The results with alkaline solutions were compared with those for acid-salt solutions with regard to the activity of the ion acting as a catalyst. The same rule which was found to be valid for the relation between reaction velocity and activity in acid-salt solutions for a number of different reactions could also be applied to alkaline salt solutions. The reaction velocity follows always the activity of the ion causing the reaction, at least as long as counteracting factors do not cause an effect and the concentration of the catalyst is not very dilute.

A possible relation of the reaction velocities in acid and alkaline salt solutions to the water equilibrium in these solutions has been considered.

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FURTHER EVIDENCE CONCERNING THE MAGNITUDE OF INTERNAL PRESSURES, ESPECIALLY THAT OF MERCURY

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RECEIVED JULY 26, 1926 PUBLISHED DECEMBER 16, 1926

Internal pressures, dependent upon the attractive forces of chemical affinity and cohesion (which make possible the existence of compounds, solids and liquids) are among the most fundamental of the properties of matter.

Even thermal internal pressures (calculated thermodynamically) are sometimes of the order of 20,000 atmospheres, yet they are obviously far less than the intrinsic cohesive and chemical pressures of compact solids. Coefficients of expansion and compression, as well as latent heats of evaporation and chemical action, indicate that these latter may often exceed 100,000 atmospheres.[1] Previous papers have sketched roughly a quantitative theory for the correlation of the data concerning these internal pressures. The present discussion corrects and amplifies the earlier work, and corroborates the previous provisional estimate of the order of magnitude and significance of intrinsic pressures by new evidence, thus strengthening the general principles of the theory, and providing a more definite outcome. The corrected values of the quantities in question are somewhat larger even than those suggested in previous papers.

1. Fundamental Equations

The present discussion is based upon the following fundamental equation of state for monatomic solids and liquids:[2]

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[1] Richards (a) THIS JOURNAL, **36**, 2417 (1914); (b) **46**, 1419 (1924); (c) **47**, 731 (1925); (d) *Chem. Rev.*, **2**, 315 (1925). This last historical paper contains many references to earlier work.

[2] Ref. 1 b, pp. 1423–1425. For a comparison of this equation with the somewhat similar, previously proposed equations of Mie and Grüneisen, see Ref. 1 d, pp. 327–329. These latter were essentially different in several important respects.

$$p + \Pi_0 \left(\frac{v_0}{v}\right)^m_T = (\Pi_\rho)_0 \left(\frac{v_0}{v}\right)^n_T + P_\theta \qquad (1)$$

In this expression p represents external pressure; Π the internal or intrinsic cohesive pressure; Π_ρ the internal or intrinsic distending (repelling or repulsive) pressure;[3] P_θ the internal thermal pressure; and v the volume corresponding to pressure p. The exponents n and m represent the rate of increase of the respective pressures with decreasing volume. The exponent m is inevitably smaller than n. Subscript T signifies the temperature at which the equilibrium is studied, and subscript 0 signifies the condition when $p = 0$. P_θ has been shown to be equal to $T\alpha/\beta$ or $-T(\partial p/\partial T)$, in which α and β are the cubic coefficients of expansion and compression, respectively.

In words: Equation 1 indicates that the condition of a solid or liquid is determined by the balance of two compressing pressures against two distending pressures—the *external pressure* p coöperating with the *intrinsic cohesive pressure* Π (both tending to diminish the volume of the solid) whereas the *intrinsic distending pressure* Π_ρ coöperates with the *thermal pressure* P_θ (both tending to expand the solid). All except the first of these four terms represent internal pressures. The second and third of the terms may be called "intrinsic" (using Lord Rayleigh's term) since they are inherent in the nature of the material, while the fourth, being dependent primarily upon heat, is less worthy to bear this latter designation. The best nomenclature is perhaps that just given (in italics); but for convenience the word "intrinsic" may usually be omitted without causing ambiguity.

Equation 1 presents the quantitative problem in the simplest form. Its solution is to be found in the ascertaining of the numerical values of the quantities involved in special cases.

In any system involving polyatomic molecules, two or more equations like Equation 1 are needful—one additional equation for each atomic region subjected to one-sided chemical stress differing in magnitude from the cohesive pressure. In molecules composed of more than one element even the cohesive pressure may differ in different parts of the molecule and hence demand more than one equation. In such cases, each equation applies only to a fraction of the molecule.[4]

Because of these inevitable complications, the problem must be attacked step by step, first considering monatomic elements, then diatomic elements, and finally more and more complex compounds. The present paper is chiefly confined to a careful study of the simplest possible case,

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[3] The intrinsic distending pressure might perhaps better be designated as, for example, Ξ instead of Π_ρ for several reasons, especially because Π_ρ is a pressure very different in character from Π, and also because the subscript ρ is inconvenient when further subscripts are needed to designate special conditions.

[4] Ref. 1 c, p. 735.

liquid mercury, but also extends the method to other isotropic elements possessing, presumably, monatomic molecules.

The history of Equation 1 is sufficiently given in another place.[1d] This equation has already been shown to be capable of representing (at least approximately) the obvious performance of solids under change of temperature and pressure.

For convenient use over a small range of volume, Equation 1 may be condensed as follows.

$$p + \Pi_0 \left(\frac{v_0}{v}\right)^m = (\Pi_p + P_\theta) \left(\frac{v_0}{v}\right)^{n'} \qquad (2)$$

This equation is less precise than Equation 1 (because the exponent n' is not wholly constant) but it is much easier to differentiate and to apply. For small volume changes, it is as accurate as the available data. At the absolute zero, n' in Equation 2 equals n in Equation 1, because then $P_\theta = 0$. At higher temperatures n' is smaller than n.

