Summary

The vapor pressures of solutions of lithium in liquid ammonia at —39.4° have been measured from the saturation point to a concentration of 60 molecules of ammonia per atom of lithium.

The saturated solution contains 3.61 molecules of ammonia per atom of lithium. With increasing dilution, the pressure rises rapidly at first and then more slowly until the region of two liquid phases is reached, when the pressure remains constant at approximately 540 mm. This pressure is only about 15 mm. below the vapor pressure of pure ammonia.

The curve is entirely regular and no indication is found of the singularities recorded by Benoit. There is no evidence indicating the existence of compounds of the alkali metals with ammonia of the nature of ammonium groups.

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INTERNAL PRESSURES PRODUCED BY CHEMICAL AFFINITY

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Recently[1] internal pressures due to cohesion have been discussed and approximately evaluated. The interpretation, which was only a preliminary sketch, was limited to isotropic elements, because they present the simplest problem.

Chemical affinity must also exert pressure in its action, and often the pressures thus produced must exceed those produced by cohesion. The present brief communication endeavors to show that the same principles which apply to cohesion may apply also to chemical affinity, bearing in mind the fact that chemical affinity acts most strongly on the portions of the atoms in immediate juxtaposition and does not envelop each atom equably over its whole surface after the manner of cohesion in an isotropic element. Just as the heat of evaporation may be accounted for by the work involved in separating atoms under the influence of the changing balance of pressures, so the heat of chemical combination may be accounted for chiefly by the work done by the more considerable pressures produced by chemical affinity.

Table I gives the results of the new method (depending upon coefficient of expansion) as applied to compounds. For this purpose, molal volume is substituted for atomic volume in Equation 3 of the previous paper;

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[1] Richards, THIS JOURNAL, **46,** 1419 (1924). This paper and other earlier papers are summarized in *J. Franklin Inst.*, 198, 1 (1924), which is a more comprehensive and less detailed discussion of the general bearings of the problem.

and the second member of the equation must be multiplied by the number (N) of atoms present in the molecule, because each atom participates in the thermal expansion. Thus:

$$\Pi_V = \frac{NR}{\alpha V_M} \tag{1}$$

Π_V is the internal attractive pressure (weighted average) at molal volume V_M, α the corresponding coefficient of expansion,[2] and R equals 83.16 cc.-megabars.

TABLE I

PROVISIONAL ESTIMATES OF AVERAGE INTERNAL PRESSURES IN TYPICAL SUBSTANCES

Calculated from the coefficient of expansion according to Equation 1

	Density	Molecular volume 20°	N	Cubic coefficient of expansion 20°	Average internal pressure
Bromine............	3.120	51.3	2	0.00112	2,900
Ethyl ether..........	0.717	106.2	15	.00166	7,080
Ethyl alcohol........	.7895	58.35	9	.00102	12,600
Xylene..............	.8811	119.1	18	.000973	12,900
Mercury............	13.546	14.8	1	.000181	31,000
Potassium chloride...	1.987	37.52	2	.0001121	38,900
Silver...............	10.5	10.27	1	.0000556	145,000
Magnesium oxide.....	3.65	11.05	2	.0000279	539,000
Tungsten............	19.10	9.60	1	.0000137	632,000

The substances named in the table are not all in the same category. Moreover, the numbers in the last column do not represent exactly the same property in the different cases. Three types may be distinguished.

I. The first category is represented by liquid mercury and the isotropic solid metals, silver and tungsten, in each of which only one kind of attractive pressure (cohesive) may well be imagined to exist.

II. In such a substance as bromine or ether, there must be a great difference between the chemical pressure and the cohesive pressure existing in the liquid—the latter (on the exterior of the molecule) being far less in magnitude than the former (which binds the atoms together within the molecule). Π_V is therefore greater than the true cohesive pressure, being augmented by a quantity due to chemical affinity.

III. On the other hand, a crystal of potassium chloride, although it may perhaps belong in Category II, is usually supposed to represent a modification of Category I. Each atom of potassium is imagined as equally attracted in all directions by the chlorine atoms around it. The outcome is in doubt; this kind of polar compound demands separate discussion.

