*Anal.* Calcd. for $C_{29}H_{27}O_2N$: N, 3.32. Found: N, 3.35.

**Tribenzylacetophenone.**—160 g. of dibenzylacetophenone was dissolved in twice its volume of toluene, 400 cc. Cooling occurred as solution progressed. Twenty-three grams of sodamide of the necessary high quality was finely pulverized and placed in a three-necked flask equipped with a condenser, a mercury-seal stirrer, and a dropping funnel. The ketone solution was introduced dropwise during two hours while the mixture was stirred and refluxed. At the end of the two-hour period, the system became purple and ammonia was evolved very rapidly. The reaction was continued for eighteen hours. Seventy-four grams of benzyl chloride, b. p. 176–178°, was then introduced at a rate of three or four drops a second. Heating and stirring were continued for twenty-four hours more. By the end of this period the purple color had given place to yellowish-brown. The flask was cooled, 250 cc. of water was added and the toluene layer separated. It was washed with water, dilute hydrochloric acid, and again with water, dried with calcium chloride and distilled on a steam-bath under slightly reduced pressure. The crude ketone which crystallized was filtered and washed with 50 cc. of methyl alcohol in which tribenzylacetophenone is but very slightly soluble, whereas the dibenzyl compound is soluble. The product, recrystallized from toluene, melted at 127–128°. The average yield of crude crystals was 135–140 g., about 68%. The unused dibenzylacetophenone was recovered. Neither the use of a larger proportion of sodamide nor longer heating had a material effect in increasing the output.

*Anal.* Calcd. for $C_{29}H_{26}O$: C, 89.23; H, 6.67; mol. wt., 390. Found: C, 89.24, 89.17; H, 6.74, 6.77; mol. wt. (ebullioscopic method with benzene), 383, 380.

**1,3-Diphenyl-2,2-dibenzylpropanol-1.**—Five grams of tribenzylacetophenone was dissolved in 400 cc. of absolute alcohol. As rapidly as possible, 50 g. of sodium was added to the solution. When the vigor of the reaction had abated, the system was heated and refluxed for half an hour, then 200 cc. of water was added to the cooled contents of the flask. The gummy organic product was heated repeatedly with portions of hot ethyl alcohol which removed the carbinol, but had little effect on any unchanged ketone. Evaporation of the alcohol yielded 2 g. of a very viscous, light yellow liquid which decomposed when heated even under a low pressure. Two grams of ketone was recovered.

When a similar experiment was conducted with isoamyl alcohol as the medium, there resulted in addition to the oil, mentioned above, a solid which, after treatment with acetone and finally with toluene, was found to be tetrabenzylmethane.

*Anal.* Calcd. for $C_{29}H_{28}O$: C, 88.77; H, 7.14; mol. wt., 392. Found: C, 88.73, 88.75; H, 7.06, 7.08; mol. wt. (Rast method), 383, 384.

**Tetrabenzylmethane.**—Four grams of tribenzylacetophenone was heated for twenty-four hours at 200° in a sealed tube with 4 g. of red phosphorus and 80 cc. of 47% hydriodic acid. The cooled tube was opened and the contents extracted with toluene. This solution was washed with aqueous potassium hydroxide and with water, and then dried with calcium chloride. Removal of the toluene left a gummy white mass which upon repeated crystallization from ethyl alcohol gave 0.5 g. of large diamond-shaped crystals melting at 164°. The yield is 13%.

*Anal.* Calcd. for $C_{29}H_{28}$: C, 92.55; H, 7.45; mol. wt., 376. Found: C, 92.50; H, 7.38; mol. wt. (Rast method), 374.

## Summary

1. Tribenzylacetophenone has been produced by a sodamide synthesis.

2. Certain derivatives of the omega-benzylacetophenones, analogous to a series of omega-benzylpinacolone derivatives, have also been prepared.

