposed the inverse integral expression, which is, however, far less intelligibly applicable. Sutherland's rather speculative although interesting communications (1886 to 1893) bearing upon the question brought no definitive evidence, but deserve mention (32).

All of these investigations (except Isaac Newton's) concerned themselves with cohesive pressure alone. In other words, among other omissions, they left wholly out of account the usually still greater pressures which must be caused by chemical affinity. Let us, then, turning back more than one hundred years, briefly glance at the few early incomplete researches which had taken chemical affinity into account.

Davy (33) in 1805 seems to have been the first to point out the great contraction which sometimes takes place when a solid compound is formed from solid elements; he inferred (in a footnote) that this contraction is greater, the greater the affinity. Sixty-five years later the same idea occurred to Müller-Erzbach (34), who showed that in many cases the contraction is greater the greater the heat of reaction, which leads to the same conclusion as Davy's, if heat of reaction is taken as representing approximately the free-energy change concerned. In the last decade of the nineteenth century the comparison was amplified by Traube (35). There were, however, many apparent exceptions to the general rule, and the idea received but a poor welcome from the physicochemical world. In the form then presented, the generalization was indeed both incomplete and inexact. None of these theorists distinguished adequately between the concomitant effects of chemical affinity and cohesion, and none considered the essential influence of the compressibilities of the factors in a reaction.

Furthermore, Traube complicated his presentation with several doubtful assumptions. Being an unqualified adherent to the van der Waals equation, he conceived of an incompressible atomic kernel and a "co-volume" ($v - b$, which, like the b of van der Waals, appears to me to be really rather a mathematical device than the index of a physical entity) and further complicated his thought by assumptions concerning "free-" and "bound-ether." These unnecessary assumptions tended not only to hide the real merit which his investigations possessed, but also to lead him astray.

Here the matter stood at the beginning of the present century. A number of physicists had interested themselves in the attracting pressure caused by cohesive forces and practically all of them had adopted van der Waals's assumption that this pressure varies inversely as the square of the volume. A very few chemists had concerned themselves with the force of chemical affinity, but had made no attempt to represent mathematically its distance effect. All of the above mentioned later experimenters and theorists of both classes had omitted to take any account whatever of the inherent distending tendency in matter except as it is represented inelastically by van der Waals's "constant" *b*, which was not adequately interpreted. Van der Waals had assumed the atoms to be incompressible, and that their kinetic impact is instantaneous. There was, concomitantly, a general tendency (which was continued far into the present century) to assume that the only variable distending potential in matter is due to heat. Although van der Waals' equation received prompt and well deserved acclaim, the importance of the internal pressures of solids and liquids had produced so slight an impression on the minds of most chemists (or even of most physicists) that these internal pressures were scarcely mentioned in the textbooks of that time. Indeed even today they occupy a very unimportant place in most chemical treatises.

Nevertheless, Young's appreciation of the fact that the concept of a variable "repulsive" or distending potential inherent in matter is necessary in addition to the cohesive pressure, had not been wholly forgotten. In an interesting paper written thirty-five years ago (before many of the publications just mentioned) Lord Rayleigh (36) evidently felt the necessity of imagining some such pressure, but he did not essay to treat it mathematically, remarking:

> The repulsive forces which constitute the machinery of this pressure are probably intimately associated with actual compression, and cannot advantageously be treated without enlarging the foundations of the theory.

He had much more to say about the attractive or cohesive internal pressure, which he called the "intrinsic" pressure; for example:

> . . . . the progress of science has tended to confirm the views of Young and Laplace as to the existence of a powerful attraction operative at

> short distances. Even in the theory of gases it is necessary, as van der Waals has shown, to appeal to such a force. . . . . Again, it would appear that it is in order to overcome this attraction that so much heat is required in the evaporation of liquids (37).

Further commenting on the question, Lord Rayleigh pointed out that the existence of great internal pressures is not only conceivable but is necessary, and that "all that we need to take into account is then covered by the ordinary idea of pressure."

Lord Rayleigh was dealing primarily not with the problem of internal pressure, but rather with that of surface tension, so that these remarks are incidental rather than basic. His pregnant suggestions might have served as the initial inspiration of my own work in this direction, if his paper had been known to me at the time. As regards the energy needed for evaporation, he accepted Dupré's equation, without analyzing its details, as a rough indication of internal cohesive pressure,—feeling with Dupré that the work of evaporation should be the mechanical equivalent of the heat involved. A concluding quotation from this paper may help to dispell a source of perplexity which sometimes influences commentors on the concepts involved in this discussion.

> It may be objected that if the attraction and repulsion must be supposed to balance one another across any ideal plane of separation, there can be no sense or advantage in admitting the existence of either. This would certainly be true if the origin and law of action of the forces were similar, but such is not supposed to be the case. The inconclusiveness of the objection is readily illustrated. Consider the case of the earth, conceived to be at rest. The two halves into which it may be divided by an ideal plane do not upon the whole act upon one another; otherwise there could not be equilibrium. Nevertheless no one hesitates to say that the two halves attract one another under the law of gravitation. The force of the objection is sometimes directed against the pressure, denoted by K, which Laplace conceives to prevail in the interior of liquids and solids. How, it is asked, can there be a pressure, if the whole force vanishes? The best answer to this question may be found in asking another—Is there a pressure in the interior of the earth? (38).