[2] Strictly speaking, α should here signify the coefficient of expansion when the total pressure ($p + \Pi + \Delta\Pi$) is kept constant ($\Delta\Pi$ being the slight change in Π due to the increased volume on heating—in this case a minus quantity). This qualification was not formulated in the previous paper (which was avowedly a mere sketch) and it does not essentially affect the present one, at least as regards the order of magnitude of the quantities concerned. It will receive detailed consideration in the near future.

I. Elements with Monatomic Molecules

The first of the categories was briefly sketched in the previous paper. The needful equation is exceedingly simple; the coefficient of expansion, α (when no external pressure is present), may be represented by the equation,

$$\alpha = \frac{R}{V_A \Pi_V} \tag{2}$$

Much more exhaustive calculations have already been completed and are soon to be published, showing that the method of treatment formulates consistently the effects of internal pressures in such simple cases, and provides for the computation of pressures from coefficients of expansion, compressibilities, and heats of evaporation; or *vice versa*. These calculations bear upon the present communication in that they support the validity of the point of view adopted, but the details must be postponed.

One aspect of the matter deserves immediate amplification, however (since it concerns intimately the present argument), namely, the computation of the internal cohesive pressure from the heat of evaporation, which involves the consideration of the rate of change of each of the opposing internal pressures with change of volume.

The following equation of state of a solid or liquid monatomic element (briefly explained in the previous paper[1]) has been shown to be reasonable and suggestive:

$$p + (\Pi)_0 \left(\frac{v_0}{v_1}\right)^m = (\Pi_p)_0 \left(\frac{v_0}{v_1}\right)^n + \left(\frac{T\alpha}{\beta}\right)_{v_1} \tag{3}$$

The values of m and n in any particular case are not necessarily the same with different elements, nor even with the same element at widely different volumes. Their difference is easily calculated at the absolute zero,[1] from the equation

$$n - m = V_A \alpha_0 / R\beta_0 \tag{4}$$

At ordinary temperatures $V_A\alpha/R\beta$ is still significant, but it yields there a quantity $(n' - m)$—where n' is a compromise value of the exponent, representing the net change with changing volume of the combined effect of the whole second member of Equation **3**. For computation $(n' - m)$ is a convenient resort; it was this quantity (8.1 in the case of mercury) which was employed in the former paper. At the absolute zero $n' = n$. The values of m may be found (at least approximately) from the data on compressibility, since the extent of curvature of the pressure-volume curve is dependent on the relative values of m and n'. This matter will be explained in more detail in a subsequent paper.

The amount of work involved in the evaporation (neglecting work done against external pressures) should be represented by the algebraic sum of the integrals (between $v_0 = V_A$ and $v_1 = \infty$) of the appropriate terms of Equation 3. In the previous paper the equation was integrated graphically for the special case of mercury, omitting consideration of $T\alpha/\beta$; formal integration yields the same result. Generalized, the integral becomes

$$W = K \Pi_V V_A \tag{5}$$

In this equation W is the work required for evaporation; K is a numerical coefficient depending upon the values of m and n'; and Π_V the initial cohesive pressure of the liquid or solid in volume V_A, which is the atomic volume. K is greatly affected by m, and but slightly affected by n', because (when the molecules become separated in the vapor) the rapid decrease of Π_p with increasing volume causes the effect of this distending pressure to give only slight assistance in evaporation; hence the work (in the form of heat) required for the process of evaporation must depend chiefly upon Π, the opposing cohesive pressure. Study of the diagram in the previous paper[1] will clarify this statement.

Hence the rate of decrease of the cohesive pressure must affect greatly the quantity of heat needed for evaporation. This latter necessity is made clear not only by the diagram, but also by the following table, which gives the respective values (found by integration) of the numerical coefficient of Equation 5 for various values of m, assuming[3] n' to be 10.

TABLE II

EFFECT ON K (THE NUMERICAL COEFFICIENT OF EQUATION 5) PRODUCED BY CHANGES IN THE EXPONENT m

n	1.4	1.5	1.6	1.7	1.8	1.9
K	2.39	1.89	1.55	1.32	1.14	1.00

This table shows that the heat of evaporation may be used for calculating the value of m, if Π is known, and the work of evaporation is considered as the primary outlet of the heat. If $n' = 7$ instead of 10, each value of K is 0.05 less than that given above. This method of calculating m is chiefly used in the present paper, in preference to that depending on compressibility.