Middletown, Conn. Received October 2, 1935

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[Contribution from the Research Laboratory, United States Steel Corporation]

# A Useful Integrated Form of the Equation for Calculating Change of Equilibrium with Temperature

By J. B. Austin

There are a number of thermodynamic equations expressing the change of equilibrium with temperature which have the general form

$$d \ln f/dT = \Delta H/RT^2 \qquad \text{I}$$

where $f$ is the equilibrium constant, vapor pressure, solubility, or some other similar quantity which characterizes a state of equilibrium, $\Delta H$ is the molar heat effect for the reaction in question at the absolute temperature $T$, and $R$ is the gas constant. If $\Delta H$ is assumed constant with $T$, this equation integrated between $T'$ and $T$ gives

$$\ln f'/f = \frac{\Delta H}{R}\left(\frac{T'-T}{T'T}\right) \qquad \text{II}$$

This relation, according to which $\ln f'/f$ is a linear function of $1/T$, has proved very useful as an aid in the critical examination of experimental observations, and even as a basis for estimating values of $f'/f$ from $\Delta H$ (or conversely) when no direct measurement is available. The ease with which it can be applied, however, can be considerably increased in a number of cases, particularly in condensed systems, by a simple transformation into an approximate form which holds over a restricted temperature range. Thus, the approximate equation shows: (1) that experimental values of $f$, whatever it may be, when plotted against $T$ on double logarithmic coördinates should fall on a straight line; (2) that if we plot on double logarithmic coördinates, not $T$ directly but a "reduced" temperature—that is, if the actual absolute temperature is divided by a suitable reference temperature, such as the melting point of the solvent in considering solubility the data for all substances which have the same entropy change in the given reaction (in the case of solubility, the same entropy of melting) fall on the same straight line; and (3) that these relations hold in many cases even if $\Delta H$ varies with $T$, so long as this variation is effectively linear over the temperature range considered. The transformed equation also leads directly to the useful empirical rules of Ramsay and Young and of Dühring.

### The Generalized Transformation

The transformation employed can be applied directly to many forms of equation I integrated on the assumption that $\Delta H$ is constant, but since the results are identical with those obtained on the basis of the general postulate that $\Delta H$ varies linearly with $T$, the discussion is confined to the latter case. If in equation I we put $\Delta H = \Delta H_0 + AT$ and integrate, we have

$$\ln f'/f = \frac{\Delta H_0}{RT'}\left(\frac{T' - T}{T}\right) + \frac{A}{R}\ln\frac{T'}{T} \qquad \text{III}$$

Now if we set $T'/T = X$, the quantity $(T' - T)/T$ in III is equal to $(X - 1)$ which is the first term in a well-known series expansion of $\ln X$[1] which is convergent for values of $X$ between 0 and 2. For values of $X$ not much different from unity, which covers nearly all the practical applications of such an equation, the higher terms of the series are negligible compared to the first one, *i. e.*, $(X - 1)$; hence for $(X - 1)$ we may substitute $\ln X$, on which basis we get the equivalent equations

$$\left.\begin{aligned} \ln f'/f &= \frac{\Delta H_0 + AT'}{RT'}\ln\frac{T'}{T} = \frac{\Delta H'}{RT'}\ln\frac{T'}{T} && \text{(a)}\\ \ln f'/f &= \frac{\Delta H'}{RT'}\ln T' - \frac{\Delta H'}{RT'}\ln T && \text{(b)}\\ f'/f &= \left(\frac{T'}{T}\right)^{\Delta H'/RT'} && \text{(c)} \end{aligned}\right\} \text{IV}$$

where $\Delta H'$ is the heat effect at $T'$.

The magnitude of the error introduced by the substitution of $\ln T'/T$ for $(T' - T)/T$ is indicated by a comparison of some typical values as given in Table I. The first two columns contain values of $(T' - T)/T$ and $\ln T'/T$, respectively; the third and fourth give values of $f'/f$ calculated from the first two columns on the basis that $\Delta H'/RT' = 10$, which is a fair average of values likely to be used in applying the equation. It is apparent that the error in this case is relatively small for values of $(T' - T)/T$ less than 0.100. If $\Delta H'/RT'$ is smaller, the error is less; if greater, the error is larger. It should be noted that since the approximation is valid for small values of $(T' - T)$—that is, when $(X - 1)$ is not far from unity—the condition for convergence of the series is fulfilled.