A more comprehensive attempt to solve the problem was undertaken at the beginning of the present century. The subject was approached independently from the chemical side. In 1901, eleven years after the publication of Lord Rayleigh's thoughtful paper, the first of the present author's early papers on atomic compressibility was published. This and the immediately succeeding papers (39) brought evidence that the atomic volume is essentially dependent upon opposing pressures, and that the large incompressible kernel of the atom is a purely imaginary, (indeed an unnecessary and irrelevant) assumption. Thus the volume of the atom was assumed to be variable. For all theoretical as well as all practical purposes, it was taken to be the appropriate fraction of the actual volume of a solid or liquid element under given conditions,—that is to say, the "atomic volume" divided by Avogadro's number. Evidence was brought forward not only showing (in independent rediscovery of the outcome of Davy, Müller-Erzbach, and Traube) that cohesion and chemical affinity exert pressure and cause diminution in this volume (just as external pressure causes similar contraction); but also showing (for the first time) that the extent of this diminution of volume is determined also by the compressibility of each atomic sphere of influence under the particular conditions concerned. It was evident, from the considerable volume-changes occurring during the act of chemical combination and the very small compressibilities concerned, that the internal pressures produced by chemical affinity must be very great.

In short, the question was reduced simply to the idea that the balance of two opposing internal pressures, together with the external and thermal pressures, is the real key to the problem, although this conclusion was not expressed as clearly as it might have been. Many actual examples, of a partially quantitative type, were adduced to confirm the reasoning. Especially the parallelism of compressibilities (40) (determined for this purpose) and atomic volumes, together with the behavior of the alkali metals on combination, supported the argument. The origin of the idea was the conviction, based upon experiment, that the quantity b of van der Waals's equation is not constant (except in an expanded gas at constant temperature, where it represents an abstraction which might be called the "collision volume" of the molecules) (41).

An important suggestion, made in the paper of 1901 (70, p. 8) was: that because the "atomic heat capacity" (i.e., the specific heat multiplied by the atomic weight) of a solid or liquid is partly due to the work involved in thermal expansion, it must be an approximate guide (in connection with the coefficient of expansion) to the amount of internal pressure present. Of course, as was there clearly indicated, not all of the heat needful to warm anything is available for work. Some of the heat must be used to provide added kinetic energy and the potential energy of temporary atomic displacement caused by vibration (42). But at any rate the heat and the work against the internal pressure (although not equal to one another) ought to be about proportional in different cases. Therefore the quotient of atomic heat capacity divided by the atomic expansion per degree $(C/V_A\alpha)$ ought to be an index of relative internal pressures (Π) in different substances. Mathematically, one might express the idea thus: $\Pi = fC/V_A\alpha$, where Π is the internal pressure, f an unknown fairly constant fraction, C the gram-atomic heat capacity, V_A the atomic volume, and α the coefficient of expansion. The inference was verified by examples and comparison with other properties. The original statement of the qualification stated above (that f must be less than unity) was overlooked by Traube (44) and by W. C. McC. Lewis (75), the former applying it partially on his own account, and the latter rejecting entirely the suggestion. A fairer estimate of the situation was made by Carl Benedicks (43), who saw that if f is taken as $1/3$, the tenets advanced in 1901 lead to the equation $\Pi = R/V_A\alpha$. This simple equation (in which, as in the previous one, Π = internal pressure, V_A = atomic value, and α = cubic coefficient of expansion while R is the gas constant) Benedicks offered only very tentatively as of distinct interest, but did not further apply numerically to the actual behavior of any form of matter. The probable significance and limitations of this equation will be discussed shortly, in connection with later work.

The American paper of 1901 seems to have stimulated Traube to calculate (in 1903) internal pressures and heats of evaporation, with results of a reasonable order of magnitude (44), by the equation of van der Waals. Traube's results were inevitably vitiated, however, by incomplete logic and by the merely approximate character of van der Waals's equation, especially as applied to matter greatly compressed either by external or by internal pressure; they were appropriately criticized by Benedicks (43). A much more exhaustive prosecution of a somewhat similar line of thought has been recently offered by J. Berger and severely criticized by van Laar (45).

Almost at the same time, in 1903, Mie (46) published an important mathematical paper which contained, perhaps for the first time, an attempt to represent *mathematically* the effect of the distending or repulsive potential of matter already mentioned as having been studied qualitatively. Mie was interested not so much in the magnitude of the internal pressures concerned, as in the calculation of the volume-changes caused by heat and by externally applied mechanical energy. His equation was therefore an energy-equation, into which, however, he introduced the idea of integrating the pressure-volume effect of cohesive pressure after the manner of Bakker (30). With the help of kinetic hypotheses, he analyzed the work involved in the volume-change of a monatomic metal, taking account of a distending as well as a compressing potential and assuming each to be a function of volume. His equation of state took the form,

$$pv_F + Av_F{}^{-1} - \frac{\nu}{3} Bv_F{}^{\left(\frac{-\nu}{3}\right)} = \frac{\nu + 2}{2} R\,\Theta$$

In this equation, the first term represents the work due to external pressure, the second that due to cohesive pressure, the third that due to distending potential, and the fourth that due to heat. The discussion of details would require too much space for the present brief history, especially because the result was not definitive.