In the case of mercury, for which there are available exceptionally complete data, the respective exponents were found from the study of compressibility to be 1.7 and 9.8. With these exponents, Equation 5 becomes

$$W = 1.32\ \Pi_V V_A \qquad (6)$$

It is of interest to see how nearly internal pressures of a number of metals calculated from the heat of evaporation with Equation 6 correspond to the

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[3] Probably n rather than n' should be used in treating the vapor, the thermal pressure being considered separately instead of in the joint quantity n'. The distinction is, however, unimportant for the present merely approximate calculation, as the effect in either case is small.

The full expression for heat of evaporation (as indicated, but not expressed symbolically in the previous paper) is as follows, according to the present point of view:

$$L_A = pv_1 + \Pi_V V_A \int_1^{v_1} \frac{dv}{v^m} - (\Pi_p)_V V_A \int_1^{v_1} \frac{dv}{v^n} + \int_0^T (C_g - C_s)dT - Q_A$$

where v_1 is the volume of the vapor, C_g the molal heat capacity of the vapor, C_s that of the solid (or liquid and solid) and Q_A the molal latent heat of melting (if a liquid is concerned). The other symbols are defined in the previous paper.

internal pressures calculated from the coefficient of expansion. The numbers are rounded off to two significant figures.

TABLE III

INTERNAL PRESSURES OF METALS

Calculated from heats of evaporation[4] by Equation 6

	$L_A = W$ (approx.)			Π	Π
	Calories	Kilojoules	V_A	From W $\times 10^{-3}$	From α $\times 10^{-3}$
K	19	80	45.4	13	7.5
Hg	14.1	60.6	14.8	31	31
Pb	46	193	18.3	80	53
Mg	34	142	13.3	81	85
Al	53	222	10.1	170	126
Ag	64	268	10.3	200	145
Cu	71	297	7.1	320	242
Fe	74	310	7.1	330	345

Evidently, in spite of considerable discrepancies between the corresponding figures in the last two columns, the order of magnitude is consistent, and the order of sequence is the same in the two columns. Therefore the exponent m is fairly uniform in each of these substances. Exact agreement of the two columns could be obtained by choosing an appropriate value for m in each case, ranging from 1.41 in the case of potassium to 1.73 in the case of magnesium. The constancy of m is too doubtful, and the available experimental values for the heats of evaporation are too uncertain, however, to make such a choice definitive at present.

In brief, heat of evaporation seems really to represent primarily work done against cohesive pressure.

II. Elements with Polyatomic Molecules, and Non-Polar Compounds

The second category of substances includes all non-polar compounds and perhaps most of the polar ones also.

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[4] The most recent calculations of gram-atomic heats of evaporation (L_A) by Johnston, and those corrected by Hildebrand, are probably the best now available for non-volatile monatomic metals [(a) Johnston, *J. Ind. Eng. Chem.*, **9**, 876 (1917). (b) Hildebrand, THIS JOURNAL, **40**, 45 (1918)]. The averages of their figures (which are hardly more than approximate) are given above. The value for the heat of evaporation of potassium has been calculated from the vapor pressures found by Kröner [(c) *Dissertation*, Leipzig, **1913**] as published by Mellor [(d) "Treatise on Inorganic Chemistry," (Longmans Green and Co.) **1922**, vol. 2, p. 456] according to the Clapeyron-Clausius equation. The value for mercury was computed in the previous paper (Ref. 1) pp. 1433, 1434 (footnotes). Only the last named has been corrected for external work and change of heat capacity; but these corrections are too small to affect the result essentially. If the internal pressures as well as m and n' are known, Equation 6 gives, of course, a means of calculating heats of evaporation, as was pointed out in the previous paper (p. 1434). For example, the heat of evaporation of gold (not known experimentally) is found to be about 61 Cal. Silver would yield the value 45 Cal. (instead of 64 as given above). Traube's values (based on the van der Waal's equation) are of the same order [*Z. anorg. Chem.*, **34**, 419 (1903)].