By differentiation of either Equation 1 or 2 at the absolute zero when $p = 0$, the following expression is obtained[5]

$$\Pi_0 = \frac{1}{\beta_0 \, (n - m)_0} \qquad (3)$$

in which $\beta_0 = (1/v_0)\,(\partial v/\partial p)_0$. Equation 3 shows that, granting that the existence of a solid is determined by a balance of pressures, the initial compressibility must be dependent under these conditions only upon the product of the total internal pressure (either compressing or distending) and the difference between the two exponents n and m. This is an important outcome, which seems to afford a basis for an adequate conception of the mechanism of the compressibility of compact substances, and explains why the compressibility of solids is so small.

At any temperature T, when $p = 0$, Equation 2 yields on differentiation an equation precisely analogous to Equation 3, namely,

$$\Pi_{0,T} = \frac{1}{\beta_{0,T} \, (n' - m)} \qquad (4)$$

where n' takes the place of n of Equation 3. Equation 4, like Equation 2, from which it was derived, may be used only over a small range of volume or temperature because n' inevitably changes somewhat with both these variables, even if n does not. For the precise treatment of large volume changes, Equation 1 must be used.[6]

When p is not zero, the differentiation of both Equations 1 and 2 leads to more complicated results, which will be discussed later.

From Equation 4 may be derived an expression for the relation of internal pressure to coefficient of expansion. As already stated, the compressibility β is related to thermal pressure P_θ thus:

[5] Ref. 1 b, p. 1426.

[6] Ref. 1 b, p. 1427.

$$P_\theta = T\alpha/\beta \tag{5}$$

Therefore:

$$[\beta_0 = T\alpha_0/P_\theta]_T$$

Substituting this value for β in Equation 4

$$\Pi_0 = \frac{P_\theta}{T\alpha_0\,(n' - m)} \tag{6}$$

all the values corresponding to $T°$.

One of the striking characteristics of the thermal pressure P_θ of a solid or liquid is the fact that it is (in monatomic metals) much greater than the pressure P_I (also a thermal pressure) which a mole of a perfect gas would exert in the same volume. That is to say, if

$$P_\theta = rP_I \tag{7}$$

the ratio r is (as a matter of fact) always greater than unity. This ratio is particularly significant because P_θ and P_I in monatomic substances are generally supposed to result from the same amount of *kinetic* energy operating in the same total atomic volume. By definition (if V_A is the atomic volume) $P_I = RT/V_A$ and hence from (7)

$$P_\theta = rRT/V_A \tag{8}$$

Substituting the value for P_θ given by (8) into Equation 6 we have

$$\Pi_0 = \frac{Rr}{V_A\alpha_0\,(n' - m)} \tag{9}$$

All the several symbols in Equations 6 and 9 refer to their values at temperature T when $p = 0$.

Equation 9 depends for its numerical fulfilment only upon the interpretation of the fraction $r/(n'-m)$, because the other quantities in the second member are definitely known. Since r was found to be probably not far from $(n'-m)$ it was assumed in previous papers to be equal to this quantity. If this were really true

$$\Pi_0 = \frac{R}{V_A\alpha} \text{ (first approximation)} \tag{10}$$

This reasoning has not been detailed in full before although it was implied in a previous paper.[7] Equation 10 was found also in other ways, the simplest being merely the comparison of the coefficient of expansion of a solid or liquid with that of a perfect gas. The agreement of these several ways, however, is not necessarily proof of verity. Indeed the reason why the different modes of obtaining it agree is because they all suffer from the same incompleteness, which has been already very briefly indicated in previous papers. The time has come for a more adequate explanation of this incompleteness.

Analyzed in detail, the expansion of a gas is very different as to its mechanism from the expansion of a solid. In a perfect gas the coefficient of expansion is measured under constant pressure (equal to the thermal pressure $T\alpha/\beta$) whereas in a solid the expansion must result from an ad-

[7] Ref. 1 b, p. 1429.

justment of three internal pressures and the small constant external pressure. In this latter case an increase of thermal pressure is balanced by the difference between a larger decrease in the intrinsic distending pressure and a smaller decrease in the intrinsic cohesive pressure. Numerically,[8] when $p = 0$,

$$\Delta P_\theta = \Delta\Pi_p - \Delta\Pi \qquad (11)$$

To illustrate the mechanism of the thermal expansion of a condensed phase, let us imagine a mass of liquid mercury, having an intrinsic cohesive pressure $\Pi_0 = 41{,}300$ (derived later) at 22°. When heated to 23°, its volume will gain 0.0181%, and Π will in consequence diminish by 14.8 megabars (if $m = 1.98$, to be shown later). The theoretical increase[9] in P_θ for 1° is 44.4 megabars (if $P_\theta = 13{,}100$ at 22°). Hence from Equation 11, $\Delta\Pi_p$ will be $14.8 + 44.4 = 59.2$ megabars. Granted that the intrinsic pressures are not affected by temperature the percentage change of Π_0 for this change of volume is therefore $100 \times 14.8/(41{,}300) = 0.0359\%$, that of Π_p is $100 \times 59.2/(41{,}300 - 13{,}100) = 0.210\%$ and that due to *volume change* alone in $(\Pi_p + P_\theta)$ is $100 \times 59.2/(41{,}300) = 0.1433\%$ (for as a matter of fact P_θ is not greatly affected by a small change of volume at constant temperature). Now because for such small changes $(1 + x)^n = 1 + nx$, these percentage changes must be to one another very nearly as the exponents m, n and n'. Thus: $m : n : n' \cong 0.0359 : 0.210 : 0.1433 = 1.98 : 11.6 : 7.91$. Incidentally, it should be noted that if $\Pi_0 = 41{,}300$, since $\beta_0 = 0.00000408$ $(n' - m)$ must be 5.93 from Equation 4 (a value consistent with those just given) since $7.91 - 1.98 = 5.93$.