Mie's excellent but incomplete theory was amplified and altered by E. Grüneisen (1911–1912), who has done valuable experimental work. The latter also, in very elaborate mathematical papers (47), computed with success compressibilities and coefficients of expansion by consideration of the work derived from four sources—external mechanical work, work done against cohesive pressure, work done by the distending potential, and work corresponding to heat. His equation of state (47b) took the form:

$$pv + n\frac{A}{v^n} - m\frac{B}{v^m} = \frac{(\mathrm{y} + 2)\mathrm{D_y} - (\mathrm{x} + 2)\ \mathrm{D_x E}}{6\ \mathrm{D}}$$

which (like Mie's) involved the use of frequency. However, he immediately concealed the two most important terms in this expression (the second and third) by combining them in a single quantity, which represents their difference. Later he simplified the full equation of state (47c). Neither Mie nor Grüneisen attempted to compute the essential internal pressures concerned; neither of them employed the expression $T\alpha/\beta$ for thermal pressure; and neither looked upon the equilibrium which determines the bulk of a solid or liquid from the point of view of a balance of pressures. They dealt primarily with energy-equations, and rested their argument upon kinetic hypotheses. Nevertheless some of their suggestions are important, as has been said. In a contemporaneous paper, Debye (48) related the quantitative connection of energy and absolute temperature to the acoustical spectrum, deriving a well-known equation for specific heat at low temperatures, and in 1914 showed that neither Mie nor Grüneisen really made use of the two different terms for opposing internal pressures in their formulas for the potential energy, but that so far as their analysis goes, the only thing needed is that deviations from the simple Hooke Law should exist—the sense of these deviations being that more potential energy-change is involved in the diminution of the volume by the amount ΔV than in an increase by the same amount. In this very interesting lecture, Debye introduced the Quantum Hypothesis into the equation of condition of a solid, considering the latter as an asymmetric oscillator. He arrived deductively at Grüneisen's Rule, but did not attempt to compute internal pressures.

The contributions of Marcel Brillouin (who corroborated Debye) should also be mentioned, as well as those of Everdingen, H. A. Lorentz, Ornstein and Zernike, and Tresling. All of these authors (59) dealt largely with the meaning of the Grüneisen rule, considered from Debye's point of view.

More or less contemporaneously with these papers, a number of suggestions appeared concerning the rate of change with changing volume, which perhaps should be mentioned. In a long series of papers, Mills (50) assumed that the force of cohesion varies inversely as the square of the distance between the molecules—an assumption which might give cohesion a rôle in determining the motions of planets and satellites. Mills' assumption was supported by Kam (51), but controverted by Kleeman (52), (who advocated assuming the fourth to the sixth power of the distance) and by Mathews (53). Winther's (54), Tryer's (53) and Tammann's (56) papers should likewise be mentioned in this connection.

Later Wohl (57) adopted an equation somewhat similar to to Grüneisen's, but was inclined to ascribe the "repulsive" force primarily to rotation. Concerning the contributions of K. K. Järvinen (58) for which nothing more than approximate accuracy was claimed, it is only necessary to call attention to the fact that his results agree with the now discredited determinations of the compressibility of mercury made by Jamin. S. Pagliani (59) considering the internal molecular forces of solid substances and their relation with the elastic properties, devised a more complicated theory, subdividing the cohesive pressure into several components. The contributions of Drude and Nernst (60), Tammann (61), and Polowzow (62) concerning internal pressures of solutions deal with systems so complicated that any attempt to derive a simple law was foredoomed to failure at the present time. The complications involved are excellently set forth in recent papers by Baxter (63).

Van Laar, who for a number of years has published interesting mathematical papers dealing more or less with internal pressures, has recently summed up his conclusions in his book (64). He employed an integral equation, depending upon the equation of van der Waals, and yielding a result very like that of Dupré, but somewhat modified by temperature terms. The well-known formulas for specific heat of Einstein (65) and of Nernst and Lindemann (66) (introducing half quanta, and preceding that of Debye) are connected with the interpretation of the phenomena under consideration, but need not be further discussed in this place. They are reviewed interestingly by Grüneisen.

Very recently important investigations have been made by several physicists, attacking the subject from an entirely different standpoint, and founding the argument upon hypotheses concerning the electronic nature of the atom. The three chief investigators in this direction have been, F. Haber, Sir J. J. Thomson, and Max Born (67). These contributions are stimulating and suggestive; but they, like Mie's and Grüneisen's, possess the inevitable disadvantage which always inheres in any deductive attempt to predict the facts when only hypothetical premises are employed. Both Thomson and Born came to the conclusion that compressibility is a function of atomic or molecular volume alone. That molecular volume is indeed one of the essential premises in the argument had been shown long before in the first comprehensive research on the compressibilities of the elements (68); but this early research showed also that molecular volume is not the only variable to be taken into account. Hence neither of these more recent suggestive discussions could be expected to yield more than approximate results. That the outcome should be as satisfactory as it was is a cause for congratulation.