Bromine, chosen as typical, is doubtless composed of loosely cohering molecules, each of which consists of two atoms bound together by a pressure much greater than the cohesive pressure. Hence the coefficient of expansion of liquid bromine must be made up of the summation of two quantities, one (the chief effect) representing the increment of volume of the cohesively compressed part, and the other (much smaller) that of the chemically compressed part of the atoms. The two pressures doubtless merge into each other gradually, but for purposes of approximate mathematical treatment it is sufficiently legitimate (at least provisionally) to define sharply these two different parts of any given atom. Thus the coefficient of expansion of such a univalent, chemically-bound atom in a solid or liquid may be represented by the following equation, which is an obvious amplification of Equation 2.

$$\alpha = x\frac{R}{V_A \Pi_1} + (1 - x)\frac{R}{V_A \Pi_2} \tag{7}$$

In this equation x is the fraction of the atom subjected to cohesive pressure, $(1-x)$ the fraction subjected to chemical pressure, Π_1 represents the cohesive pressure, and Π_2 the chemical pressure.

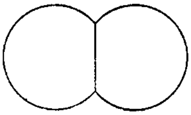

Fig. 1.—An imaginary Longitudinal Section of the Bromine Molecule.

The exact shape of this section (which is bounded by curves supposed to indicate regions possessing equal repelling potential) can be drawn only after much more knowledge has been obtained. Probably the true figure would be more nearly an ellipse than that drawn above. The extent of compression between the atoms is roughly inferred from the actual changes of volume suffered by bromine on combining with other substances. It is supported by the inferences of A. O. Rankine [*Trans. Faraday Soc.*, **17**, 719 (1922)].

The fraction x is the most uncertain of these quantities. The diagram. Fig. 1, gives graphic suggestion of the problem. One may infer that the intense chemical affinity binding the atoms certainly affects less than half and probably more than one sixth of each. Probably, also, x possesses different values in different compounds, depending upon the intensity of the affinities concerned. The assumption, $x = 0.8$—a compromise between the probable limits—will be made in the argument which follows. Ultimately, when more exact experimental data are at hand, the quantity x may perhaps be determined precisely. The numerical outcome can then be easily corrected to correspond.

On the assumption, $x = 0.8$, the cohesive pressure Π_1 of bromine is found from Equation 7 to be somewhat over 2,300 megabars, or about four-fifths of the value given in Table I.

The question now arises: is it possible to compute the cohesive pressure of such polyatomic substances, as well as of monatomic elements, in independent fashion from the heat of evaporation? There follows a table containing results for the internal cohesive pressures of several substances with polyatomic molecules, thus obtained with the help of Equation 6, on the provisional assumption that the exponents m and n' are the same as those in mercury. Molal volumes and molal heats of evaporation naturally take the place of gram-atomic values in the equation. Many more cases are available, but those given will suffice.

TABLE IV

ESTIMATES OF INTERNAL PRESSURES IN TYPICAL COMPOUNDS

Calculated from the heat of evaporation by Equation 6

	Molecular volume 20°	Heat of evaporation Kilojoules per gram-molecule	Π_1 Internal cohesive pressure
Bromine	51	28.2	4,200
Ethyl ether	106.1	25.7	1,900
Ethyl alcohol	58.35	43.0	5,700
Water	18	40.8	17,500

Although these values for Π are of the same order of magnitude as those in Table I, wide individual differences exist. The reasons for the differences are: First: Table I gives values for *compounds* greater than the true cohesive pressures (as was shown in the case of bromine) because its quantities include also the effect of chemical pressure. This is especially the case when atoms of large valence (such as carbon) are present; they must expose very little surface available for cohesive pressure, and are concerned primarily with chemical pressure. Table IV is free from this complication. Second: the values of the exponents of the volume ratios may differ in different substances. These exponents affect Table IV, but not Table I. Allowing for these superposed effects, it appears that each mode of determining internal pressure supports (at least approximately) the other.

If now the heat of evaporation is assumed to give an exact measure of the pressure, the exponent m can be calculated from it, if $(n'-m)$ is known. For bromine, substituting in Equation 5 the corrected value $\Pi = 2300$, also $V_M = 51$, and $W = 28$, the value of K is found to be 2.4. Since in bromine $n'-m = 5.5$, Table II (as corrected in the sentence immediately following it) shows that $m = 1.41$.