Now, $P_\theta = 13{,}100$ is a definite thermodynamic conclusion drawn from experimental results, and P_I is just as definitely equal to $RT/V_A = 1657$; hence, $P_\theta/P_I = 7.91 = r$; and evidently $r = n'$, since n' was found above to be also 7.91.

If thus $r = \alpha V_A/\beta R = n'$, by substitution in Equation 9 we obtain

$$\Pi_0 = \frac{n'}{(n' - m)} \frac{R}{V_A \alpha} \qquad (12)$$

The foregoing exposition is an illustration, not a proof, of the equality of n' and r. It depends upon the value of Π, taken in the first place; and that in turn is intimately related to $(n' - m)$ through Equation 4. Moreover it ignores small superposed complications. This exposition is nevertheless of value as showing that the ratio r of the two thermal pressures is closely connected with the exponent n'.

If, when a monatomic condensed phase is being expanded by heat, enough external pressure (as calculated from m) is added to keep the total

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[8] Algebraically, if Π is considered as a positive pressure, it would be more logical to consider the other two as inherently negative.

[9] The actual increase in P_θ is slightly less than this, because α is slightly diminished below its normal value by decrease in heat capacity. This superposed complication is discussed later.

pressure ($\Pi_0 + \Delta\Pi_0 + p$) constant, the coefficient of expansion will, of course, be slightly smaller than α_0, and may be represented by $(\alpha_0 - \kappa_0)$. This new kind of "isoholopiestic" dilatation (or dilatation under constant total pressure) would appear to be the logical measure of the expansibility of a condensed phase for comparison with that of a perfect gas, which also is measured under constant total pressure. Thus it is possible to correct the incompleteness of Equation 10 in another way, as follows.

$$\Pi_0 = \frac{R}{V_A\,(\alpha - \kappa)_0} \tag{13}$$

The value of κ may be found if Π_0 and m (already defined) are known, because $\Delta\Pi = p$ is dependent upon the volume ratio $(v_0/v_1)^m$ and the change of volume $(\alpha - \kappa)$. Mathematically, because α is very small:

$$\Delta\Pi = \Pi_0\,(1 + \alpha_0 - \kappa_0)^m - \Pi_0 \cong \Pi_0 m\,(\alpha - \kappa)_0 \tag{14}$$

Furthermore,[10] from the nature of the case,

$$\kappa = \beta_0 p_\kappa = \beta_0 \Delta\Pi \tag{14a}$$

assuming that β is essentially constant over the small range of volume concerned.

Hence, from Equations 13, 14 and 14a

$$\kappa_0 = Rm\beta_0/V_A \tag{15}$$

Equation 12 may be easily derived algebraically from Equations 4, 13 and 15. If $n' = r$, Equations 4 and 12 give the same value (41,300 megabars) for Π_0 as Equation 13, but not otherwise. The last named equation may be obtained in a fashion entirely independent of n'.

In another way, also, Equation 13 furnishes evidence that probably $n' = r$. With mercury, $\kappa_0 = 0.0000453$. The fractional isoholopiestic change of volume $(\alpha_0 - \kappa_0)$ per degree at 22° will therefore be $(0.0001812 - 0.0000453)$; which is 0.01359%. But under these conditions the thermal pressure increases by $\alpha/\beta = 44.4$ megabars, and (because the decrease in Π_0 has been compensated) this must equal the decrease in the total distending pressure, $\Delta\Pi_p$, which is due to Δv, alone. Hence, the increase in volume being only 0.01359%, and the small change of P_θ due to *volume* being neglected, it is evident that the exponent n' of the volume ratio must be $44.4/(41{,}300 \times 0.01359) \cong 7.91$ as before. In this expression m plays only a subordinate role; hence, one can hardly avoid the conclusion that r really equals n'. Moreover, it will be seen that this conclusion corresponds better with the change of dilatation and compressibility under pressure than any other reasonable assumption.

For these reasons Equation 10 is seen to be only a first approximation, and all the other mutually consistent numbered equations in this paper are now accepted as representing the more probable mathematical solution of the problem. If in the future a yet more satisfactory value for r is

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[10] In this expression β must be in terms of megabars, since it is to be used later in connection with $R = 83.15$.

found, the equations can be easily modified accordingly. So far as can now be seen, such change could hardly be more than a slight correction, because the present well-supported assumption is surprisingly consistent with both the facts and the various ramifications of reasoning involved.

2. The Value of m (Mercury)

None of the preceding equations affords a means of determining the value of m, since a change in the assumption of this quantity affects all equally. For example, if $m = 2$ (instead of $m = 1.98$) the value of Π_0 is increased 0.3%. On the other hand, the second derivatives of the volume change (for example, changes of compressibility with pressure, later formulated in Equations 20 and 21) should provide an exact value for m if the experimental data were accurate enough. Unfortunately, they are not, since a degree of precision at present unattainable is needed. In a former study[1b] the problem was approximately solved by comparison with data from "synthetic" curves depending upon assumed values of m and n', in connection with hyperbolic equations founded on the same data. This partly graphic method suffered from the same disadvantage, but at least it indicated the order of magnitude of Π_0, m and n'.

On the basis of this outcome it seemed probable, however, that the heat of evaporation of a monatomic solid or liquid ought to be able to supply exactly the knowledge needed for the computation of m. The intrinsic work involved in the evaporation must be a function solely of the intrinsic pressures and of the exponents m and n (not n'). The exponent n has, however, but slight effect (negative); the work of evaporation is chiefly due to the intrinsic cohesive pressure and its exponent m. With a given heat of evaporation, an increase in the assumed value of m causes Π_0 also to increase, but in this case much more rapidly than in the case of the preceding equations. Hence, by means of a nomogram or by successive approximations it is possible to find precise values for Π and m which alone will conform to all the phenomena concerned. The same result may be obtained by algebraic substitution, but this yields a very complicated expression, less convenient than that of the other methods.