Some of those who advocate the electronic explanation believe that both the repelling and attracting forces are due to the same cause, and that the condition of equilibrium is one not of opposition but rather of a kind of neutrality. This view involves the assumption that Coulomb's Law is greatly modified at short range (perhaps by quantum forces). A simple definitive explanation along this line seems far to seek.

Is it indeed possible to gain exact quantitative knowledge, from any source, concerning a problem so recondite, dealing with concealed pressures so mutually entangled and so far removed from the range of actual experiment? Recently (in 1916) Jeans has written: "The effect of the forces of cohesion is too complex for an exact mathematical treatment to be possible" (69); and this feeling has been at times shared by others, including the present author. Nevertheless, the question is so fundamentally important that even an incomplete answer is vastly better than none.

The attracting and repelling tendencies which determine the behavior of solids and liquids are different in many ways from any other forces in nature. It would appear, then, that for their understanding and evaluation one must pursue an inductive quest, relying in phenomenological fashion upon the actual effects which are produced by the powerful influences involved. That is to say: the basis for the determination of internal pressures would seem to be found in the actual behavior of solids and liquids under the action of thermal and mechanical energy. This proposition was indeed implicitly recognized by many of the earlier authors already quoted. That density, coefficient of expansion, specific heat, heat of evaporation, and compressibility, as well as many other properties of matter having to do with physical and chemical condition, must be dependent upon internal pressure, was especially emphasized in 1901 (70).

At that time, and in the immediately following years (71), it was shown that in all probability, as a general rule, the greater the coefficient of expansion, the less the internal pressure; again, the greater the compressibility, the less the internal pressure; and yet again, the greater the decrease of compressibility with increasing external pressure, the less the internal pressure. Nevertheless data were lacking for numerical calculations leading to an exact quantitative theory.

In 1922, however, the remarkable work of Bridgman on the compressibility of thirty metals to 12,000 atmospheres' pressure, was published (72). These results, which had been kindly communicated to me by Professor Bridgman some months before publication, promised at last a means of penetrating more deeply into the mystery. Bridgman's thermodynamic treatment of them was primarily concerned only with external pressures, and he made no attempt to compute from them the much greater internal pressures involved. Nevertheless they furnished an exceptionally good basis for inference concerning these internal pressures, especially because many of the metals studied were isotropic and therefore presented a simple and more intelligible basis of analysis of the problem than is possible where more than one intensity of internal cohesive pressure is present at the same time in the same substance.

The opportunity was immediately grasped, and the first hopeful outcome was the discovery of a very simple hyperbolic interpolation equation (73) which represents with great precision the effect of pressure and temperature on the volume of heavy metals such as gold and silver. This equation took the form

$$(p + P)\ (v - B_1) = k_1 + cT$$

In it p is the external pressure applied by a pump and measured by a gauge; P represents (but is not necessarily exactly equal to) the hidden internal cohesive pressure which holds the metal together; v is the volume; B_1, k_1, and c are constants; and T is the absolute temperature. The agreement of this equation with the actual results for many heavy metals was within the limit of error of experiment, and an approximate agreement existed even with the more compressible alkali metals. Somewhat similar equations had previously been used over short ranges for organic substances by Tumlirz and Tammann (74). Their treatment of temperature was, however, inadequate and not illuminating, and their equations were merely first approximations as regards the behavior of the complex substances concerned.

The above stated equation is an energy-equation, analogous to that of van der Waals,—although the B_1 value is smaller in magnitude than the b of the latter's treatment. But we are concerned primarily with pressures, and not with quantities of energy; because the equilibrium which exists in a solid or liquid at ordinary temperatures must be really a balance of pressures. Therefore this expression was reduced to an equation of pressures by dividing it through by the volume $(v - B_1)$ as follows:

$$p + P = \frac{k}{v - B_1} + \frac{cT}{v - B_1}$$

The transformed equation still has four terms, but now each represents a pressure. The first term, p, is simply the external pressure; the second represents pressure caused by *cohesion*, the third represents that portion of the *distending*, "repulsive" or repelling tendency which is independent of heat, and the last, the remainder of the distending pressure, caused by heat. The *compressing* tendencies are in the left-hand member, and the *distending* tendencies in the right.