The cohesion of bromine at ordinary temperatures is roughly represented by the foregoing considerations. Let us now turn to the main object of this paper, namely, the pressure effect of the chemical affinity binding the atoms.

A new difficulty is encountered, however, in applying these considerations to the heat of thermal dissociation of the bromine molecule.[5] The pressure produced by chemical affinity must exist only on *one side* of each atom concerned, not all around it. Evidently a given amount of work, measured as heat, must produce a much greater pressure when applied over a small portion of the atom (by this one-sided action) than when applied on all sides. This inference may be represented mathematically by substituting the quantity zV_A for V_A in Equation 5, where z is considerably less than unity, and has much the same significance as $(1-x)$, of Equation 7. The quantity z is assumed, like $(1-x)$, to be 0.2; because, even if the two quantities are not exactly identical, they must have the same order of magnitude and probably vary in the same way. The pressure produced by chemical affinity between two combined atoms of bromine is then, from Equation 5:

$$\Pi_2 = W/KzV_A = 960{,}000/(2.4 \times 0.2 \times 25.5) = 78{,}000 \text{ megabars}$$

Although this value, 78,000, will doubtless need revision in the future, it seems to be at least of the right order of magnitude. The outcome is reasonable, in relation to the more simply calculated cohesive pressures of metals. For instance, it is not far from the internal pressure found for calcium, 66,000 megabars. Bromine begins to dissociate appreciably at a red heat (perhaps 600°)[5] and calcium begins to evaporate appreciably at about the same temperature.[6] In chlorine, of course, the cohesive pressure must be less than in bromine, and the chemical pressure greater (the latter, found in the same way, is about 100,000 megabars). In iodine the cohesive pressure must be greater than that in bromine, and the chemical pressure less (perhaps 13,000 and 57,000 megabars, respectively).

The fact that a similar method of treatment, involving the same value of K, yields a reasonable result as regards both cohesive and chemical pressures reinforces the conclusion that these two are probably both manifestations of the same attracting tendency, as well as the conclusion that the heat of chemical reaction, like the heat of evaporation, is due primarily to the work done by the attracting pressure. To this large effect (in the case of chemical affinity, as well as in the case of cohesion) must, of course, be added algebraically the heat change due to change of heat capacity, and that needed for the work involved by the external pressure. These last two minor effects have been neglected (except as regards mercury) in the present treatment, but should receive consideration in a definitive analysis.

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[5] The reaction $2\text{ Br} = Br_2$ has been found to yield 46 Cal. or 192 kj. per mole by Bodenstein [*Z. Elektrochem.*, **22,** 327 (1916)] and also by Henglein [*Z. anorg. allgem. Chem.*, **123,** 137 (1922)]. Correspondingly, $2\text{ Cl} = Cl_2 + 54$ Cal., and $2\text{ I} = I_2 + 34$ Cal. These data are only approximate and are affected by temperature and degree of dissociation.

[6] Pilling found the vapor pressure of calcium to be 0.01 mm. at 600° and 0.2 mm. at 700° [*J. Inst. Metals,* **25,** 170 (1921) as quoted by Mellor, Ref. 4 d, vol. 3, p. 632 (1923)].

There is good reason to believe that similar conditions hold in all non-polar compounds, of which bromine was selected at random as a type. The study of such compounds as the chloride of iodine would be interesting, but the experimental data are not yet adequate. In anisotropic elementary solids (such as bismuth), of which both the coefficient of expansion and the compressibility vary according to the direction chosen in the crystal,[7] the situation is similar to the case of liquid bromine, except that in a crystal the anisotropic molecules must be consistently oriented. The fact that a crystal built up of only one kind of atom can possess different pressure relations in different directions affords additional evidence that each atom may be compressed by combined atoms more firmly on one side than on another, even when the atoms are all alike.

More complicated compounds involve, of course, greater complications of treatment, but not necessarily the introduction of new principles. For complete analysis each element in a compound demands a separate equation of the type of Equation 7. The second member of each of these equations must have a number of terms equal to the number of different kinds of atomic union present. The total coefficient of expansion is, therefore, to be considered as being made up of the sum of a number of small effects.