The intrinsic or internal work of evaporation is of course less than the total heat of evaporation, L, by the external work done against p. This latter is equal to $p(v_2 - V_A)$ or essentially (at 22°) to 2.45 kilojoules ($=$ 24,500 megabars $\times$ cm.^{3} $= RT$) per gram molecule. The relation of the intrinsic work ($L - RT$) thus found to the intrinsic pressures concerned depends, of course, upon the mathematical expression which defines their changes with changing volume. Van Laar[11] in an interesting analysis of the problem has offered a solution which takes into account the changes

[11] Van Laar, "Die Zustandsgleichung von Gasen und Flüssigkeiten," Leopold Voss, Leipzig, **1924**, especially p. 238.

in the a and b of the equation of van der Waals, but otherwise uses this latter equation as the basis of his reasoning. From the present point of view his analysis seems to be unnecessarily complicated. Kuenen[12] also applies finally the equation of van der Waals.

Another method of treatment, more directly applicable to the present point of view, assumes, $L = \int_{v_1}^{v_2} P_\theta dv$, which seems to be reasonable.[13] For P_θ one may substitute its value as given by Equation 1. Upon integrating the resulting expression between volumes V_A and v_2 (when $v_2 = \infty$) the following equation is obtained. This treatment is equivalent to equating the difference between the amounts of work (obtained by integration) involved in the two intrinsic pressures with the amount of intrinsic work corresponding to the corrected heat of evaporation ($L - RT$). The latter method of reaching the result is less confusing than that from Equation 1 with regard to the several signs involved. By both methods:

$$m = \frac{\Pi_0 V_A}{L - RT + \Pi_\rho V_A/(n - 1)} + 1 \qquad (16)$$

Egerton[14] has recalculated the results for the vapor pressures of mercury found by Smith and Menzies and by Knudsen for various temperatures. Taking the average of these results for 22°, the atomic heat of evaporation is found to be 14.69 Calories = 614,000 megabars × cm.^{3}, a value which may be substituted for L in Equation 16. v_2, the volume of vapor, is about 1.5×10^{10} cc. (since the vapor pressure of mercury at that temperature is only 0.0012 mm.), a volume so large that the intrinsic work involved in further expansion is negligible. Assuming $\Pi_0 = 42{,}000$ megabars as a first rough approximation based on Equation 13, m is found from Equation 16 to be about 2. A nomogram and further approximations taking account of the

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[12] J. P. Kuenen, "Die Zustandsgleichung der Gase und Flüssigkeiten und die Kontinuitätstheorie," Friedrich Vieweg und Sohn, Braunschweig, **1907**, p. 124.

[13] Probably this value of L should be corrected slightly for the kinetic energy expelled or taken in (as the case may be) in the process of evaporation, which is related to the change of heat capacity, during this process. Previously (Ref. 1 b, p. 1433, footnote) the correction was taken as equal to the difference in "heat content" of the liquid and gaseous phase between 0°K. and room temperature. This was evidently an excessive estimate, for an important part of the heat used in raising the mercury from the absolute zero to 20°C. must be stored as potential energy. The latent heat of melting belongs in the latter category and should not have been included. Assuming equipartition, the amount of kinetic energy in the liquid must be very nearly equal to that in the vapor. In any case the correction is evidently small, and would not affect m by as much as 0.5%; it may be neglected in the present discussion, since any possible error would not affect the essential argument. The specific heats, however, give a means of computing the heat of evaporation at the absolute zero—an outcome which is the real bearing of an expression given elsewhere (Ref. 1 c, p. 734 footnote). A somewhat similar expression was given by Egerton (Ref. 14, p. 9).

[14] Egerton, *Phil. Mag.*, [6] **39**, 8 (1920).

effect of slight changes in m on the results of the earlier equations show that the following are the only values which satisfy simultaneously all the preceding equations (except, of course, Equation 10, which is only a first approximation,[15] as already explained): $m = 1.975 \pm 0.01$; $\pi_0 = 41{,}300$.

The value of m thus found is the average value which corresponds to the actual area in a pressure-volume diagram (similar to Ref. 1 b, p. 1433) representing $(L-RT)$. Most of the area, however, is covered during the very first stage of the separation of the atoms, between volumes V_A and $8V_A$, that is, before the distances between the atomic centers have doubled. The fact that the result 1.98 agrees so nearly with the value $m = 2$ (found by van der Waals as the best for gases) seems to show that m is nearly constant for the whole range of expansion—a rather unexpected outcome.

Accordingly, the value $m = 1.98$ (for mercury) has been used throughout this paper as the best evaluation available at present.

3. Confirmation from Changes of α and β (Mercury)

A good test of these considerations and equations is the study of the effect of moderate additional external pressure upon compressibility and coefficient of expansion. Here the effect of known and measurable external pressure is compared with the effect of the hidden intrinsic pressures, and thus an unimpeachable criterion for judgment is available. Erroneous assumptions concerning the intrinsic pressures would lead almost inevitably to inconsistent results. It will be seen that the agreement of prediction with fact is within the limit of experimental error, and hence that the treatment is justified.