Here we have experimental evidence that a distending potential, independent of heat, is an important influence in the balance of pressures. It is indeed, except in very volatile substances, much greater than the thermal pressure. The latter (the fourth term in the immediately preceding equation) was shown, by a process of reasoning too extended for exposition here, to be equal to the absolute temperature multiplied by the coefficient of expansion and divided by the compressibility, ($T\alpha/\beta$)—one of Dupré's old expressions. Thermodynamically it is a valid quantity, equal to $-T(\partial p/\partial T)_v$. This quantity represents only one of the four opposing pressures, namely, that due to thermal energy. In the case of very volatile substances, $T\alpha/\beta$ is indeed not very much less than the total distending pressure, but with non-volatile substances this thermal pressure is only a small part of the total tendency which resists compression. If the sole distending tendency in matter were this one, due to heat, (14b, page 626) matter would shrink to zero volume at the absolute zero of temperature;—for example, Kamerlingh Onnes' apparatus for liquefying helium would have been reduced to very small dimensions before the liquid could have been obtained.

An obvious difficulty in the preceding equation is the assumption of the constancy of the quantity representing cohesive pressure, P, whereas really this pressure must increase very rapidly with decreasing volume. If this latter conclusion is true, in order that the equation may (as it does) represent the facts, the expression for the distending tendency $k/(v - B_1)$ must also increase with decreasing volume. Therefore a different method of stating the second and third terms is needful.

In its most general form the equation of state of any condensed phase composed of a single species of monatomic molecules under definite conditions may evidently be expressed by the simple equation[1]

$$p + \Pi = \Pi_\rho + T\alpha/\beta$$

in which Π depicts the true internal cohesive pressure (represented roughly by P in the preceding equation) and Π_ρ depicts the true internal repelling or distending pressure independent of heat. But because each of these internal pressures must be assumed to change with changing volume, as has been said, the following amplification (73b) presents a much better picture of the situation:

$$p + \Pi_o \left(\frac{v_o}{v_1}\right)^m = \Pi_{\rho_o} \left(\frac{v_o}{v_1}\right)^n + \frac{T\alpha}{\beta}$$

This equation (in which Π_o and Π_{ρ_o} correspond to the volume v_o) appears to be rather complex, but the ideas concerned are really simple enough. It is easy to see that (at ordinary temperatures) since Π_o is larger than Π_{ρ_o}, whereas n is larger than m, the difference between the actual changes in the second and third terms with moderately changing volume might very well be equal to the increase in p—a supposition which would explain the approximate validity of the simpler hyperbolic equation already given. So far as present analysis can show, m is usually not far from 2, being often about 1.7. The exponent n is much larger than m; if it were not, all matter would collapse under slight external pressure.

The above equation combines the static and the dynamic points of view by virtue of its use of the dimension of pressure as the key to the situation—for pressure may be exerted either by a steady push (as in the cases of p, Π, and Π_ρ) or by a succession of kinetic impulses (as in the case of $T\alpha/\beta$). The impulsive pressure

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[1] This equation represents mathematically the basic idea in the author's work since 1901. The idea was perhaps somewhat vaguely expressed at first, but it had assumed very definite form shortly afterwards (71, pp. 2435–2437). See also 73a, p. 425, and the paper written in collaboration with E. Saerens (67).

produced by heat must cause an oscillation determined in its range by the rate of increase and falling off of the two great static opposing internal pressures. It appears to act in the whole volume occupied by the atom. Obviously when any given thermal impulse is great enough to over-balance the above-mentioned equilibrium, the atom (or molecule) carrying the impulse must be set free,—i.e., evaporate. The situation appears to be well adapted to furnish a suitable mechanism for the physical and chemical reactions necessary for constructing a workable universe and a physical basis of life.

The new equation for monatomic elementary substances, thus independently developed, seems to make possible the weaving together into a consistent fabric many of the diverse threads which other investigators had gradually accumulated. It contains, like the equations of Mie and Grüneisen, a term for each of the four separate tendencies affecting the volume of a condensed phase. It gives prominence to the third term depicting the non-thermal distending or repelling tendency in matter, which has been so often neglected. In keeping the second and third terms separate from one another it emphasizes their essentially opposite nature. It installs as the fourth term a quantity which seems to express the true thermodynamic magnitude of thermal pressure, $T\alpha/\beta$ (or $-T\left(\frac{\partial p}{\partial T}\right)_v$). It shows, on the other hand, that this last term does not represent (as Dupré (8) and others (75) appear to have thought) the whole of the distending tendency in matter. Finally it assigns to the exponents of the two volume ratios symbols (m and n) which are independent of the gas-equation of van der Waals, and which challenge evaluation on the basis of the behavior of the condensed phase itself under mechanical and thermal pressure.

The most important distinguishing feature of the new equation is the treatment of the two opposing pressures Π and Π_p as separate entities, operating presumably by different mechanisms. This feature is probably that least acceptable to many physicists, who may prefer dealing merely with the difference $(\Pi - \Pi_p)$, after the manner of Grüneisen, Kleeman (52) or Eucken (83), or else prefer maintaining (as has been said) that equilibrium is a neutral point in an hypothetical electrical system governed by anomalous quantum forces. But if as it appears, the exponent m is the same (somewhat less than 2) with many substances (81, p. 734) and since, furthermore, both thermal expansibility and latent heat of evaporation as well as chemical heat probably point toward pressures of the full magnitude of Π, does not the individual quantity Π acquire real significance? And is not then the use of the mere difference between Π and Π an evasion of the issue? Moreover, the dissociation of the treatment of these two tendencies has much to recommend it, not merely for mathematical convenience, but also because of analogy with other physical phenomena. In general, when in a series of observations a maximum or minimum exists, strong evidence is afforded that two different mechanisms are at work. Such an inflection appears in the relations of the internal forces to distance,—an inflection too marked to be accounted for without the assumption of a concrete distending tendency other than heat. The fact that Π and Π_p must ultimately be referred to forces does not invalidate the treatment of these tendencies as pressures concomitantly with external and thermal pressures.