Any explanation of the ultimate cause of the great pressures, thus inferred, is not here attempted. Gravitation doubtless constitutes but a negligible part of cohesive attraction. The apparent existence of a specific attracting force of great intensity, decreasing as the fourth or fifth power of the distance, presents now even more than formerly a tempting field for theoretical speculation.

III. Polar Compounds

The third class of substances included in Table I, namely, polar compounds such as potassium chloride, offers new complications. First among these is the question as to the distance effect of the electrical attraction, which in such substances probably adds its influence to that of ordinary cohesion or affinity of a non-polar kind. Again, the question as to the existence of diatomic molecules (as distinguished from macroscopic molecules) is important.

Nevertheless, it is worth while to apply here also the method already used with non-polar compounds. Equation 1 gives 38,900 megabars as the net effect of cohesive and chemical pressure in crystals of potassium chloride.[8] (Table I.) On the other hand (if the heat of evaporation is

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[7] Bridgman, *Proc. Nat. Acad. Sci.*, 10, 411 (1924).

[8] This value is supported by Slater's value for $\frac{1}{\beta}\left(\frac{\partial \beta}{\partial p}\right)$ [*Phys. Rev.*, 23, 488 (1924)]. I have found (as will be shown in a later paper) that $\Pi = \frac{n'}{n'-m}\beta\left(\frac{\partial p}{\partial \beta}\right)_v$. For KCl the result is 47,000 megabars—a result as near 39,000 as could be expected, considering the difficulty of the experimental determination.

49 Cal. and $K = 2.4$, as with bromine and potassium) the cohesive pressure (taken alone) of potassium chloride is found (Equation 5) to be 22,000 megabars. Both of these values, although reasonable as representing the cohesive pressure, are far less than the expected chemical pressure of the union of potassium with chlorine, for this compound is thermally decomposed only at very high temperatures. The fact that the two values are of the same order of magnitude shows that m is not very different in this polar compound from its value in the other cases.

Independent evidence concerning the chemical pressure of the union of potassium and chlorine atoms may be secured (as in the case of bromine) from the heat of thermal dissociation of the vaporized salt. The total energy change of dissociation may be calculated by adding to the heat of formation of solid potassium chloride (106 Cal.) the heat of vaporization of metallic potassium (19 Cal.)[4] and half the heat of dissociation of chlorine molecules into chlorine atoms (27 Cal.(?)),[5] and subtracting the heat of evaporation of potassium chloride (50 Cal.). The result is 102 Cal. According to von Weinberg[9] this quantity was found to be 136 Cal. by a more round-about process involving solutions. An average, $K + Cl = KCl + 120$ Cal. (500 kj.) is sufficiently certain for the present purpose. Each of the two different atoms, potassium and chlorine, must be compressed up to the final pressure Π_2, and two pairs of pressure-volume curves constructed, one for each substance. Assuming, however, that the values of K are (as they appear to be) about the same in each case, the two effects may be considered as added together and treated by Equation 5 in a manner analogous to the case of bromine. If, then, one-fifth of the molecular volume of solid potassium chloride is taken as representing the one-sided effect of the chemical pressure, Π_2 is found to be about 280,000 megabars, a first approximate estimate of the pressure which exist between the potassium and chlorine atoms in vaporized potassium chloride. This pressure is in the neighborhood of the internal pressure of copper found from the coefficient of expansion and also independently from the heat of evaporation (Table III) by simpler reasoning involving fewer assumptions. The temperature necessary to cause incipient thermal dissociation of potassium chloride is in fact probably at least as high as that necessary to cause incipient evaporation of this metal.[10] Therefore the result is not unreasonable; its consistency indicates that the energy change concerned is really of an order of magnitude corresponding to the pressures inferred from the present argument.

If the pressure of 300,000 megabars still persists in one-fifth the bulk of potassium chloride in the crystal form, the cohesive pressure in the

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[9] Von Weinberg, *Z. Physik,* **3,** 337 (1920). A convenient resumé of the work of others is found in Mellor's Treatise, Ref. 4 d, p. 537.

