3. In every case the current was directly proportional to the voltage and directly proportional to the number of reacting molecules.
4. The ratio of ions to reacting molecules was in every case exceedingly small, about 1 pair of ions for 10^{13} molecules reacting. It is likely that ionic recombination prevents all but a minute fraction of the ions from reaching the electrodes.
5. The experimental facts which have been obtained substantiate the electronic hypothesis for the constitution of matter and the electron theory of chemical bonds. It is apparent that at the moment of reaction there is an electronic rearrangement wherein the fall of potential between certain electrons and their parent nuclei has materially changed.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

THE INTERNAL PRESSURES OF SOLIDS

BY THEODORE WILLIAM RICHARDS

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Everything points toward the existence of very great internal pressures in solids. These pressures appear to be caused by chemical affinity and cohesion; they must be intimately connected with the circumstances which determine the very existence of solids and also of liquids. Although they give little obvious outward indication of their presence, they are nevertheless of great importance and interest in their direct bearing upon any theory of atomic structure, as well as in their indirect bearing upon most of the chemical and physical properties of matter. The present paper briefly outlines a recent attempt to add to the knowledge of this subject; it is a sketch rather than a finished picture.

Both the chemical affinity and the cohesion which are assumed to cause these pressures may well be due, at least in part, to electrical attractions and repulsions, as current theories demand. No attempt is made in the present sketch, however, to seek the ultimate source of the agencies involved, or to define how the atomic domain is filled. The effort has been rather to discover how internal pressures behave—to trace their effects on some of the cardinal properties of matter.

One of the first desiderata in the study of these pressures is the discovery of the hitherto unknown laws which determine the relation of the volume of liquids and solids to external pressures, as well as to the great internal pressures which exist within them. Any such study, like any other attempt to solve an entirely unsolved problem of this type, must depend upon the determination of the facts concerned, and must proceed inductively from these facts. Hence the very valuable experimental investigations of Professor Percy W. Bridgman,[1] upon which many of the following conclusions depend, as well as my own experimental work, have been used in the elucidation of the subject in so far as the behavior of solids under high external pressures is concerned.

Recently[2] it has been shown that the change of the volume of solids under pressure conforms in many cases to a simple type of hyperbolic interpolation-equation, which holds with unexpected exactness for dense, compact solids, and roughly for voluminous ones. The physical meaning of this equation is a matter of interest; it is of importance in its relation to the theory of the solid and liquid state. Accordingly the equation has been investigated in detail.

The equation, as published, took the form

$$(p + P)(v - B_1) = k \qquad (1)$$

Its analogy to the equation of van der Waals is obvious; but it differs from the latter in that P is assumed to be independent of volume. In Equation 1, p indicates external pressure, P represents a function involving internal cohesive pressure, v records the volume at any given pressure p, B_1 is a fractional volume which indirectly represents the resisting tendency, or "repulsive potential" of the atom, and k is a constant, determined by the other quantities. In the papers referred to, P was interpreted as giving a new means of inferring the existence of great internal pressures in solids. That its values are of the same order of magnitude as these pressures was guessed from the fact that the P values often correspond rather closely with the values of the internal pressures computed from the rule of Dupré—which latter is by no means beyond reproach, however, as will be seen.

This hyperbolic equation may be modified to include the effect of temperature, by introducing a temperature function into k (conforming to the obvious analogy with the gas-law). Here, however, k must be split into two parts, one of which is independent of temperature and the other depicts the temperature effect. Thus modified, the equation assumes the form (in which T signifies the absolute temperature)

$$(p + P)(v - B_1) = k_1 + cT \qquad (2)$$

By differentiation at constant temperature when $v = 1$ and $p = 0$, the compressibility, $\beta_0 = \left(\frac{\partial v}{\partial p}\right)_T = (1-B_1)/P$. Furthermore, by subtracting two equations (with $p = 0$) at temperatures T and $T + \Delta T$ (ΔT being small), $c = P(\Delta v/\Delta T)$. Substituting (from above) $P = \frac{(1-B_1)}{\beta_0}$ and

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[1] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58,** 163 (1922).

[2] Richards, *Proc. Nat. Acad. Sci.*, 9, 73 (1923); THIS JOURNAL, **45,** 422 (1923).

In 1923 the author was unaware that an analogous equation had been applied to organic liquids (with which it accords only over a comparatively short pressure-range) by Tumlirz, *Sitz. Akad. Wiss. Wien,* IIa, **118,** 203 (1909) and Tammann, *Ann. Physik.,* [4] **37,** 975 (1912). Their treatment of temperature is inapplicable to the present case.

noting that (since v is 1 when $p = 0$) $\Delta v/\Delta T = \alpha_0$ (the initial coefficient of expansion) we have

$$c = P\alpha_0 = \frac{\alpha_0(1 - B_1)}{\beta_0} \tag{2a}$$

which has the dimensions of energy divided by temperature. This expression holds exactly only when $p = 0$, but it serves as a convenient first approximation when the volume is not far from unity. Since α and β both vary, these symbols must be carefully defined as to conditions. Present knowledge of the changes in α is, however, in a very crude state.

For convenience in identifying the several quantities (some of which are unusual) employed in this paper, the following table of definitions of symbols is appended.