The four unknown quantities Π_o, Π_{p_o}, m, and n could theoretically be determined by four equations, involving different relative volumes and pressures, and representing the actual behavior of an isotropic element, provided that m and n were unchanging in value. But this last proviso is not necessarily fulfilled, although for a comparatively small range of volume definite values may be assumed without serious error. The range of volume experimentally available with comparatively incompressible substances is of necessity small.

A more convenient method of advance was found in the study of a series of "synthetic" pressure-volume curves, built up on definitely assumed internal pressures and exponents, and in the comparison of these with the pressure-volume curves actually exhibited by isotropic substances. This study can not be detailed here. It sufficed to show that the Π_o values are of the order of magnitude of the P in the hyperbolic interpolation equation; and that when m is 2 and n is 7, the two quantities P and Π are nearly equal. Increasing n increases P and diminishing n diminishes P in relation to Π. From these considerations also, the initial compressibility β_o at the absolute zero (where $T\alpha/\beta$ is 0) was found to be $\beta_o = 1/(\Pi_o\ (n - m))$—an important relation which may be used for the direct computation of Π_o when the difference $(m - n)$ is certainly known, or of $(m - n)$ where Π_o is known (77, p. 733).

These considerations make possible the approximate determination of the internal pressures in the isotropic metals, depending upon the experimental results of Bridgman. It appears that Π_o is, for example in the case of silver, about 160,000 megabars. The amount of calculation involved is great and has not yet been applied to many other cases, but there seems little doubt that the outcome is reasonable and that the equations just given afford an adequate picture of the behavior of isotropic solids. Very recently J. E. Jones, from a study of solid argon (76) has confirmed in a remarkable manner not only the point of view, but also some of the quantitative aspects of the development.

This outcome is supported in rather striking fashion by an entirely different method of approach depending upon facts of a different kind, namely, by the study of the coefficient of expansion, a property like compressibility concerned with the great internal pressures existing in solids and liquids. That the coefficient of expansion is primarily dependent upon internal pressure was perhaps first emphasized (70) in 1901 as has been already indicated above.

The coefficient of expansion of a solid or liquid is always much less than that of a perfect gas. The probable reason for this difference may well be as follows: In solids and liquids the pressure produced by heat must be only a small part of the total pressures concerned (as is shown by the foregoing equations) whereas in the case of a perfect gas the energy of heat must cause the whole distending effect. Is it not then reasonable to draw an inference concerning the magnitude of this greater pressure from the comparison of the two coefficients of expansion? The coefficient of expansion of silver at 20° is about one sixty-first of that of a perfect gas. The kinetic energy involved is generally believed to be identical in the two cases. May it not then be that the total pressure involved in the expansion of silver is sixty-one times that which a gram-atom of a perfect gas would exert in the same volume? If this is the case in general, the internal pressure of a metal at 20°, for example, would be

$$\Pi = \frac{RT}{V_A} \frac{0.00341}{\alpha_s} = \frac{R}{V_A \alpha_s}$$

This expression makes precisely the above comparison (73b). In it Π, as before, signifies cohesive internal pressure; T, absolute temperature; R, the gas-constant; $0.00341 = 1/T = \alpha_g$ (the coefficient of expansion of a gas) α_s the coefficient of expansion of the solid; and V_A the atomic volume. The above equation is identical with that tentatively suggested but not applied by Benedicks (43) in entirely different fashion upon the basis of an earlier proposition (70).

From the point of view here adopted, this equation is, however, only a first approximation. The expansion of a perfect gas is measured under constant pressure, whereas the expansion of a solid is measured under a slightly changing *total* pressure (although under a constant *external* pressure); for as the solid expands the internal pressure Π must diminish; and even if the external pressure is kept constant, the total pressure against which the energy of heat is acting must be diminished during the expansion. In order to be entirely consistent, then, α should here signify the coefficient of expansion when the total pressure $(p + \Pi + \Delta p)$ is kept constant (Δp being the slight change in p necessary to replace the small loss of Π due to the increased volume on heating (77). The correction is, however, a small one; it leads to values of Π slightly higher than the uncorrected values. Its exact amount can not be precisely determined until the constancy of Π in constant volume with changing temperature has been proved (78).

At very low temperatures the equation needs modification for the little understood reason which causes the failure of Dulong and Petit's Law. The "Grüneisen Rule" that for a given substance α is approximately proportional to C (the molecular heat capacity), indicates this parallelism. Evidently a more correct expression is that advocated (and expressed in words, but not in symbols) in 1901 (70), namely,

$$\Pi = f\ (C/V_A\alpha)$$

At ordinary temperatures $C = 3R$ approximately, and $f = 1/3$. At very low temperatures C/3 is no longer equal to R. Further discussion of this aspect of the matter must be postponed.