[10] See Ref. 4 d, vol. 3, pp. 46 and 515.

solid substance, calculated from Equation 7, is 32,000 megabars. Thus the chemical pressure in the vapor is found to be about nine times as great as the cohesive pressure in the solid.

A brief table including eight other similar salts may be of interest for comparison. The coefficients of expansion, α, are due to Baxter,[11] as are also the molal volumes. The values for U (the heat of dissociation of the vapor) are computed from the value already given for potassium chloride on the reasonable assumption that these values are roughly proportional to the heats of formation (found by de Forcrand)[12] of these analogous salts. All the values are given in round numbers, for obvious reasons. The chemical pressures (Π_2) are those calculated for the dissociated molecules in the vapor. The cohesive pressures (Π_1), as given, are calculated by Equation 7 on the assumptions that the chemical pressures persist in the solids and that $x = 0.8$ as before.

Table V

Approximate Estimates of Cohesive and Chemical Pressures in Nine Halides of Alkali Metals

Alkali Halide	$\alpha \times 10^6$	V_M	U Kilojoules	Π_1 (in solid) $\times 10^{-3}$	Π_2 (in vapor) $\times 10^{-3}$
NaCl	115	27.05	490	43	380
NaBr	120	32.13	440	34	290
NaI	135	40.91	390	24	200
KCl	112	37.52	530	32	280
KBr	118	43.30	480	26	230
KI	118	53.12	430	20	170
CsCl	136	42.34	530	23	260
CsBr	139	47.99	500	19	220
CsI	146	57.60	440	15	160

If the molecules of these solid halides are macroscopic (that is, if each crystal is a single molecule) each atom, both of metal and halogen, must be subjected on all sides to the same pressure, which might be called a "chemical cohesive pressure."[13] Its value in crystals of the nine salts above (as found from Equation 1) must then be, respectively, 52,000, 42,000, 29,000; 39,000, 32,000, 25,000; 28,000, 23,000, 19,000. Such a condition is not impossible; the many-sided action of the residual affinity producing cohesion might conceivably be able to overcome the more intense one-sided action of the chemical combination. In that case, however, each metal and halogen might well be called a hexad—a questionable outcome. Discussion of the conflicting evidence on this question will be postponed.

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[11] Baxter, This Journal, **38**, 259 (1916). The value of α for potassium chloride employed is an average of the results of many observers.

[12] De Forcrand, *Compt. rend.*, **143**, 863 (1906); **152**, 27 (1911).

[13] Attention in this connection should be called to the very recent papers by J. C. Slater [*Phys. Rev.*, **23**, 488 (1924)] and E. Saerens [*J. chim. phys.*, 21, 265 (1924)].

In each of these series of pressure values (both those in Table V and those just given) the pressures found for sodium salts are all greater, and those for cesium salts all less, than those for the corresponding potassium salts. For bromides the pressures are always less than for chlorides; and for iodides, less than for bromides. These relations appear to be consistent with other properties of these substances, such as fusibility and solubility of salts.

Obviously the several values of Π_2 given in the last column of Table V are only tentative, and will doubtless need revision. Nevertheless, these values are significant *relatively to one another*, because they have all been calculated by the same methods, and they indicate at least the order of magnitude of the several quantities. Furthermore, they present the fundamental problems concerned in a more vivid manner than is possible without their aid.

Summary

The object of this paper, which is merely preliminary and makes no attempt at precision, is to suggest some of the problems necessarily involved in any attempt to evaluate the great internal pressures determining the existence of chemical compounds and of solid and liquid substances. In order to exemplify a possible method of treatment, tentative numerical results, calculated by a consistent method, are recorded. The actual values of the cohesive pressures thus obtained are much more trustworthy than those of the chemical pressures; but at least, the latter are clearly shown to be generally much greater than the former. Both may well be due in part to the same original causes, working in a different manner in the two cases. The outcome shows that the heat energy needed for evaporation or thermal dissociation is probably of the same order as the work needed to overcome the respective pressures concerned, taking account of the estimated volumes involved; hence it furnishes a conceivable picture of the *raison d'être* of heat of evaporation and of chemical reaction. The necessary assumptions are neither complicated nor unreasonable.

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