The necessary equations for the computation are

$$\Pi_0 + \Delta\Pi + \frac{n'}{n'-m}\,p \cong -\frac{v}{\beta_p\,(n'-m)} \tag{17}$$

and

$$\Pi_0 + \Delta\Pi + \frac{n'}{n'-m}\,p \cong \frac{n'}{(n'-m)}\,\frac{R}{(V_A)_0\,\alpha_p} \tag{18}$$

The former (Equation 17) is the mathematical outcome[16] of the differentiation of Equation 2 when p is finite: Equation 18 is obtained by substituting the approximate equation $\beta_p \cong \alpha_p V_A/n'R$ (easily obtained from Equations 5 and 8 if $n' = r$) in Equation 17, noting that under pressure p,

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[15] The preliminary value $m = 1.7$ used in the previous papers corresponds to $\Pi_0 = 31{,}000$, which is not compatible with Equations 12 and 13, having been derived from Equation 10.

[16] I am indebted to Professor P. W. Bridgman for suggestions regarding the first part of the present paper, especially for his emphasis on the value of following out the exact mathematical consequences of the theory in spite of the merely approximate nature of Equation 2, and for the rather subtle exact differentiation leading to Equations 17 and 19, which depends on the definition $\beta_p = (1/v_0)(\partial v/\partial p)_T$ in accordance with his data as published, and not upon the frequently used $\beta_p = (1/v)(\partial v/\partial p)_T$.

the volume V_A becomes $(V_A)_0 v$, when v is $1-\beta_p$, approximately.[17] Neither of these equations is exact, since n' doubtless changes somewhat with changing volume. Nevertheless, with small volume changes they may be used as first approximations.

On comparing Equations 17 and 18 it is seen that the coefficient of expansion is indicated as having a somewhat less percentage decrease with growing pressure than the compressibility. This is in accord with most of Bridgman's observations,[18] although the uncertainty of these as regards dilatation under pressure is shown, for example, by the two mutually inconsistent values 0.62 and 4.5 for $(1/\alpha)_0(\partial\alpha/\partial p)_0$ for two samples of calcium.

Equations 17 and 18 agree as well as could be expected (considering their inherent incompleteness and the possible experimental error) with the actual behavior of mercury, as is shown by Table I. This records Bridgman's results[19] reduced to the megabar standard and corrected for a slight error (discussed later) in the first result for the compressibility of iron (which was used for comparison in the work on mercury) together with the calculated values. $V_A = 14.81$ and $v_0 = 1.004$, corresponding to $p = 0$ at 22°C.

Table I

Verification of Equations 17 and 18

Mercury at 22°

p	$\Delta v/v_0 \times 10^5$	Coefficient of expansion $\times 10^6$ Calcd.	Obs.	Compressibility $\times 10^6$ Calcd.	Obs.
0	0	[181]	181	4.08	4.04 (?)
1000	397	174	173	3.91	3.90
2000	784	168	167	3.75	3.77
3000	1153	162	164	3.61	3.64
4000	1511	157	159	3.47	3.50
5000	1857	151	155	3.34	3.36

The average difference between the calculated and observed values of the compressibilities is less than 0.7%, which is no greater than the probable error of the pressure readings upon which the compressibilities depend. It is rather surprising that the agreement at the higher pressures is as good as it is, since the approximate equations used become distinctly faulty when $\Delta v/v > 0.01$. On the other hand if the old values, $\Pi_0 = 31{,}000$ and $(n'-m) = 7.91$, are used, the compressibility at $p = 5{,}000$ is calculated as only 3.26×10^{-6}, instead of 3.36, a difference of 3%, distinctly greater than the probable error of experiment. Thus Equation 17 favors $\Pi_0 = 41{,}300$ as against $\Pi_0 = 31{,}000$, and simultaneously favors $r = n'$ as against $r = n'-m$.

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[17] Equation 18 reduces to one previously given (Ref. 1 d, p. 339, middle of page) if n' is replaced by $(n' - m)$ in the numerators, when Π becomes 31,000—the former provisional value, now rejected in favor of $31{,}000\ n'/(n' - m) = 41{,}300$.

[18] Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 221, 222 (1922).

[19] Bridgman, *ibid.*, **47**, 380, 381 (1911).

The effect of change of *temperature* on α and β is more complicated than the effect of change of pressure. Grüneisen[20] has presented an approximate solution of this problem; but although his solution applies well to the *compressibility* of copper, platinum and iron, the agreement as regards dilatation is not so good. In the case of mercury, for example, α_0 is actually very nearly constant between 0° and 40°, increasing slightly as the temperature rises, although the atomic heat *decreases* nearly 1% over that range.[21] Evidently the coefficient of expansion is not in this case exactly parallel with atomic heat. From the present point of view, one perceives that if the atomic heat of mercury did not behave in this abnormal manner, the coefficient of expansion would increase more rapidly than it does with rising temperature, after the manner of most other liquid substances. All these things must be taken into account in the final reckoning of minor subsidiary effects, which must include also the changes of P_θ and n' with change of volume. This must be postponed.

The differentiation[16] of Equation 17 (that is, the second differentiation of Equation 2) yields the equation

$$\frac{1}{\beta}\frac{\partial\beta}{\partial p} = \frac{n' + \dfrac{m\,(n' - m)\,(\Pi_0 + \Delta\Pi)}{n'p + (n' - m)\,(\Pi_0 + \Delta\Pi)} + 1}{n'p + (n' - m)\,(\Pi_0 + \Delta\Pi)} \tag{19}$$

from which, if $p = 0$ (and therefore $\Delta\Pi = 0$) we obtain

$$\Pi_0 = -\frac{n' + m + 1}{n' - m}\,\beta_0\left(\frac{dp}{d\beta}\right)_0 \tag{20}$$

Unfortunately, Bridgman's experimental method is unreliable when $p = 0$. He extrapolated from 1150 atmospheres' pressure (with the help of only a single determination at 575) by an interpolation formula which is doubtless merely approximate. Hence, Equation 20 cannot be tested by experimental data. That it is consistent with the preceding equations is, however, shown by the fact that the calculated values for β_0 and $(d\beta/dp)_0$ (taken from the next to the last column in the preceding table) when substituted in Equation 20, give the value $\Pi = 41{,}500$.