Symbol	Meaning
α	cubic coefficient of expansion, referred to v_0, or v_T or v_p, as specified
β	cubic coefficient of compression (compressibility) as specified
B_1	a constant fractional volume indirectly determining (in Equations 1, 2 and 3) internal distending pressures
B_θ	a fraction of unit volume $= 1 - P_\text{I}/P_\theta$
c	$P\alpha_0$
D	density
f	a ratio of quantities of energy used in computation
k	a constant at $T^\circ = k_1 + cT$
k_1	a constant quantity of energy independent of temperature
L_A	gram atomic latent heat of evaporation
m	exponent of volume ratio indicating change of cohesive pressure Π
n	exponent of volume ratio indicating change of distending pressure Π_ρ
p	external pressure
P	a constant function related to internal cohesive pressure
P_I	the pressure exerted by a mole of perfect gas in volume V_A
P_θ	$T\alpha/\beta$ = thermal pressure : distending pressure produced by heat energy
Π	internal cohesive pressure
Π_ρ	internal distending pressure, independent of temperature (each of the last two applies to pressures between atoms)
R	the gas constant = 8.32 joules per degree Centigrade or 83.16 cc. megabars per degree
T	absolute temperature
v	volume
V_A	atomic volume

The supplementary equations necessary for calculating the values of P and B_1 from Equation 2 at any given temperature (making the initial volume unity, while v_1 is the volume at p_1, and v_2 the volume at p_2) are as follows:

$$f = \frac{p_1(1 - v_2)}{p_2(1 - v_1)}, \quad P = \frac{fp_2 - p_1}{1 - f}, \quad B = \frac{(p_2 + P)\,v_2 - P}{p_2}$$

When these values have been obtained the sum $k_1 + cT$ follows as a matter of course, and the volume of the substance under any given pressure is easily found.

Suitable partial differentiation of Equation 2 yields (with very compact substances) an expression for compressibility, $\left(\beta = \frac{1}{v_0}\left(\frac{\partial v}{\partial p}\right)_T = -\frac{k}{(p+P)^2}\right)$; hence, even if it were of no further service, the equation would be useful. The derivative giving the coefficient of expansion is less exact, because c is not wholly constant; but with the more compact metals it may be assumed as constant without serious error. With very compressible substances such as potassium, c varies widely as the volume changes, and the equation is far from satisfactory.

That this equation agrees within the limit of error of experiment with the actual figures of very compact substances is shown by Table I, which gives the results calculated for copper, silver and gold[3] as compared with

TABLE I

COMPARISON OF HYPERBOLIC EQUATION WITH OBSERVED VALUES

In terms of megabars

GOLD (α = 0.0000432)

Equation $(p + 160{,}000)(v - 0.90726) = 12{,}813 + 6.91\ T$

	Volumes at 20°			Volumes at 75°		
p	Obs.	Calc.	Error $10^4\Delta$	Obs.	Calc.	Error $10^4\Delta$
0	1.00000	(1.00000)	0.0	1.00237	(1.00237)	0
2,000	0.99883	0.99885	+ .2	1.00120	1.00120	0
4,000	.99770	.99772	+ .2	1.00006	1.00005	−0.1
6,000	.99658	.99659	+ .1	0.99895	0.99893	−0.2
8,000	.99550	.99550	.0	.99787	.99784	−0.3
10,000	.99445	.99444	− .1	.99682	.99678	−0.4
12,000	.99343	.99343	.0	.99590	.99573	−1.7

SILVER (α = 0.0000556)

Equation $(p + 200{,}780)(v - 0.7978) = 37{,}327 + 11.16\ T$

0	1.00000	(1.00000)	0	1.00306	(1.00306)	0
2,000	0.99801	0.99801	0	1.00103	1.00099	−0.4
4,000	.99606	.99605	− .1	0.99904	0.99905	+0.1
6,000	.99415	.99413	− .2	.99708	.99710	+0.2
8,000	.99227	.99225	− .2	.99516	.99519	+0.3
10,000	.99043	.99045	+ .2	.99326	.99332	+0.6
12,000	.98862	.98860	− .2	.99144	.99144	0

COPPER (α = 0.0000484)

Equation $(p + 255{,}490)(v - 0.8131) = 44{,}120 + 12.38\ T$

0	1.00000	(1.00000)	0	1.00266	(1.00266)	0
2,000	0.99855	0.99855	0	1.00117	1.00119	+0.2
4,000	.99712	.99712	0	0.99971	0.99974	+0.3
6,000	.99572	.99571	−0.1	.99825	.99831	+0.6
8,000	.99433	.99432	−0.1	.99685	.99691	+0.6
10,000	.99296	.99296	0	.99545	.99552	+0.7
12,000	.99163	.99162	−0.1	.99407	.99416	+0.9

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[3] Bridgman has carefully made and recorded results upon many other metals at different temperatures. The present method of treatment is equally applicable to most of these. See Ref. 1.

Bridgman's observed values (recalculated from his smoothed curves in terms of megabars[4] instead of kg./sq. cm.). The results of Equation 2 for silver, for example, depend upon the following values for the constants: $P = 200{,}780$, $B_1 = 0.7978$, $k_1 = 37{,}327$, $c = 11.16$—values which are easily found algebraically from the temperature coefficient and three points on the curve where, respectively, $p = 0$, 6000 and 12,000. Many other similar and equally satisfactory results for other slightly compressible metals have been computed; those given in Table I will serve as examples.

Thus in a single equation the pressure-volume-temperature relations of a compact solid are expressed satisfactorily over a fairly wide range. The precise physical meaning of the several terms is, however, veiled.

By dividing through by $(v-B_1)$, the equation becomes

$$p + P = \frac{k_1}{(v - B_1)} + \frac{cT}{(v - B_1)} \tag{3}$$

This equation of pressures is interesting, not only because it has been shown to hold (in the form given by Equation 2) very exactly for compact substances, but also because it gives a further insight into the nature of the pressure equilibrium in solids. Clearly it demands the existence of a balance of four pressures, the first being p, the external pressure; the second P, representing the cohesive pressure (which is for the present assumed to be constant); the third $k_1/(v-B_1)$—which represents a distending pressure independent of temperature and increasing as the volume diminishes; and the fourth $cT/(v-B_1)$ another distending pressure caused by the kinetic effect of heat. The value of this last term may be easily calculated: from its mode of derivation, $c = \alpha_0(1-B_1)/\beta_0$; hence $cT/(1-B_1)$ is simply $T\alpha_0/\beta_0$ (where α_0 is the initial cubic coefficient of expansion, and β_0 the initial compressibility). The quotient α_0/β_0 is the so-called "pressure coefficient;" thermodynamically it equals — $\left(\frac{\partial p}{\partial T}\right)_v$. The thermal distending pressure $T\alpha/\beta$ usually does not change greatly in compact solids with moderate change of volume. It may, of course, be exactly computed when α and β are known for the conditions concerned. For convenience, this quantity $T\frac{\alpha}{\beta}$ will be designated the "thermal pressure" (although others have used this term in other senses) because no other term seems to be fitting.