## Applications

### I. Solubility Relations in Ideal Solutions

**A Complete Immiscibility in Solid Phase.**—Since there are a number of advantages deriving from the use of the approximate equation in specific applications, a number of examples will be considered. The first is that of the lowering of the freezing point of an ideal solution from which one component separates as a pure phase on cooling; that is the components are completely miscible in the liquid but completely immiscible in the solid. Under these conditions $\Delta H' = \Delta H_m$ the heat of fusion of the solvent, $T'$ is the melting temperature of the pure solvent, and $f = N_2$, the mole fraction of solvent in the liquid at $T$. Obviously $f' = N_2' = 1$, hence equation IV may be written in the equivalent forms

$$\left.\begin{aligned} \ln N_2 &= \frac{\Delta H_m}{RT_m}\ln T/T_m && \text{(a)}\\ \log N_2 &= \frac{\Delta H_m}{RT_m}\log T - \frac{\Delta H_m}{RT_m}\log T_m = \\ &\qquad \frac{\Delta H_m}{RT_m}\log T + \text{const.} && \text{(b)}\\ N_2 &= (T/T_m)^{\Delta H_m/RT_m} = (T_m/T)^{-\Delta H_m/RT_m} = \\ &\qquad \text{const. } T^{\Delta H_m/RT_m} && \text{(c)} \end{aligned}\right\} \text{V}$$

TABLE I

COMPARISON OF VALUES OF $f'/f$ CALCULATED FROM $\frac{T' - T}{T}$ AND FROM $\ln T'/T$

| $\frac{T' - T}{T}$ | $\ln T'/T$ | $f'/f$ calcd. from $\Delta H'/RT' = 10$<br>$(T' - T)/T$ | <br>$\ln T'/T$ | Difference, % |
|---|---|---|---|---|
| 0.010 | 0.0100 | 0.904 | 0.904 | 0 |
| .0200 | .0199 | .818 | .819 | + 0.12 |
| .0500 | .0488 | .606 | .613 | + 1.1 |
| .0750 | .0724 | .472 | .484 | + 2.5 |
| .1000 | .0954 | .367 | .385 | 4.9 |
| .2000 | .1830 | .135 | .160 | 11.0 |

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(1) See, for example, Hudson, "The Engineers Manual," John Wiley and Sons, Inc., New York, 1917, p. 35.

Equation V shows that if we plot $N_2$ against $T/T_m$ on double log paper, the data for all ideal solutions in the same solvent should fall on the same straight line; moreover, that these straight lines all radiate from a single point ($N_2 = 0$, $T/T_m = 1$) and that for any solvent the angle between its characteistic line and the temperature axis depends only on the magnitude on $\Delta H_m/RT_m$. Consequently, by plotting a few guiding lines for integral values of $\Delta H_m/RT_m$ or $\Delta H_m/T_m$, the line for any given solvent can be quickly and easily drawn, provided, of course that $\Delta H_m$ and $T_m$ are known. On the other hand $\Delta H_m$, if not known, can be rapidly estimated by plotting the available data for appropriate solutions and drawing the best straight line through them. It should be noted that $\Delta H_m/RT_m$ is $1/R$ times the entropy of melting of the pure solvent, which is approximately the same for many chemically related substances; hence, when plotted in this way, the straight lines for many related substances as solvents coincide, a fact which is useful in estimating solubility in the absence of any direct measurement of $N_2$ or $\Delta H_m$.

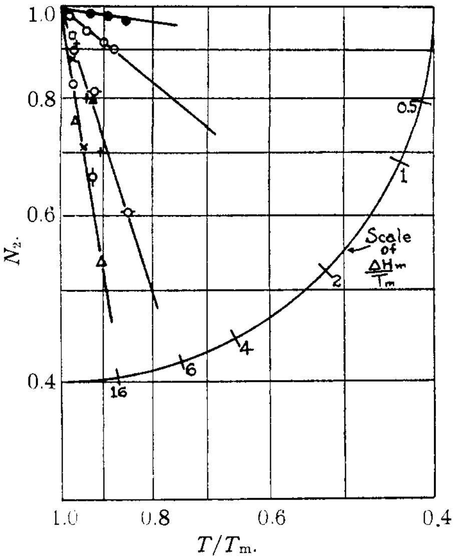

Fig. 1.—Solubility relations in systems with immiscibility in the solid phase plotted on double log coördinates using a reduced temperature according to eq. Va. Solid lines are calculated from heat of melting of solvent (component *italicized*): △, *anorthite*-diopside; □, *NaCl*-$Na_2Cr_2O_7$; ⦶, *diopside*-anorthite; ▲, *NaCl*-CsCl; ×, *diopside*-albite; -○-, *NaCl*-$Na_2SO_4$; ⊙, *magnesium*-nickel; +, *NaF*-NaCl; ●, *iron*-iron carbide.