Equation 19 yields for mercury $(1/\beta)\,(\partial\beta/\partial p) = 3.89 \times 10^{-5}$, at 3000 megabars' pressure, whereas the observed value is 3.57×10^{-5} (calculated from the observed data in Table I), but the possible accumulation of experimental error is certainly as large as 9%. The value derived from the calculated numbers in the next to the last column of Table I is 3.85×10^{-5}. Equation 19 thus gives, like Equation 20, a possible means of calculating Π_0; but in this case, as well as in the preceding, the result is limited in accuracy by the extreme difficulty of observing with precision the quan-

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[20] (a) Ref. 24; (b) *Ann. Physik,* [4] **39,** 279 (1912).

[21] For a convenient critical discussion of C_p for mercury, see J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, **1923,** Vol. 4, p. 720.

tity $(\partial\beta/\partial p)$. Nevertheless, the outcome supports (although somewhat lamely) the conclusion that $P_\theta/P_I = n'$ within the possible limit of experimental error.

By the combination of Equations 4 and 20 there is obtained a numerical quantity, given in the last column of Bridgman's table, $-(1/\beta^2)_0(\partial\beta/\partial p)_0$. This is thus found to be equal to $(n' + m + 1)$, which corresponds exactly with the above calculations if $\partial\beta/\partial p = 181 \times 10^{-12}$ for mercury. The result is in all probability very near the actual value. Experimental difficulty precludes exact numerical confirmation with less compressible substances, but on the average the experimental values of this quantity for various metals are of the right order (in most cases less than 20). Bridgman's[22] interpretation of these figures is different but perhaps not irreconcilable. Grüneisen found for the *adiabatic* compressibility β_s the somewhat similar expression $-(1/\beta_s^2)\ (\partial\beta_s/\partial p) = m + n + 3$. The more useful new equation

$$-(1/\beta^2)_0\,(\partial\beta/\partial p)_0 = n' + m + 1 \tag{21}$$

appears to afford the most convenient method of finding the effect of pressure on compressibility at very low pressures.

4. Effect of Changing Atomic Heat

Equations 12 and 13 may be supposed to apply exactly only at temperatures at which $R = C_v/3$ (wherein C_v is the atomic heat capacity in constant volume).[23] In other words, they hold only when thermal vibration in the solid or liquid under consideration is unrestricted by those inadequately known circumstances which modify the law of Dulong and Petit and cause the vanishingly small specific heats of substances at very low temperatures. That this qualification is reasonable and in accord with Equation 12 is evident, for r could be supposed to equal n' only if the same amount of *kinetic* energy exists in both P_θ and P_I. Grüneisen's rule,[24] which points out that α varies as C_v, reinforces this conclusion, since Π can hardly be supposed to increase greatly as the temperature decreases, unless a change of state ensues. Thus

$$\Pi = \frac{C_v}{3V_A\,(\alpha - \kappa)} \tag{22}$$

is probably the true expression for Π in a monatomic solid.[23b] This equation reduces to Equations 12 and 13 at ordinary temperatures with most metals.

Very few data adequate for testing the effect of changing atomic heat exist. The best example, perhaps, follows. The atomic heat of copper between —190° and +17° averages 5.03 cals./°C. or 210 mgbr. × cm.^{3}/°C., whereas that for ordinary temperatures is practically $C_p = 3R = 250$.

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[22] Ref. 18, pp. 219, 221.

[23] Compare (a) Lewis, This Journal, **29,** 1165 (1907); (b) Ref. 1 d, p. 339.

[24] Grüneisen, *Verhandl. deut. physik. Ges.*, **13,** 491 (1911).

The ratio of the atomic heats in constant volume is about the same. Substituting C/3 for R in Equation 12 and noting that the coefficient of expansion of copper over the lower range is 0.000040 (Henning[25] found 0.000043 and Lindemann[26] 0.000037) whereas that at ordinary temperatures is 0.0000483, the value of Π at ordinary temperatures is found to be 376,000 (the details of calculation are given later) and that calculated for the lower range (if the same value of n' is used) is 385,000. Clearly the concordance is within the limit of error of experiment. This outcome is indeed a foregone conclusion in the light of the relationship indicated by Grüneisen's rule, even though this rule is not entirely exact.

It is not worth while at present to follow these particular considerations further. Data of greater accuracy, both as regards atomic heats and coefficients of expansion over wide temperature ranges are necessary before a complete inductive analysis of the situation can be possible. Equations 12 and 13 will be used here only in cases practically free from these complications, although the latter may exist to a minor extent in most substances.

5. Similar Treatment of the Data for Other Metals

Since, therefore, all the various corollaries of Equations 1 and 2 lead to consistent results which agree with the facts within the recognized limit of error of the experiment and the degree of approximation of the equations in the case of mercury, it is worth while to record the treatment of other isotropic substances in the same way.

Table II gives revised values of Π_0 for the several metals previously reported, now calculated on the basis, $r = n_0' = \alpha_0 V_A/\beta_0 R$. Except for minor changes in the choice among conflicting experimental data (notably in the case of calcium), the final values are simply the earlier multiplied by $n'/(n'-m)$. The data in the first five columns are all determined by experiment.[27] In default of adequate experimental data on the heat of evaporation of many of these substances, m has been assumed to be 2.00 throughout. Any possible error in this assumption may easily be corrected on the basis of future experimental evidence, if necessary. The values of Π_0 (which follow necessarily from these data if the above theory is accepted) have been usually rounded off to the nearest kilomegabar (1000 megabars). The possible error due to experimental inaccuracy may often exceed 2%.