All the quantities involved in Equation 3 are assumed to be constant excepting p, v and T. The assumption of constancy of P and B_1 places all the variation of *internal* pressure upon $k/(v-B_1)$. Nevertheless, although from a pragmatic point of view this procedure appears to be

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[4] The megabar is the pressure of 1,000,000 dynes (or 1019.8 g. at 45° of latitude per sq. cm). It is 0.987 "atmosphere," and may be called the "absolute atmosphere"

justified, it cannot be considered as anything but a fortunate compromise, for any actual increase in P might in fact be entirely hidden (as far as change of volume is concerned) by a decrease in B_1, which latter decrease would of course increase the quantity $k/(1-B_1)$. The fact that Equation 3 corresponds very well with the observations does not therefore preclude the possibility that both the compressing and the distending internal pressures increase as the volume diminishes.

For the adequate representation of this possibility, another equation, similar as to the qualitative nature of the terms employed, but based upon the true (but as yet unknown) opposing internal pressures, is necessary. For this purpose, the designations Π and Π_p are hereafter used for the true cohesive and distending pressures, respectively, in order to distinguish these true values from the temporary values P and $k_1/(v-B_1)$, which have hitherto been used for the purposes of definition as being at least qualitatively related to the true values.

Based thus upon Equation 3, the true equation of the pressures existing within a solid, takes the form

$$p + \Pi = \Pi_p + P_\theta \tag{4}$$

in which the first and last terms are identical with the corresponding terms in Equation 3 while the quantities Π and Π_p differ from the corresponding terms in Equation 3 by a like (as yet unknown) amount, x. In this new equation Π and Π_p are assumed to be independent of temperature, but not independent of changes of volume. Π is the true cohesive pressure; Π_p is that part of the true distending pressure which is not due to heat.

Equation 3 thus affords confirmation of the assumption (based upon long experience) which was made in a former paper,[5] namely, that the fundamental equation representing equilibrium in all forms of matter should take, at any given temperature and pressure, the form of Equation 4.

The two internal pressures Π and Π_p are the chief topic of the present sketch; they deserve much more careful study.[6] Because of the fact that

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[5] Richards, THIS JOURNAL, **45**, 425 (1923). On lines 6–9 of the page just cited Equation 4 is expressed in words.

Of course, in a perfect gas Π and Π_p are each zero, hence Equation 4 reduces to $p = (P_\theta)_v$. The last term is still equal to $T\alpha/\beta$, since in a perfect gas $T\alpha = 1$ and $1/\beta = p$, —if compressibility is defined as $\frac{1}{v_p}\left(\frac{\partial v}{\partial p}\right)_T$. If compressibility is defined as the fraction of the volume change produced by a unit of pressure, its value under pressure p is $\beta = 1/(p+1)$. When the gas is under great pressure, this refinement of definition is practically unnecessary.

[6] The history of the knowledge of these pressures covers many years. Newton long ago saw the necessity of imagining an attracting cohesive force. Young [*Phil. Trans.*, **1805**, p. 81] and Laplace discussed somewhat arbitrarily the same tendency. As the late Lord Rayleigh pointed out [*Phil. Mag.*, **30**, 285 (1890)], their arguments are obscure. Lord Rayleigh saw that a "repulsive" or repelling force is necessary to withstand this attraction. Most chemists and physicists have thought until very recently

only the *difference* between their changes is manifest outwardly, at least in the study of pressure-volume effect, they are particularly difficult to evaluate.

Probably each of these true pressures increases rapidly with diminishing volume. This conclusion is supported by many circumstances, among them the otherwise unexplained changes in α and c already mentioned; its probability will become clearer in the sequel. Certainly Π_ρ increases more rapidly than Π as the volume decreases (at least when the ordinary compressibility of the solids is concerned). This is essentially proved by Equation 3. Moreover, if Π_ρ did not increase more rapidly than Π, the external pressure which causes the diminution in volume would cause a complete instantaneous collapse to a more stable condition. Such a collapse, indeed, probably occurs in the act of the formation of allotropic forms produced by pressure but it need not concern the present discussion. Thermal pressure should also be considered in the analysis.

The reasonable assumption (which few will contest) may then be made that both internal pressures increase as the volume decreases. This assumption was made also by Grüneisen. (Ref. 6.) Thus the equation of state for a solid may be amplified as follows,

$$p + \Pi_0 \left(\frac{v_0}{v_1}\right)^m = (\Pi_\rho)_0 \left(\frac{v_0}{v_1}\right)^n + (P_\theta)_{v1} \qquad (5)$$