In order to illustrate the usefulness of these relations a few typical data have been plotted in this manner in Fig. 1. The solutions selected are all high temperature systems—metals, fused salts and silicates—because they cover a relatively wide range of values of $\Delta H_m/T_m$; but the method applies equally well to any substantially ideal solution. It should be noted that the condition for proper application of the equation is met in that the value of $T/T_m$ is never far from unity, even though a relatively wide range of temperature is included.

The points on the lowest line are for three silicate solutions taken from Bowen's study of the system diopside ($CaO \cdot MgO \cdot 2SiO_2$)–anorthite[2] ($CaO \cdot Al_2O_3 \cdot 2SiO_2$)–albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). Following Bowen the molecular weights are taken as 217, 278 and 263, respectively. The full line is the calculated curve based on the directly determined heat of fusion of anorthite (105 cal. per gram).[3] It is evident that the solubility data are in excellent accord with the values calculated from $\Delta H_m$ for anorthite. Since anorthite and diopside are very similar, this agreement indicates that the entropy of melting of silicates of this type is very nearly the same and is close to 16 e. u.

The next curve compares the experimental data for four fused salt solutions, as given in "International Critical Tables" (Vol. IV), with the line calculated from the entropy of fusion of sodium chloride. Not only do the points for three solutions in sodium chloride as solvent fall on the line but those for a solution of sodium chloride in sodium fluoride come very close to it, indicating again that the behavior of solutions in related solvents can be represented by a single line with ample accuracy for many practical purposes.

The third line represents the solubility of nickel in magnesium as determined by Hanson and Payne,[4] compared with the solubility calculated from the entropy of fusion of magnesium. In this case it was demonstrated by direct measurement that the maximum solid solubility of nickel in magnesium is of the order of 0.1% so that the system closely approaches the ideal case of zero solid solubility. It should be noted that the entropy of fusion of magnesium is practically 2, which is a good average for that of most elements; hence $\Delta H_m/RT_m$ is close to one, which greatly simplifies the calculations.

(2) N. L. Bowen, *Am. J. Sci.*, **40**, 161 (1915).

(3) Vogt, "Das Silikatschmelzlösungen," Vol. II Videnskabs.-Selskabets Skrifter, I Math. naturv. Klasse, 1904, No. I.

(4) Hanson and Payne, *J Inst. Metals*, **54**, advance copy (1934).

The uppermost curve in Fig. 1 gives the effect of carbon ($Fe_3C$) on the $\alpha \longrightarrow \gamma$ transformation temperature of iron, as taken from Sato[5] and is included, first because it shows that the equation applies to solid solutions and solid transformations as well as to liquid solutions and melting; and second because it is a good example of a transformation which has a very small entropy change (0.2 e. u.).

In Fig. 2, the data for the silicates have been plotted directly on double-log paper. The heat of fusion calculated from the slope of these curves is: for anorthite, 39,900 cal. per mole (107.5 cal. per gram) in good agreement with the directly determined value (105 cal. per gram); for diopside 20,000 cal. per mole or 93 cal. per g. in satisfactory agreement with the experimental value (approximately 100 cal./g.).[3]

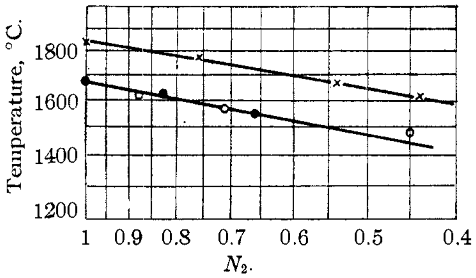

Fig. 2.—Solubility relations in some silicate systems plotted on double logarithmic coördinates according to eq. Vb. The solvent is the component *italicized*. ○, *Diopside*-anorthite; ●, *diopside*-albite; ×, *anorthite*-diopside.

Equation Vc is especially interesting because it shows that *the addition of a given mole fraction of solute lowers the (absolute) melting point of all solvents of related composition, i. e., those for which $\Delta H_m/T_m$ is the same, by the same percentage;* or *the solubility of a given solute at an absolute temperature which is a given fraction of the melting temperature is the same for all such solvents.* In other words, if $N_2$, the mole fraction of solvent, is plotted against $T/T_m$ on rectangular coördinates, a single solubility curve is obtained for all ideal solutions in a given solvent, or for all ideal solutions in which the solvents have the same entropy of melting, thus providing a convenient way of representing a large number of data on a single curve or family of curves. An illustration of this method of plotting is given in Fig. 3.