However this may be, the equation

$$\Pi + \Delta\Pi + p = R/V_A\alpha$$

gives at ordinary temperatures a good means of predicting rather closely the effect of pressure on the coefficient of expansion and compressibility, as will be shown in a subsequent paper. For example, the coefficient of expansion of mercury under 3,000 megabars pressure (p′) is computed to be $\alpha_p' = R/14.75\ (31{,}000 + 515 + 3{,}000) = 0.000163$, whereas Bridgman's experimental value is 0.000164, both being referred to V_A at 0°C. The value $\Delta\Pi = 515$ is calculated on the assumption that $m = 1.7$; it represents here the increase of cohesive pressure due to the diminished volume caused by the external pressure, $p' = 3{,}000$.

Taking everything into consideration, it accordingly appears that

$$\Pi = C/3V_A\alpha; \quad \text{or} \quad R/V_A\alpha$$

(for ordinary temperatures) may therefore be accepted as a promising, if not rigorous, means of computing internal pressures, which gives results somewhat, but not much, too low. Accordingly, table 1 is given to show the approximate internal pressures in a number of isotropic* metals compared in this way, R being 83.16 megadyne-cm./°C.

These pressures are very large, but not unreasonably so. That at least they are not far from the right order of relative magnitude

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* "Isotropic" is used here in its original sense and not as synonymous with "amorphous."

is likely. Moreover the fact that they are about equal to values computed from the pressure-volume curves alone (that is to say, from compressibility), strongly supports their approximate accuracy. If volatile liquids possess internal pressures of the order of a thousand or more atmospheres, as is generally conceded, the magnitude of these values for metals is not excessive. They are not far from the values calculated by Traube (44) from the equation of van der Waals. Griffith has found experimentally values of the same order of magnitude from the tensile strength of glass fibers (79).

TABLE 1

Approximate internal pressures of isotropic metals based on atomic volumes and cubic coefficients of expansion (at 20°C.)

METAL	COEFFICIENT OF EXPANSION	ATOMIC VOLUME	INTERNAL PRESSURE
Caesium	300	71	4,000
Potassium	245	45.4	7,500
Sodium	215	23.7	16,300
Mercury	181	14.8	31,000
Lead	85	18.3	53,000
Calcium	50	25.3	66,000
Magnesium	74	13.3	85,000
Aluminum	65.5	10.1	126,000
Silver	55.6	10.3	145,000
Gold	43.2	10.2	189,000
Copper	48.4	7.1	242,000
Palladium	34	8.77	279,000
Tantalum	24	10.9	315,000
Nickel	38	6.7	327,000
Cobalt	37	6.85	329,000
Iron	34	7.1	345,000
Platinum	26.4	9.1	347,000
Tungsten	13.7	9.6	632,000

The heat of evaporation of mercury affords support for the corresponding value given in the above table, and therefore indirectly for the other values. When the attracting and repelling pressures and m and n are known, one should be able to compute from the second equation on page 334 the work required for pulling the atoms apart—in other words, for evaporating the substance. This work (when corrections for such small concomitant effects as external work and heat expelled because of change of heat capacity are made) should be equal to the heat of evaporation. The difference between the pressure-