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that the "repulsive" force (or rather pressure) is entirely due to heat. This view seems to be taken, for example, by W. C. McC. Lewis [*Trans. Faraday Soc.*, **7,** 94 (1911)] as well as by Hildebrand [THIS JOURNAL, **44,** 504 (1921)] who used $T\alpha/\beta$ as the internal pressure, although it is only one of the distending pressures in a solid or liquid. Long before this a few others had perceived the need of imagining a distending tendency independent of heat. This idea was the basis of the theory of atomic compressibility [*Proc. Am. Acad. Arts Sci.*, **37,** 1 (1901)]; see also for details, the Faraday Lecture [*J. Chem. Soc.*, **99,** 1207 (1911) and THIS JOURNAL, **36,** 2437 (1914)]. Doubtless independently, G. Mie used this concept in relation to other phenomena [*Ann. Physik,* 11, 657 (1903)]. Mie's theory was amplified by E. Grüneisen, who has done valuable experimental work on compressibility. Especially in a very elaborate mathematical paper [*Ann. Physik,* **39,** 257 (1912)] he computed compressibilities and coefficients of expansion from a point of view similar to that herewith presented. More recently the idea of opposing pressures has been accepted by many physicists, for example, Langmuir [THIS JOURNAL, **38,** 2235 (1916)]. M. Born, in numerous papers [in particular, *Ann. Physik.*, **61,** 87 (1919); also in "Der Aufbau der Materie," Berlin, **1922**] has endeavored to predict internal pressures on an electrical basis. Haber's work in a similar direction should also be mentioned (*Sitzb. Preuss. Akad. Wiss.*, Berlin, **1919,** p. 506) and likewise that of Sir J. J. Thomson, "The Electron in Chemistry" (Franklin Institute, Philadelphia, 1923). The validity of these views is discussed by Richards and Saerens, THIS JOURNAL, **46,** 946 (1924). Discussions bearing upon internal pressures, often in relation to surface tension, have been published by Eötvös, Walden, Stefan and others too numerous to mention. A complete bibliography concerning internal pressures would occupy far too much space for publication here. So far as I know, however, none of the investigators on this subject has pursued exactly the independent lines of thought herewith presented.

in which Π_0 and $(\Pi_p)_0$ represent the values of these quantities when $p = 0$, v_0 the corresponding volume, and v_1 the volume under pressure p, and in which n is ordinarily greater than m. The exponents m and n may change with changing volume—that is to say, the compression curve is probably not simply exponential. Hence their values, with those of Π and Π_p, cannot be determined by merely observing the volume at four different external pressures. Nevertheless, they can be determined, at least approximately, in other ways, as will be seen. There is indication that over a small range of volume, approximate constancy in m and n may be assumed without danger of serious error.

This equation appears to represent adequately the pressure equilibrium in a solid composed of monatomic molecules. Its relation to the hyperbolic interpolation equation is interesting. When constructed on the same series of points (representing the volume changes in curves of known antecedents or of a given metal under pressure) these two different equations show, by comparison, that while P is in general of the same order of magnitude as Π, the two are exactly equal only when the exponents m and n have certain relative values. The extended study which led to an understanding of the mutual relations of the P and Π under different circumstances cannot be explained in brief space. It is enough to say here that when n is considerably greater than m, P is somewhat greater than Π. This is the case with silver and mercury, chiefly discussed below. On the other hand, when the exponents are not very unequal, Π is greater than P. Thus P is not identical with the true internal pressure, Π, but is closely related to it.

From these considerations, also, the initial compressibility β_0 at the absolute zero (where $P_\theta = 0$) was found to be

$$\beta_0 = \frac{1}{\Pi_0\,(n - m)}, \tag{5a}$$

an important relation, which may be used for the direct computation of Π_0 when the difference $(n-m)$ is certainly known, or of $(n-m)$ when Π_0 is known.

On this basis it is possible to construct a curve for a given metal; for example, silver, of which the experimental values have already been recorded. In this case $B_1 = 0.7978$, a value which indicates the *average* of the exponents to be about 5. Choosing $m = 1.7$ and $n = 8.5$ for several reasons[7] (the chief being that the *difference* between the exponents is

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[7] That the exponent of the repelling tendency should be so large is no new idea. For instance in 1914 I made the following statement [THIS JOURNAL, **36**, 2436, 2437 (1914)]: "Whether the atom consists of 'substance,' of whirling electrons, of complete vacuity, or merely of a repellent force. . .the present research shows that the effect increases inversely as a very high power of the distance." The high power of the distance may reasonably be held responsible for the phenomena which led J. H. Jeans [*J. Chem. Soc.*, **123**, 3398 (1923)] to maintain that the atom is "infinitely hard." This condition would be attained if $n = \infty$.

found to be 6.8, shown by the coefficient of expansion as will be indicated later), it is easily possible to show that the following equation of state represents rather closely the case of silver.

$$p + \Pi\left(\frac{v_0}{v_1}\right)^{1.7} = (\Pi_p)\left(\frac{v_0}{v_1}\right)^{8.5} + \left(\frac{T\alpha}{\beta}\right)_{v_1} \qquad (6)$$

This equation is easily solved, if one remembers that when p is zero $\Pi = (\Pi_p) + (T\alpha/\beta)$, by substituting corresponding values for p and v_1 for a single point. The values for Π_0 and $(\Pi_p)_0$ are found in the case of silver to be, respectively, 160,680 and 144,510 (since P_θ equals 16,170 when $p = 0$; and 16,520 when $p = 10{,}471$ and $v_1 = 0.9900$, as derived from the experimental results of Bridgman given in Table I). The equation then becomes, at 20°

$$p + 160{,}680\left(\frac{v_0}{v_1}\right)^{1.7} = 144{,}510\left(\frac{v_0}{v_1}\right)^{8.5} + \left(\frac{T\alpha}{\beta}\right)_{v_1} \qquad (7)$$

This equation is easily solved for other values of p. Thus at volume 0.995 (if P_θ is taken as halfway between the values given above, or 16,345) p at 20° is found to be 5090, whereas Bridgman's value was 5111, corresponding to an error in the volume of 0.00002, or only 0.002%. This is as close as could be expected, considering the uncertainty which lack of exact knowledge of the coefficient of expansion at different pressures introduces into the problem. Small errors would be enormously magnified in the calculation, which leads to very large magnitudes from very slight changes of volume. For these reasons among others, Equation 5 although a step forward, evidently does not provide a wholly satisfactory solution of the problem.