It should be noted that the conclusion given in italics in the preceding paragraph is a rule for solutions exactly analogous to the rule of Ramsay and Young for vapor pressures which, as will be shown later, can be derived in the same way as equation Vc. It also leads to a rule for solutions analogous to the Dühring rule for vapor pressure. Thus if we plot the temperature at which a given substance has a given solubility in one solvent as ordinate and the temperature at which it has the same solubility in a "related" solvent (one whose entropy of melting is the same, or nearly the same) as abscissa, the experimental points should fall on a straight line whose slope is the ratio of the melting temperatures of the solvents.

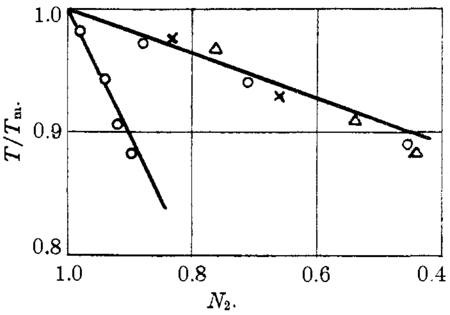

Fig. 3.—Solubility relations plotted on Cartesian coördinates using a reduced temperature according to eq. Vc. The solid lines are calculated from the heat of fusion of the solvent which is the component *italicized:* ×, *Diopside*-anorthite; ○, *diopside*-albite; △, *anorthite*-diopside; ●, *magnesium*-nickel.

It is also obvious that equation Vc in the form $N_2$ = const. $T^{\Delta H_m/RT_m}$ where the constant is $(T_m)^{-\Delta H_m/RT_m}$, enables one to draw in the actual solubility curve on linear coördinates with very little effort. Furthermore, the equation in this form demonstrates the factors which govern the shape of the solubility curve when plotted as $N_2$ against $T$. Clearly, when $\Delta H_m/RT_m = 1$ the solubility curve is a straight line between ($N_2 = 1$, $T = T_m$) and ($N_2 = 0$, $T = 0$); when $\Delta H_m/RT_m > 1$ the curve lies above this straight line and is concave to the $N_2$ axis, and when $\Delta H_m/RT_m < 1$ the curve is below the straight line and is convex to the composition axis. These relations, illustrated schematically by the curves in Fig. 4, are easily checked by considering a specific example. If $\Delta H_m/RT_m = 2$ equation Vc is a parabola passing through the origin ($N_2 = 0$, $T = 0$) and the melting point ($N_2 = 1$, $T = T_m$) and is symmetrical about the $N_2$ axis; whereas if $\Delta H_m/RT_m = 0.5$,

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[5] Sato, *Tech. Repts. Tohôku Imperial Univ.*, **8**, 27 (1928).

the curve passes through the same two points but is symmetrical about the $T$ axis at the $N_2 = 0$ side. Actually the equation would not hold over this range, but it does hold as $N_2$ approaches unity and in this region has the same form as if it were valid to $N_2 = 0$. It is concluded, therefore, that if the entropy of melting is close to 2, as it is for most of the elements, the solubility curve is substantially a straight line; if it is greater than 2, the curve is concave to the composition axis; if it is less than 2, the curve is convex to this axis, and in each of the last two cases the curvature becomes less as $N_2$ approaches unity. From this reasoning it is clear that if the curvature of the solubility line changes sign, then $\Delta H$ has changed in such a way that $\Delta H_m/RT_m$ has passed from its initial value through unity. These points are illustrated by Fig. 5, which shows data for three types of solution plotted as $N_2$ against $T$.

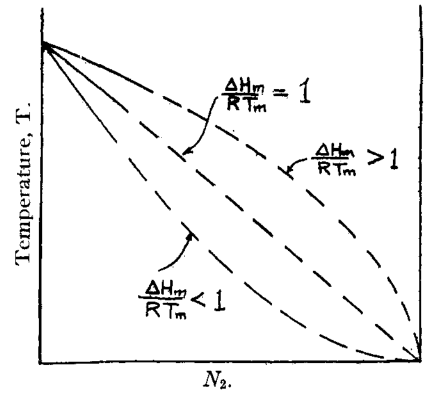

Fig. 4.—Schematic chart showing the relation between the entropy of melting and the curvature of the solubility line in a system in which there is no solid solubility.