The testing of these data by means of Equation 17 is of importance, since by this means evidence may be obtained concerning the question

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[25] Henning, *Ann. Physik*, [4] **22**, 631 (1907).

[26] Lindemann, *Physik. Z.*, **12**, 1197 (1911).

[27] The compressibilities recorded below are chiefly those determined by Bridgman, Ref. 18, p. 219. They essentially confirmed the earlier work of the author and his collaborators.

TABLE II

INTRINSIC COHESIVE PRESSURE OF NINETEEN ISOTROPIC ELEMENTS (REVISED), WITH ESSENTIAL DATA AT 20°C.

	$\alpha_0 \times 10^6$	$\beta_0 \times 10^6$	P_θ megabars	n'_0	$V_{A,0}$ cc.	Π_0, kilo-megabars
Cesium	300 (?)	66 (?)	1,340	3.90	71	8
Potassium	245	34	2,100	3.92	45.4	15.3
Sodium	215	15.8	4,000	3.90	23.7	33
Mercury	181	4.08	13,100	7.91	14.8	41.3
Lead	85	2.4	10,340	7.75	18.3	72
Calcium	72	5.76	3,660	3.80	25.3	95
Lithium	169	8.8	5,630	3.07	13.3	106
Magnesium	76	3.04	7,300	4.00	13.3	164
Aluminum	65.5	1.36	14,000	5.85	10.1	191
Silver	55.6	1.01	3,690	6.76	10.3	208
Gold	43.2	0.58	21,800	9.10	10.2	243
Copper	48.3	.73	19,390	5.64	7.1	376
Palladium	34	.53	18,800	6.76	8.8	396
Tantalum	24	.49	14,500	6.49	10.9	455
Platinum	26.4	.37	21,000	7.81	9.1	465
Nickel	38	.54	20,600	5.65	6.7	508
Cobalt	37	.55	19,700	5.56	6.9	510
Iron	34	.60	16,600	4.84	7.1	587
Tungsten	13.7	.30	13,400	5.27	9.6	1020

as to whether $n' = r$ with other metals besides mercury. Lead may be taken as an example, chosen at random. Here (according to Bridgman) $\beta_0 = 2.41 \times 10^{-6}$ (reduced to the megabar standard at 20°); $\alpha_0 = 85 \times 10^{-6}$; $V_A = 18.3$; $P_\theta = 10{,}340$; $P_I = 1333$. Therefore, $n' = 7.75$. The exponent m is assumed to be 2 (that for mercury being 1.98). Therefore from Equation 4, $\Pi_0 = 72{,}200$. At 5000 megabars Δv is evidently (from β) about 1.1%, which affords basis for the calculation of $\Delta\Pi = 1600$. From Equation 18, using these values, $\beta_{5000} = 2.1 \times 10^{-6}$; and from Equation 18, $\alpha_{5000} = 0.000076$, whereas Bridgman's observations[28] give 2.2 and 0.000078, respectively.

Particularly interesting and important is the case of iron, which served as the basis of all Bridgman's work, and for which he obtained two somewhat different series of results. In one of his series $(1/\beta)(\partial\beta/\partial p) = 0$, and in the other $(1/\beta)(\partial\beta/\partial p) = 7 \times 10^{-6}$. Another method of calculation (as valid as that employed above) will be used in order to compute the result on the present basis. Here $\beta_0 = 0.60 \times 10^{-6}$; $\alpha_0 = 34 \times 10^{-6}$; $V_A = 7.1$; $n' = 4.84$; and if $m = 2$, the correction $Rm\beta_0/V_A = \kappa = 14.1 \times 10^{-6}$. Hence from Equation 13, $\Pi = 589{,}000$ megabars. For 10,000 megabars $\Delta v = 0.0058$, $\Delta\Pi$ is 6800, and Equation 17 gives $\beta_{10{,}000} =$

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[28] Bridgman's values (although not always the best under low pressures) are used throughout this paper for the sake of consistency because his results for high pressures seem to be the best yet secured. Considering the very great experimental difficulty, his work with high pressure was, indeed, masterly. See Ref. 27.

0.57×10^{-6}. Any possible error in the assumption of m could not affect greatly the result, which falls between Bridgman's two results (0.59 and 0.56) for 10,000 atmospheres. As regards the average compressibility between $p = 0$ and 10,000, Bridgman's first result was 5.95, his second 5.78; the present value, 5.85, is again between the two experimental ones. In each case the second result is somewhat favored. Bridgman himself was inclined to reject wholly the first experiments. All these values are reduced to the megabar standard, Bridgman's[29] having been originally given in terms of kg./sq. cm. Given α_0 and β_0, the above calculation requires but very few minutes, instead of months of experimental labor.

Table III gives a typical value of β_p for each of most of the foregoing elements. The change of compressibility with small changes of volume of cesium and potassium are not known accurately enough to make the comparison in their cases significant, and the very incompressible metals could not be expected to yield better experimental results than iron. Table III contains the results of Equation 17 as applied to the other metals in Table II. In most cases $\Delta v/v$ is of the order of 1%. The "observed" values are computed by subtracting $p(\partial\beta/\partial p)$ according to Bridgman from the respective results for β_0 given in Table II.