There is, however, another method of attacking the matter which, granting a reasonable assumption, gives a much more definite outcome. This method depends upon the coefficient of expansion—a property allied to compressibility and like the latter concerned with the great internal pressures existing in solids and liquids.

The coefficient of expansion of a solid is always much less than that of a perfect gas. The probable reason for this difference may well be found in the inference (drawn from Equation 3) that in solids the pressure produced by heat must be only a small part of the total pressures of cohesion and repulsion involved, whereas in the case of a perfect gas, the kinetic energy must be the whole distending effect. An inference concerning the magnitude of this greater pressure may then be drawn from the comparison of the two coefficients of expansion.

The coefficient of expansion, $\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{T}$, of a compressed mass of perfect gas at 20° is always 0.00341, whatever the volume, because, as has been said, heat is the sole distending influence. The cubic coefficient of expansion of silver at 20° is only 0.0000556; that is to say, it is less than $^1/_{61}$ of that of a perfect gas $(1/T)$. From this point of view the total pressure involved in the expansion of silver should be 61.2 times that which a gram atom of a perfect gas would exert in the same volume. Since this latter (which may be called P_I) is easily computed from the gas law and the atomic volume $V_A = 10.27$—being simply (in megabars) RT/V_A, or at 20° the quantity $24{,}360/V_A = 2374$—the internal pressure of silver would appear to have the value 145,000 megabars.

$$\Pi = \frac{R}{V_A\alpha} = \frac{24{,}360}{V_A} \times \frac{0.00341}{0.0000556} = 145{,}000 \qquad (8)$$

(R is the gas constant, 83.16, expressed in cc. megabars per centigrade degree.)

This simple mode of calculating internal pressures is supported by many other considerations. Some of the reinforcing arguments may be of interest; but those readers who are interested rather in the outcome than in details will probably prefer to turn at once to Table II, several pages further on.

Another way of approaching the computation of internal pressure from these premises is the following. On comparing the thermal pressure ($T\alpha/\beta$) with the ideal pressure (P_I) which a perfect gas would exert in the same space (that is in the atomic volume of the particular substance concerned), the thermal pressure is seen to be always greatly in excess of the ideal pressure. In other words, the solid system may be, for the sake of argument, supposed to act as if the restricting or repelling tendency had confined the energy of heat into a bulk smaller than the atomic volume. The practicable fraction of the whole is represented by the quotient of the ideal pressure divided by the thermal pressure—which fraction may be depicted (in analogy to Equation 1) by the expression $(1-B_\theta)$. From its method of derivation, it is equal to $24{,}360\ \beta/T\alpha V_A$, at 20°C., or $R\beta/\alpha V_A$.

This B_θ is a different quantity from B_1 used in the hyperbola (Equation 1), although not dissimilar in kind. Each value of the new quantity, β_θ, belongs only to a *single point* of the curve, whereas the old quantity B_1 was obtained as an *average* value, derived from the whole experimental range, and indissolubly linked with the nature of the hyperbola. When (as appears to be often the case) the exponents of the volume ratios in Equation 5 change with changing volume, B_1 is greatly affected. Hence B_θ and B_1 could not be expected always to agree. Clearly, however, the new quantity, B_θ, is a much safer basis for the calculation of the internal pressure than was the old quantity B_1, because at any one point it is unaffected by the progressive change of the exponents. Moreover, if the picture of the balance of pressures herewith presented is a correct one, the reciprocal of $(1-B_\theta)$ must approximately equal $(n-m)$, according to the following equations. Since $\Pi_0 = 1/\beta(n-m)$ (approximately), and also $\Pi_0 = \frac{RT}{V_A} \times \frac{1}{\alpha T}$, we have

$$n - m = \frac{V_A}{RT} \times \frac{T\alpha}{\beta} = \frac{P_\theta}{P_I} = \frac{1}{1 - B_\theta} \text{ (approximately)} \qquad (8a)$$

(in which P_I signifies the pressure which a gram-atom of a perfect gas would exert in the volumes V_A). On the other hand, B_1 (of Equation 1) bears somewhat the same relation to P that B_θ bears to Π. When m is 2 and n is 7, the two quantities B_1 and B_θ are nearly equal. Thus it appears that B_θ gives the means of computing approximately $n-m$, while on the other hand B_1 gives an approximate clue to $^1/_2(m + n)$ as already stated. These two together, then, go far towards solving the problem in hand. Most of these relations are rendered somewhat inexact at high temperatures by the simultaneous presence of thermal pressure. At the absolute zero the compression curves would be simpler in character than they are at ordinary temperatures.

Let us proceed to the calculation of the internal pressure, on this basis. B_θ is the quantity which must be subtracted from the atomic volume so that the remainder shall act (as regards *temperature*) according to the gas law. The remaining portion may be assumed to act also as regards *pressure* according to the gas law. In other words, since B acts as if it were an incompressible portion of the substance in one case (although, of course, it is in fact only a mathematical function representing indirectly the resistance to compression), it probably will act thus in the other case likewise. Then since the pressure of a greatly compressed perfect gas is always the volume divided by the compressibility, $\Pi = \frac{1-B_\theta}{\beta}$. If into this latter expression the value of $1-B_\theta$ (calculated from the thermal pressure) Equation 8a is introduced, any eccentricity of compression should be eliminated, because the same quantity $(1-B_\theta)$ is considered with respect to the pressure produced by heat, as well as to the pressure produced mechanically. The treatment may be considered as somewhat analogous in logic with the highly useful method of treating the abnormalities of the so-called "Law of Mass Action" by means of the "*activities*" of G. N. Lewis. All the disturbing irregularities are banished into this quantity B_θ, which is then mathematically eliminated. This consideration leads to exactly the same conclusion as that expressed above, thus:

$$\Pi = \frac{1 - B_\theta}{\beta} = \frac{1}{\beta} \times \frac{RT}{V_A} \times \frac{\beta}{T\alpha} = \frac{R}{V_A\alpha} \qquad (9)$$

The result is precisely that of Equation 8. It is, indeed, identical with the other in premises, and therefore in outcome; but the point of view from which it is approached is somewhat different; hence the new argument may assist in the understanding of the problem.