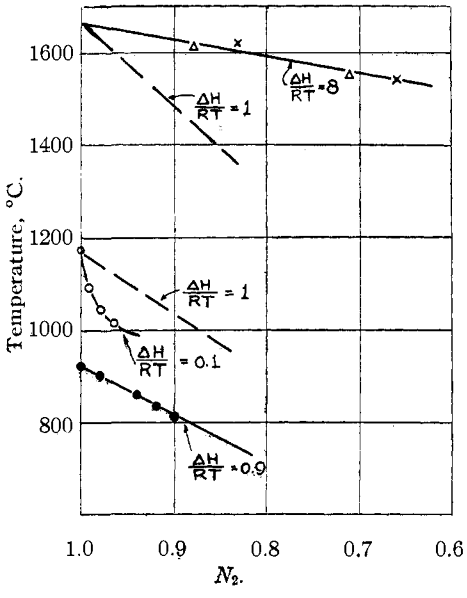

Fig. 5.—Chart illustrating the relation between the entropy of melting and curvature of the solubility line. △, *Diopside*-albite; ×, *diopside*-anorthite; ○, *iron*-iron carbide; ●, *magnesium*-nickel.

There is another interesting transformation which can be applied to equation V. It is a well-known fact that the value of $-\ln X$ approaches $(1 - X)$ as $X$ approaches unity; hence, as $N_2$ approaches unity, that is, in a dilute solution, $-\ln N_2$ can be replaced by $(1 - N_2)$ or $N_1$, the mole fraction of solute in the liquid at $T$. On this basis we have

$$\mathrm{d}N_1/\mathrm{d}T = -\Delta H_m/RT^2 \qquad \text{VI}$$

which is the van't Hoff freezing point equation for dilute solutions. By the methods already indicated this becomes

$$\left.\begin{array}{lr} N_1 = \dfrac{\Delta H_m}{RT_m}\ln\dfrac{T_m}{T} = -\dfrac{\Delta H_m}{RT_m}\ln T/T_m & \text{(a)} \\ N_1 = -\dfrac{2.3\,\Delta H_m}{RT_m}\log T + \text{const.} & \text{(b)} \\ T = T_m\, e^{-N_1T_mR/\Delta H_m} = T_m\, e^{-aN_1} & \text{(c)} \end{array}\right\} \text{VII}$$

In this case plotting on semi-logarithmic coördinates gives a straight line. The advantages of these equations for dilute solutions are in general those mentioned for equation V and need not be discussed in detail again. Data for the silicates and for magnesium which have been plotted on this basis are shown in Fig. 6.

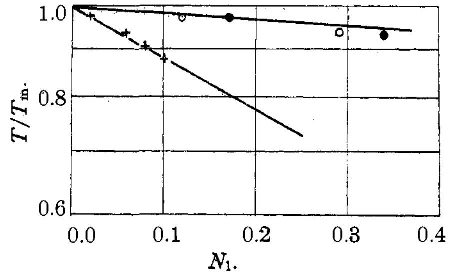

Fig. 6.—Solubility relations in some high temperature systems plotted on semi-logarithmic coördinates using a reduced temperature according to eq. VIIa. ×, *Magnesium*-nickel; ○, *diopside*-albite; ●, *diopside*-anorthite.

**Case 2. Miscibility in the Solid Phase.**—The second general case to be considered is that of a system showing solubility of the components in the solid phase (or in the low temperature form in the case of a solid transformation). In this case $\ln N_2$ is replaced by $\ln N_1/N_s$ where $N_1$ and $N_s$ are the mole fractions of solvent in the liquid and solid, respectively,[6] and we have

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[6] The solvent is taken as the component whose heat of melting and melting temperature are used, usually the component present in the largest concentration.

$$\left.\begin{aligned} \ln N_l/N_s &= \frac{\Delta H_m}{RT_m} \ln T_m/T = \\ &\qquad - \frac{\Delta H_m}{RT_m} \ln T/T_m && \text{(a)} \\ \log N_l/N_s &= - \frac{\Delta H_m}{RT_m} \log T + \text{const.} && \text{(b)} \\ N_l/N_s &= \left(\frac{T}{T_m}\right)^{-\Delta H_m/RT_m} = \\ &\qquad \text{const. } T^{-\Delta H_m/RT_m} && \text{(c)} \end{aligned}\right\} \text{VIII}$$