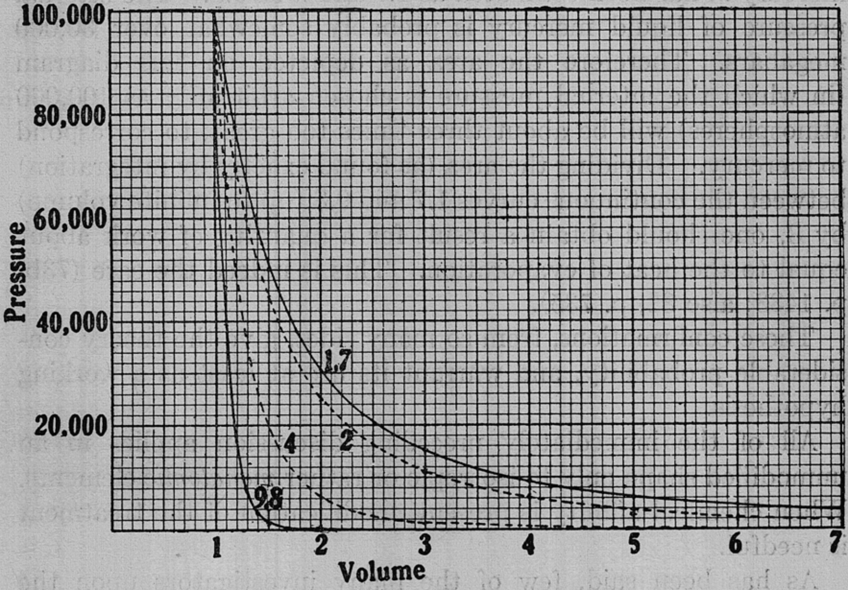

FIG. 1. THE WORK OF EVAPORATION DONE AGAINST COHESIVE PRESSURE

Multiples of the atomic volume are plotted as abscissae (abscissa 1 corresponding to the atomic volume of the condensed material). Pressures in megabars are plotted as ordinates. The difference between any two integrals, that is to say, the *area* between any upper curve (representing the decrease of cohesive pressure with increasing volume) and any curve below it (representing the decrease of internal repelling pressure with decreasing volume) represents the work required to separate molecules from a condensed condition to a distended vapor. This diagram holds precisely only at the absolute zero, thermal pressure not being included in it. It assumes that the internal pressure in the liquid or solid is 100,000 atmospheres; for any other internal pressure, the appropriate fraction or multiple of the differences between integrals gives the corresponding work.

volume integrals of the second and third terms of this equation constitute the chief part of the energy in question. This difference is represented by the *area* between any two curves in the diagram (fig. 1) in which the numbers on the face of the diagram near the curves represent the exponents of the volume ratio.

On the other hand the equation of Dupré is represented by the rectangle at the left of ordinate 1. Evidently, for any reasonable values for n or m, the area between the curves will be of about the same order of magnitude as Dupré's expression. In the case of mercury m has been estimated as 1.7 and n as 9.8. The internal pressure of liquid mercury is probably somewhat over 30,000 megabars. Therefore the area as depicted on this diagram (in which the internal pressure is chosen arbitrarily as 100,000 atmospheres) will be about three times too great, to correspond to mercury. Dividing the area (as found exactly by integration) between the continuous curves 1.7 and 9.8 (up to infinite volume) by 3, one should obtain a result for a quantity of work about equal to the heat of evaporation. This is indeed the case (73b, p. 1433; also 81, p. 735).

These confirmations, from so many sides, give the theory considerable probability, and warrant its use at least as a working hypothesis.

All of the immediately preceding discussion applies in an unmodified shape only to isotropic or rather *monatomic* elements. When chemical affinity is present, modification of the treatment is needful.

As has been said, few of the many investigators upon the subject have included chemical affinity in their consideration. Yet this force is no less important than cohesion, which in many respects it resembles (84). Like cohesion, chemical affinity must produce very great pressures which fall off very rapidly as the attracting atoms recede from one another (2, 80); and like cohesion, chemical affinity may in many cases be overcome by the energy of heat. The similarity is great enough to warrant the application of the foregoing principles, inferred from one set of phenomena, to the more complicated situation presented by the other. New difficulties arise in the treatment, due not only to the fact that in a compound at least two different elements are present at the same time, but also to the probability that each chemically combined atom is subjected to different intensities of pressure on different portions of its surface. Nevertheless, the venture seemed to be worth making, since even a vague outcome would be better than none.

Accordingly, within a few months (81) the method of treatment outlined in the immediately foregoing pages has been expanded to include the pressures produced by chemical affinity. The outcome shows that the same principles which apply to cohesion may apply also to chemical affinity, bearing in mind the fact that chemical affinity acts most strongly on the portions of the atoms in closest juxtaposition and does not envelop each atom equably over its whole surface after the manner of cohesion in an isotropic element. Just as the heat of evaporation may be accounted for chiefly by the work involved in separating atoms under the influence of the changing balance of pressures, so the heat of chemical combination may be accounted for chiefly by the work done by the more considerable one-sided pressures usually produced by chemical affinity. This verifies a much earlier prediction based upon the relation of volume-change to heat of reaction (82). Even the recent discussion was inevitably tentative, because the portion of the atom involved by the one-sided action of chemical affinity is not easily defined. Nevertheless it was possible to show that the amount of work which may be done by the chemical union of two atoms is of the order of magnitude of the heat evolved. Of course, for completeness in this case, as in the other, correction must be made (on the basis of the so-called third law of thermodynamics) for the change of heat capacity during the reaction.

The equations presented by the most recent investigations thus seem not only to explain the pressure-volume-temperature behavior of solids, and liquids, but also to give a roughly quantitative picture of the *raison d'être* of heat of evaporation and of chemical reaction. Further investigation now in progress must proceed slowly, partly because of the time needed for calculation, and partly for the reason which halted Newton at a much less advanced state of the inquiry, namely, the lack of "a sufficiency of experiments." But nevertheless, although incomplete, the knowledge already gained, step by step, through the successive advances of many investigators, gives a conceivable and rational picture of the action of the mechanism whereby solids and liquids (forming the framework of the universe) maintain their equilibrium. What the basic causes of the great pressures indicated may be, cannot yet be definitely decided. Perhaps these causes may be entirely electronic, but of course the demonstration of such a cause can be complete only when it is conclusively shown that electrical attractions and repulsions may really be capable of producing the very great but balanced pressures which are indicated by the actual behavior of condensed matter.

Incomplete although our knowledge of internal pressures may still be, one feels that at least something has been accomplished toward the fulfilment of Newton's parting injunction: "It is the Business of experimental Philosophy to find them out."

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