Long ago[8] it was pointed out that the atomic heat of a metal, divided by the change of atomic volume caused by the change of 1° in temperature, yields a quantity which appears to have a close relation to cohesive affinity. This quantity, which is approximately $3R/V_A\alpha$, is now seen to have more

[8] Richards, *Proc. Am. Acad. Arts Sci.*, **37**, 8 (1901).

significance than has usually been accorded to it. It is three times the internal pressure as computed above. Study of Boltzmann's analysis of the law of Dulong and Petit shows the probable reason for the factor 3, and thus brings specific heat also into the list of properties which support the present argument. The details are too voluminous for discussion here.

The agreement of the outcomes of these three trains of thought seems to indicate that the expression reached by each of them gives an indication of internal pressure worthy at least of provisional acceptance.

With very compressible substances, such as potassium, Π is found to increase rapidly as p increases. For example, when $p = 12{,}000$, $\Pi = 25{,}000$, although under atmospheric pressure the value of the latter is less than one-third of this quantity. The comparison of the changes in Π (as well as in Π_p, which is easily calculated for each pressure) with different elements is highly interesting, but would take too much space for discussion here.

The possible effect of temperature on cohesive affinity is another aspect of the subject which should be noted. The assumption has been implicitly made that this is negligible except as affected by change of volume—all of the temperature effect having been thrown into P_θ. The justification of this assumption lies in the outcome, since the equation seems to be at least approximately fulfilled. Nevertheless, it is possible that Π is somewhat affected by temperature. On comparing the values of Π, calculated from the coefficients of expansion at different temperatures, one finds that in all the cases considered in this paper, Π diminishes as the temperature rises—an effect doubtless primarily due to increase in volume, as the above argument predicts. This diminution is, however, sometimes more and sometimes less than is demanded by the change of volume and the most probable values of m and n. Whether the slight discrepancies are due to inaccuracy in our knowledge of coefficients of expansion or to slight changes in Π with temperature alone, is a question which must remain, for the present, in abeyance. The effect is rather one of a second order. If Π changes with temperature, all of the equations discussed in this paper must be somewhat modified accordingly, but the effect can hardly be great enough to influence the general conclusions herewith drawn.[9]

That these considerations cannot apply without modification to cases where superposed effects are present, is obvious. A negative coefficient of expansion, of course, would mean an impossible negative pressure, if it were not caused by some superposed effect. So far as we know, however,

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[9] In this connection a paper by Grinnell Jones [THIS JOURNAL, **31**, 192 (1909)] is of interest. This paper deals with the effect of temperature in special cases of chemical affinity; but since chemical affinity resembles cohesion in so many ways, its bearing on the present case is significant.

it is usually if not always thus caused. In the case of water, for instance, there is every reason to believe that the abnormal expansion is due partly to true expansion and partly to the change of volume incident to shifting polymerization. It is impossible, therefore, to use at present the coefficient of expansion of water at ordinary temperatures as a direct means of determining its internal pressure. In compounds or alloys in general, as well as in metals having polyatomic molecules, the interpretation is likewise not simple. In such cases the more compressed portions of the atoms will have a smaller coefficient of expansion than the less compressed portions. The result will be an average in which the two effects are superposed, and will probably vary in proportion to their relative preponderance. Thus the fact that the internal pressure of sodium chloride, for example, determined in this way, is only about 40,000 atmospheres, does not show that the pressure due to the chemical affinity concerned is only about 40,000 atmospheres, unless it can be proved that each atom of chlorine and sodium is affected on all sides by the same pressure. These matters, together with many other aspects of the subject will be discussed in a later paper.

From Equation 9, by due transposition, it appears that

$$\beta = \frac{\alpha V_A (1 - B_\theta)}{R} \tag{10}$$

This equation affords a plausible picture of the reason why α and β with different chemical elements, or with a given compressible element at

TABLE II

ESTIMATES OF THE INTERNAL PRESSURE OF ISOTROPIC METALS BASED ON MOLECULAR VOLUME AND CUBIC COEFFICIENT OF EXPANSION AT 20° AND UNDER ATMOSPHERIC PRESSURE

Arranged in the order of magnitude

Metal	Coefficient of expansion × 10^6	Molecular volume	Internal pressure in megabars
Cesium	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

different volumes, do not in fact show a constant ratio. The product $V_A\ (1-B_\theta)$ varies from less than 1 cc. to more than 20 cc. in different elements. The equation just recorded is similar in significance to Dupré's empirical equation for similar organic substances, namely $\beta = k\ \frac{\alpha T}{D^2}$.

Table II gives a few estimates of the internal pressures computed in this way,[10] according to the expression $\Pi = 83.2/V_A\alpha$.

These values are plausible. That at least they are not far from the right order of *relative* magnitude is likely. The other properties which are associated with strongly knit texture would lead one to expect some such order of succession as is here indicated. Moreover, the different modes of approach in the present paper give outcomes reasonably consistent. For example, in the case of silver the hyperbolic equation gave 200,800 as the value of P. The probable values of m and n indicate that this result is probably about 20% greater than the true value of Π, which is thus shown to be about 160,000. The value of Π from the coefficient of expansion is 145,000—quite as near to the former values as could be expected.