These equations are entirely analogous to equations V, and show that by plotting $N_l/N_s$ against $T/T_m$ or against $T$ directly on double log paper, a straight line having the slope $\Delta H_m/RT_m$ should be obtained. Equation VIIIa shows that the lines again radiate from a common point, as is evident from Fig. 7 which shows a few typical data plotted in this manner. The lowest curve is for anorthite-rich solutions of albite and anorthite,[2] and the middle one is for the albite-rich end of this system plotted so as to fall on the graph instead of above it as it normally would. The uppermost curve shows the ratio $N_l/N_s$ at the eutectic temperature of each of a series of aluminum alloys.[7] The full lines are those calculated from the directly-measured heat of fusion while the dashed line (for albite) is the best straight line through the data. The entropy of fusion of albite is considerably lower than that of anorthite, indicating that $\Delta H_m/RT_m$ does not have the same value for all silicates; nevertheless, the agreement demonstrated previously between the entropy of fusion of diopside and anorthite, which are closely related chemically, suggests that the silicates can be classified into a small number of groups, the members of each group having the same entropy. The comparison of silicates emphasizes that Fig. 1 is nothing more than a special case of Fig. 7—the value of $N_s$ being unity in the former. The data of Fig. 1 can therefore be plotted on Fig. 7, and the lines for anorthite and diopside would coincide. The uses of equation VIIIb are apparent and need no further discussion.

While the equations as given are derived for melting phenomena, it is obvious that they apply equally well to the boiling point of solutions of a volatile solute in a volatile solvent. Thus by making $\Delta H_m$ the heat of vaporization, $T_m$ the boiling point and changing $N_l$ and $N_s$ to $N_v$ and $N_l$, the mole fractions of solvent in vapor and liquid, respectively, we get

$$\left.\begin{aligned} \ln N_v/N_l &= \frac{\Delta H_v}{RT_v} \ln \frac{T_v}{T} = - \frac{\Delta H_v}{RT_v} \ln T/T_v && \text{(a)} \\ \log N_v/N_l &= - \frac{\Delta H_v}{RT_v} \log T + \text{const.} && \text{(b)} \\ N_v/N_l &= (T/T_v)^{-\Delta H_v/RT_v} = \\ &\qquad \text{const. } T^{-\Delta H_v/RT_v} && \text{(c)} \end{aligned}\right\} \text{IX}$$

Since these equations are precisely analogous to equations VIII whose application has been considered, no further discussion is needed, except to state that for a non-volatile solvent, $N_v = 1$ and the equations simplify to the form analogous to equation V.

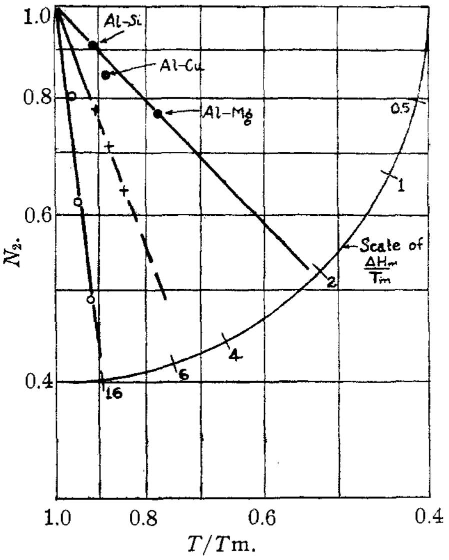

Fig. 7.—Solubility relations on systems having solid solubility. plotted on double logarithmic coördinates using a reduced temperature according to VIIIa. The solid lines are calculated from the heat of melting of the solvent which is the component *italicized:* ○, *Anorthite-albite*; +, *albite*-anorthite; ●, *aluminum* alloys at eutectic temp.

**Other Applications.**—In a purely formal way the approximate equations are valid for any quantity whose variation with temperature is given by equation I, and apply therefore to the equilibrium constant of a reaction, vapor pressure, dissociation pressure or electron emission. Actually, the change in these quantities with temperature is such that the restriction of keeping $T'/T$ less than 1.2 imposes a serious limitation so that the equations are useful in only a few special cases.