TABLE III

COMPRESSIBILITY UNDER PRESSURE

	$p \times 10^{-3}$	β_p (obs.)	β_p calcd.
Sodium	1	14.8 (?)	14.4
Mercury	5	3.36	3.34
Lead	5	2.2	2.1
Calcium	2	5.6	5.35
Lithium	2	8.4	8.2
Magnesium	4	2.73	2.68
Aluminum	3	1.33	1.32
Silver	10	0.91	0.92
Gold	10	.52	.52
Copper	10	.68	.69
Iron	10	.59 .56	.57

These values are perhaps as satisfactory as could be expected. Their discrepancies are of the order of the uncertainty of the pressure measurements upon which the compressibilities depend. *The change of compressibility* with pressure has, of course, a much larger probable error. Some of the elements show a somewhat greater and some a less change of compressibility with pressure than is demanded by the accepted assumption $n' = r$. It would appear, therefore, that at least on the average this assumption is justified. More accurate treatment of the whole subject must await yet more accurate experimental results, as well as a more de-

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[29] Ref. 18, p. 174.

tailed and meticulous study of the concomitant but subordinate influences involved in the change of heat capacity with temperature, and in the change of n' with volume.

Evidently the equations under consideration give the means of calculating with good approximation both compressibilities and coefficients of expansion under high pressure, from data corresponding to $p = 0$, if the change of volume is not great.

A comparison of the values of n' for different metals is not without interest, since the quantity n' is important; indeed, it is the keystone of the whole structure. As given above, it depends upon two thermodynamic pressures. If it could be evaluated in any way independent of P_θ, the quantities Π_0 and β could easily be calculated from the coefficient of expansion alone, since $\beta = V_A\alpha/n'R$. The most obvious property of a substance (from a hypothetical point of view) likely to be allied with n' is density, for P_θ would naturally be supposed to depart more widely from P_I the more compact the substance. The figures bear out this inference, since n' (as may be seen in Table II) is smallest in the case of lithium and largest in the case of gold, being high also in platinum, lead and mercury. Nevertheless, density is evidently not the only determining factor as regards n', since platinum, although denser than gold, has a smaller value for n'. In spite of such discrepancies, nevertheless, an approximate value for n' is given by the empirical equation $n' = 3.0 + 0.3\,D$. A large majority (14 out of 19) of the values in Table II are thus fairly well represented; but the values thus obtained for aluminum and lead are considerably smaller than P_θ/P_I whereas those for platinum, tantalum and tungsten are distinctly greater. No convincing explanation for these particular divergences has been found. Probably the small increase in density caused by external pressure increases slightly both n and n'.

The approximate relation of n' to density makes the new equation $\beta = V_A\alpha/n'R$ very similar to an empirical equation published some years ago,[30] taking account of the fact that (roughly) α increases (in the comparison of different elements) as the absolute melting point decreases. It is also closely related to an old empirical equation of Dupré's.

Heats of evaporation calculated from these data by means of Equation 16 (after transposition, assuming $m = 2$) are essentially equal to those calculated in a previous paper.[4]

6. General Considerations

Of course the modification of the treatment which makes $P_\theta/P_I = n'$ (instead of $n' - m$) should be applied also to the consideration of the pressure produced by chemical affinity,[1c] as was indeed suggested at the time. Nevertheless, this alteration makes no essential difference in the logic

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[30] Richards, THIS JOURNAL, **37**, 1652 (1915).

of the argument previously advanced, although it modifies details of both conclusions and results. If the present point of view stands the test of time, these modifications can easily be applied in the future. The main ideas of the paper in question remain unchanged.

The distinguishing feature of this discussion is, as before, the treatment of the two opposing pressures Π_0 and Π_p as separate entities, operating presumably by different mechanisms. This feature is perhaps that least acceptable to many physicists, who may prefer dealing merely (but more rigorously) with the difference between these two pressures $(\Pi - \Pi_p)$ after the manner of Grüneisen or Eucken, or else may prefer maintaining that the equilibrium is a neutral point in a hypothetical electrical system governed by quantum forces. But if, as it appears, the exponent m is about the same (about 2) with many substances,[31] 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_0, does not the individual quantity Π_0 acquire real significance? And does not then the use of the mere difference between Π_0 and Π_p omit one of the most important aspects of the case? "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."[32]

Even if the future should demand further modifications of the point of view and of the conclusions herewith presented, the present consistent theory should remain useful as a close approximation at least; for this theory makes it possible to compute some of the physical properties of substances under high pressure which would otherwise demand laborious and time-consuming experimentation of a very difficult kind. Whether any treatment of non-polar affinities by classical electrodynamics could do as well is doubtful.

The most significant outcome of these considerations—an outcome which far transcends the successful prediction of individual properties—is the support which they afford for the theory of balanced pressures upon which they are based. It is unlikely that the rather subtle effects of external pressure and temperature should be thus capable of prediction within the

[31] Ref. 1 c, p. 734.

[32] Ref. 1 d, p. 336.

limits of experimental error if the theory were unsound. Certainly as a working hypothesis its adequacy has been severely tested, and has not been found wanting. The present paper, dealing with the simplest possible cases, clears the way for a more exact discussion of more complicated cases, especially those concerned with chemical phenomena.

Summary

This paper not only amplifies various previously recorded equations concerning internal pressure (adding a correction which had been suggested, although not applied before), but it also provides new evidence as to the magnitude of the internal pressure of monatomic elements drawn from the change of compressibility and the change of expansibility with increasing pressure. The most important detail is the new and better supported definition of the rate of change (n') of the intrinsic distending pressure with changing volume. In this respect alone this paper supplants those preceding it. In general, the paper demonstrates the necessity of imagining very great internal pressures in order to account for the actual values of compressibility and coefficients of expansion of condensed phases. Values of these intrinsic cohesive pressures are given for 19 elements. A mathematically consistent and rather simple approximate treatment is capable of predicting the behavior of these properties under high pressure within the limit of experimental error. This fact is demonstrated by definite calculations concerning several typical elements. Such properties are with great difficulty determined experimentally, but are very easily computed with the help of these considerations. The paper thus affords support for the theory of balanced pressures (which seems to give an adequate picture of the action of cohesive and chemical affinities), and serves as a necessary introduction to the detailed treatment of more complicated cases.

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