Furthermore, Equation 7 shows that a pressure of about this magnitude will cause a pressure-volume-temperature surface of precisely the type exhibited by silver if the exponents of the volume ratios are, respectively, 1.7 and 8.5, which are not improbable. Applied to other metals, the comparison sometimes yields more consistent results than with silver, in other cases less consistent results; but all the values seem to me to point toward probable order of magnitude not far from those indicated in the table. Comparisons of the values of m and n with different metals, and with a given metal under varying conditions, are interesting, but would require much space, and must be postponed to a later communication.

The values receive support from their relation to the corresponding heats of evaporation. Not many isotropic elementary substances have had their heats of evaporation determined; but that of mercury, at least, is known, and this metal therefore serves as the best example. The heat of evaporation may be supposed to consist of at least three parts; the work required for separating the molecules, the heat set free by change of heat capacity, and the work done against external pressure. The last two are easily computed; the first (with which we have now to do) is by far the greatest. According to the present point of view, the work involved in separating the molecules should be capable of computation when the volume effects of the opposing pressures are known.[11]

The idea is perhaps best presented graphically, computing the curves

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[10] The values of the coefficients of expansion are due to many experimenters, especially to Henning, Grüneisen and Fizeau. Landolt and Börnstein's "Tabellen" give as usual a convenient résumé, with references: pp. 333 and 352 (1912).

[11] Compare Eucken, *Z. Elektrochem.*, **28,** 6 (1922).

for Π and Π_ρ in relation to increasing volume. This is done approximately in the diagram herewith presented. The superposed effects of thermal pressure, as well as those caused by the possible changes of exponents of Π, including gravitation, are disregarded in this preliminary computation. They could hardly affect the order of magnitude of the outcome. The area between the two curves shown in the graph represents (with the foregoing qualifications) the work corresponding to the evaporation of a gram atom of mercury from the liquid state. The internal cohesive pressure Π is taken as 31,000 megabars, computed from the equation $\Pi = R/\alpha V_A$. Values for n and m of Equation 5 are computed from Bridgman's data concerning mercury[12] which give $B_\theta = 0.877$; $B_1 = 0.824$. Therefore $m + n = 11.50$ and $n-m = 8.1$, hence m and n equal, respectively, 1.7 and 9.8. The curves are drawn accordingly. Evidently this area represents

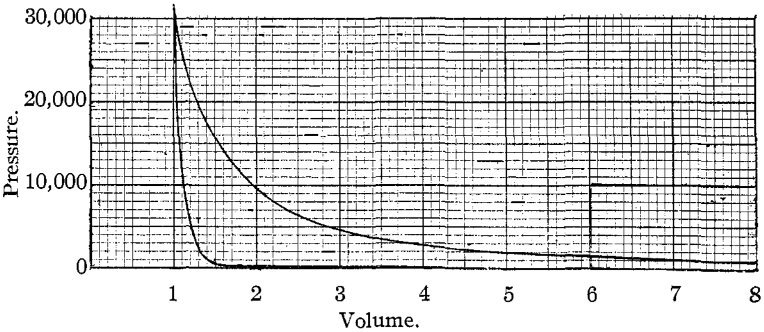

Fig. 1.—Work due to pressure-volume effect involved in the evaporation of mercury (20°).

Pressures in megabars are plotted in the direction of ordinates; volumes in terms of multiples of the atomic volume are plotted as abscissas. Hence each small square represents 1.48 liter-megabars. The total area between the curves (to infinite volume, easily calculated from a convergent series) is about 410 times that amount, or 60.6 kilojoules.

an amount of work roughly corresponding to the heat of evaporation. The number of squares included between the curves in the diagram is about 310; and nearly one-third as many again (easily found by the summation of a convergent series) correspond to the extension to infinite volume, or about 410 in all. Each square corresponds to 0.148 kj. and the total area corresponds to about 60.6 kj. Subtracting 5.3 kj. (the heat *given out* by change of heat content[13]), the heat of evaporation is found to

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[12] Bridgman, *Proc. Am. Acad. Arts Sci.*, **47**, 347 (1911). The P of the hyperbolic interpolation equation for mercury is 42,460, c is 8.25 and k, is 5028 at 20°.

[13] The amount of heat required to raise 1 gram atom of mercury from 0° K. to 293° K. is about 1593 cal. plus the latent heat of melting (560 cal.) or 2153 cal. (that is, 9.0 kj.). The amount of heat necessary to raise mercury vapor in extremely attenuated condition over the same range would presumably be $1.5\ RT = 3.7$ kj. The difference, 5.3 kj. is presumably the amount of accumulated heat displaced in the change from

be 55.3 kj. instead of 55.6 kj.[14]—an agreement so close that it must be partly fortuitous. Of course the area may be defined mathematically with greater exactness, but the data do not warrant greater precision at present.

Striking although this confirmation is, it cannot be considered as proof. A lower value of the internal pressure, together with lower values of n and m might yield a similar result. Moreover, even if correctly evaluated, the exponents m and n may vary; if this variation is similar in each, the result would not be much affected, but if different, its effect might be considerable. The above statement, nevertheless, is enough to show that both the internal pressure and the exponents employed are consistent with one another and with the heat of evaporation, as to the order of magnitude

Incidentally, it should be noted that the exponent of the volume effect of the cohesive pressure $m = 1.7$ is not far from the value 2 assumed in the equation of van der Waals. Taken in connection with the reasoning just detailed, this last coincidence seems to afford additional support to the whole argument. Not all metals have this value of m, however.

Furthermore, this diagram shows why the old equation of Dupré:[15] Cohesive pressure $= L_A/V_A$ (in which L_A is the atomic heat of evaporation) gives a reasonable value for the internal pressure; because the work corresponding to the area between these curves, is, by chance, not far from $\Pi \; V_A$ (in the case of mercury, 46 kj.). It would appear, then, that Dupré's rule (although not founded on a logical analysis of the process of evaporation) may be used as an approximate guide, at least in many cases, to the internal pressure.