There are, however, certain interesting aspects of the equations for some of these quantities, particularly the one for vapor pressure. Thus, if $f'$ in IVc is the vapor pressure at $T'$ of a liquid

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[7] Fink and Freche, *Trans. A. I. M. M. E.*, **111**, 304 (1934).

whose normal boiling point is $T$, it follows that for "related liquids," *i. e.*, those whose entropy of vaporization is the same, at the same vapor pressure

$$T_1/T_2 = T_1'/T_2' = \text{constant}$$

which is the empirical rule of Ramsay and Young.

Dühring's rule also follows from IVc, for considering a given pressure we write

$$\left(\frac{T_1'}{T_1}\right)^{\Delta H_1'/RT_1'} = \left(\frac{T_2'}{T_2}\right)^{\Delta H_1'/RT_2'}$$

and for "related liquids"

$$T_1' = T_1/T_2T_2' = \Delta H_1'/\Delta H_2' \times T_2'$$

which is the equation for the Dühring line. It also indicates that the slope of the Dühring line is the ratio of the absolute boiling temperatures or the heat of vaporization of the liquids chosen.

It is also possible to give some basis to Guldberg's empirical rule that for many liquids the normal boiling point is two-thirds of the absolute critical temperature. Thus, denoting the values of the quantities at the boiling point and critical point by the subscripts b and c, it can be shown on the basis of IVc that $T_b/T_c = (^1/P_c)^{-\Delta H_b/RT_b}$ Since $P_c$ for most liquids is of the order of magnitude of 60 atmospheres, and by Trouton's rule, $-\Delta H_b/RT_b = -11$, the ratio $T_b/T_c$ is roughly 0.7.

## Summary

By a simple transformation the equations relating the change of solubility with temperature can be changed into an approximate form which is in many cases more convenient for interpolation or extrapolation than the original equations. Thus it is shown that experimental values of these quantities fall on a straight line when plotted against the temperature, or the reduced temperature, on double logarithmic coördinates. The approximate equation for vapor pressure leads directly to the rules of Ramsay and Young and of Dühring.

KEARNY, NEW JERSEY RECEIVED JULY 13, 1935

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. JOHN'S UNIVERSITY]

# The Formation and Composition of Lithium Aluminate

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## Introduction

According to Allen and Rogers,[1] an insoluble aluminate of lithium is formed when aluminum is dissolved in a solution of lithium hydroxide. Analysis of the air-dried substance for alumina and water led them to assign the formula, $LiH(AlO_2)_2 \cdot 5H_2O$. As a result of conductometric measurements on the saturated solution of the substance, similarly prepared, Prociv[2] concluded lithium and aluminum were present in the ratio of 0.8Li:2Al, which, he says, is an atomic ratio of approximately 1Li:2Al. According to him lithium aluminate may also be precipitated by the addition of a solution of lithium hydroxide to a solution of an aluminum salt or by adding a solution of a lithium salt to a solution of an alkali aluminate. On ignition, he claims, the compound is converted into $Li_2O \cdot 2Al_2O_3$. Dobbins and Sanders[3] describe the formation of lithium aluminate by the addition of dilute ammonia to a solution containing a lithium and an aluminum salt, in the presence of phenolphthalein as an indicator. However, they claim the compound contains lithium and aluminum in atomic ratio of 2Li:5Al and, as a result of a series of ignitions assign the formula, $2Li_2O \cdot 5Al_2O_3$, for the ignited product.

Thus there is disagreement as to the composition of lithium aluminate prepared by different methods. This might be attributed to a variation of conditions, *i. e.*, alkalinity, relative ionic concentrations or temperature, in the different methods used. Concerning temperature, Allen and Rogers[1] and Heyrovsky[4] suggest precipitation at low temperatures, (near 0°), to prevent decomposition of the aluminate.

Since the compound has not been extensively studied, this investigation was undertaken in order, (1) to determine conditions for the precipitation of lithium aluminate from a solution of an aluminum salt, (2) to determine, by analytical means, the atomic proportions of lithium to aluminum in the substance precipitated, (3) to

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(1) Allen and Rogers, *Am. Chem. J.*, **24**, 304 (1900).

(2) Prociv, *Collection des Travaux Chimique de Tchecoslovaquie*, **1**, 95 (1929).

(3) Dobbins and Sanders, THIS JOURNAL, **54**, 178 (1932).

(4) Heyrovsky, *J. Chem. Soc.*, **117**, 1013 (1920).