The graphic method just outlined, of course, affords a means of computing the heats of evaporation of any isotropic element for which α and β are known at several points. Thus the atomic heat of evaporation of a gram atom of silver at 20° is found to be about 190 kj., if $\Pi = 145{,}000$ and $m = 2$ (or somewhat less than 2). The same method may be applied to the heat of chemical combination, but the discussion of this process (which involves additional complexities) must be postponed to a later paper.

There is nothing inherently improbable in the great magnitude of these pressures. The same principles applied to organic substances yield values of about the order (some thousands of atmospheres) usually ascribed to these substances.[16] If, for example, ethyl acetate possesses an internal

liquid to attenuated vapor at 20°. The estimate of the average gram atomic heat capacity (5.45) is from the results of many experimenters. For a résumé, see Mellor, "Inorganic and Theoretical Chemistry," Longmans, Green and Co., **1923**, vol. 4, p. 720.

[14] Numerous experimenters have found from 62 to 77 cal. per gram (or 52 to 65 kj. per gram atom) at the boiling point. The careful vapor-tension determinations of Pfaundler at 56.3° and 98.8° give 58 kj. per gram atom at 83°. Subtracting the external work at 20° (2.4 kj.) the value 55.6 kj. is obtained.

[15] A. Dupré, "Théorie Mécanique de la Chaleur," Paris, **1869**, p. 158.

[16] See Hildebrand, THIS JOURNAL, **38**, 1459 (1916).

pressure of several thousand atmospheres, mercury may well possess an internal pressure of 31,000 atmospheres.

Comparison of these pressures with the gross behavior of metals is not uninteresting. The changes in metals under stress are of course influenced, not by any one pressure alone, but by the balance of all. When a metal is stretched, for example, p (in the direction of stress) becomes a minus quantity, and both Π and Π_p must decrease, the latter more rapidly than the former. That the attracting or cohesive pressure falls off rapidly has been shown qualitatively by experiment,[17] as well as by the application of Equation 7. Hence the cohesive pressure must be greatly diminished before the moment of fracture. When the metal finally yields, the break occurs gradually, in successive places (unless the substance is exceedingly hard)—as may easily be inferred from examination of the fracture. The molecules tear apart by degrees, rather than all at once. In confirmation of this view, the great difference in breaking stress between the hardened (or drawn) and the annealed condition of a metal may be cited. Both of these circumstances tend to make the breaking stress (which, even as it is, sometimes amounts to thousands of atmospheres) much smaller than the true cohesive pressure of the unstressed metal.[18] The present considerations concerning internal pressures give promise of interesting mathematical relations to the theory of elasticity.

One cannot but wonder that so little account is taken of these very large cohesive pressures in the literature of physical chemistry. Chemical affinity must often exert still greater pressures.

As already stated, this paper is rather a report of progress than a final treatment of the subject. The manifold relations which it involves underlie the whole basis of the physics and chemistry of compounds, and of solids and liquids. Many other relations have already been studied in further elucidation of its complexities; these are necessarily omitted from lack of space. Much more remains to be done in the future.

Summary

This paper contains a brief analysis of the nature of an approximate hyperbolic pressure-volume equation for solids, namely,

$$(p + P)(v - B_1) = k_1 + cT \qquad (1)$$

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[17] T. W. Richards and W. T. Richards, *Proc. Nat. Acad. Sci.*, **9**, 379 (1923)—a paper which contains a record of an experimental attempt to estimate gravimetrically the distance effect of chemical affinity, together with a brief bibliography of the conclusions of others on this topic,

[18] The very fact that a slight change in treatment, which can hardly affect cohesive affinity, causes so great a change in breaking stress, shows that the latter is inadequate to give the full value of the cohesive effect. Modern evidence concerning the slipping (or gliding) of molecular layers, as well as concerning amorphous interstitial matter, appears to be consistent with this conclusion.

It discusses the relation of this hyperbolic equation to an equation of state, in which each of the quantities has definite physical meaning. This latter equation takes the general form,

$$p + \Pi\left(\frac{v_0}{v_1}\right)^m = \Pi\left(\frac{v_0}{v_1}\right)^n + \left(T\frac{\alpha}{\beta}\right)_{v1} \qquad (5)$$

The exponents m and n may be inferred to change with any considerable change of volume. The data for compressibility and coefficient of expansion appear to be inadequate, as yet, for the rigorous determination of their rate of change. This question seems to be the chief obstruction to a complete solution of the problem.

In the perfect gas Π and Π_p are, of course both zero at all temperatures; the compressibility of a gas depends at finite temperatures entirely upon P_θ. With a perfect gas at the absolute zero all the terms of Equation 5 become zero.

The truth of the following expression, as regards simple isotropic solids,

$$\Pi_0 = \frac{1}{\beta\,(n - m)} \qquad (5a)$$

at the absolute zero seems to be probable; this expression throws new light on the meaning of the compressibility of solids and liquids.

Furthermore there is described a method which (although not free from assumption) gives a plausible means of calculating the internal pressure of isotropic elements from the coefficient of expansion by means of the equation,

$$\Pi = \frac{R}{V_A\alpha} \qquad (8)$$

Assuming that this holds true, it can be used to determine $(n-m)$ by combination with (5a). Thus $n-m = V_A\alpha/R\beta$.

Relatively to one another, the internal pressures of a number of isotropic metals seem to be given reasonable values by these considerations. The heat of evaporation affords confirmatory evidence. It is notable that the existence of these great pressures is often ignored.

Even after making due allowance for possible errors in the necessary assumptions involved in the reasoning, these equations all point to the existence of very great internal pressures in solids, especially in such metals as iron, platinum and tungsten.

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