

THE COMPLETE CALCULATION OF ACTIVITY COEFFICIENTS FROM FREEZING POINT DATA

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Despite the importance of the freezing point method for the calculation of activity coefficients, it has not yet been made to yield results of high precision. For their well-known application of the method to sodium chloride solutions, Lewis and Randall (1) were forced to use data very limited in range and accuracy. In addition to experimental uncertainties, they permitted several simplifying approximations to enter their calculations.

It is the purpose of this investigation to examine the various approximations; to remove those not permissible in a precise calculation; to introduce into the calculation heat of dilution data recently made available; to discuss the precision of the calculation as a whole; and finally, to point out possible sources of remaining errors. The difficulty of the extrapolation of Lewis and Randall's j function to infinite dilution is not discussed in this paper. The problem of extrapolation has been treated for potassium chloride solutions by Spencer (2) with a method which Scatchard (3) has found to agree well with his recent measurements.

Our needs will be adequately met by a calculation of the ratio of the activity coefficient, γ , to the value of γ at 0.1 molal. Harned and Nims (4) have determined this ratio, $\gamma/\gamma_{0.1}$, by means of electromotive force measurements. In table 1, column 4, their data at 25°C. are presented for comparison with the activity coefficients calculated from freezing points. In the second column are tabulated values of $\gamma'/\gamma'_{0.1}$ calculated from γ' , the "provisional values" obtained by Lewis and Randall when they neglected heats of dilution. In the third column are values of

$\gamma/\gamma_{0.1}$ derived from their "final values" of the activity coefficient, γ . If the electromotive force results are not greatly affected by dissolved electrode materials or side reactions, Lewis and Randall's $\gamma/\gamma_{0.1}$ for a 4 molal solution is about 6 per cent in error.

Since the freezing point method does not involve such uncertainties as side reactions, dissolved electrode materials, etc., it is very important that its precision be improved as much as possible. The development of the following equations is necessary.

TABLE 1

Activity coefficients from various sources

The first line of initials indicates sources of activity coefficients; the second, sources of freezing point data; the third, sources of relative heat contents. The last line in the table shows the per cent deviation at 4 molal from the results of Harned and Nims, adopted as a tentative standard.

γ ϑ x	$\gamma'/\gamma'_{0.1}$ L + R L + R ...	$\gamma/\gamma_{0.1}$ L + R L + R L + R	$\gamma/\gamma_{0.1}$ H + N	$\gamma/\gamma_{0.1}$ Y L + R Y + M	$\gamma/\gamma_{0.1}$ Y I. C. T. Y + M
<i>M</i>					
0.2	0.940	0.942	0.940	0.944	0.942
0.5	0.855	0.863	0.873	0.871	0.871
1.0	0.789	0.815	0.843	0.827	0.839
2.0	0.768	0.828	0.860	0.845	0.851
3.0	0.786	0.882	0.924	0.901	0.908
4.0	0.823	0.959	1.017	0.978	0.988
Per cent . .	19	5.7	(0.0)	3.8	2.9

Let the molal heat capacity of ice minus that of water be represented as a function of *Centigrade* temperature, thus:—

$$\Delta C_p = \Delta\Gamma_0 + \Delta\Gamma_1 t + \Delta\Gamma_2 t^2 + \Delta\Gamma_3 t^3 \quad (1)$$

Then the molal heat of solidification, ΔH_s , is given by the following expression, in which ΔH_θ represents its value at the freezing point, θ , of the solvent.

$$\Delta H_s = \Delta H_\theta + \Delta\Gamma_0 t + \frac{\Delta\Gamma_1 t^2}{2} + \frac{\Delta\Gamma_2 t^3}{3} + \frac{\Delta\Gamma_3 t^4}{4} \quad (2)$$

Adopting the procedure and symbols of Lewis and Randall (p. 282 et seq.), but retaining more terms in our series, we obtain the following two equations for the temperature variation of the activity of the solid solvent, a_s . The symbols and those of subsequent equations are explained in table 2.

TABLE 2
Explanation of symbols

$A_1 = \frac{\Delta H_\Theta}{R\Theta^2} = -\frac{1}{55.508 \lambda}$	
$B_1 = 2 \frac{\Delta H_\Theta}{R\Theta^3} - \frac{\Delta \Gamma_0}{R\Theta^2}$	
$C_1 = 3 \frac{\Delta H_\Theta}{R\Theta^4} - 2 \frac{\Delta \Gamma_0}{R\Theta^3} + \frac{\Delta \Gamma_1}{2R\Theta^2}$	
$D_1 = 4 \frac{\Delta H_\Theta}{R\Theta^5} - 3 \frac{\Delta \Gamma_0}{R\Theta^4} + \frac{2 \Delta \Gamma_1}{2 R\Theta^3} - \frac{\Delta \Gamma_2}{3R\Theta^2}$	
$E_1 = 5 \frac{\Delta H_\Theta}{R\Theta^6} - 4 \frac{\Delta \Gamma_0}{R\Theta^5} + \frac{3 \Delta \Gamma_1}{2 R\Theta^4} - \frac{2 \Delta \Gamma_2}{3 R\Theta^3} + \frac{\Delta \Gamma_3}{4R\Theta^2}$	
$B_2 = -\frac{55.508}{2.3026} B_1$	$D_2 = -\frac{55.508}{2.3026} D_1$
$C_2 = -\frac{55.508}{2.3026} C_1$	$E_2 = -\frac{55.508}{2.3026} E_1$

$$d \ln a_s = (A_1 + B_1 \vartheta + C_1 \vartheta^2 + D_1 \vartheta^3 + E_1 \vartheta^4 + \dots) d\vartheta \quad (3)$$

$$d \ln a_s = A_1 d\vartheta + B_1 \vartheta d\vartheta + \frac{C_1 \vartheta d(\vartheta^2)}{2} + \frac{D_1 \vartheta d(\vartheta^3)}{3} + \frac{E_1 \vartheta d(\vartheta^4)}{4} + \dots \quad (4)$$

From these we derive equation 5 for the calculation of the activity of the solvent, a_1'' , at any specified temperature, and equations 6 and 7 for the evaluation of γ , the activity coefficient of the solute at the same temperature.

$$2.3026 \log a_1'' = \left(A_1 \vartheta + \frac{B_1 \vartheta^2}{2} + \frac{C_1 \vartheta^3}{3} + \frac{D_1 \vartheta^4}{4} + \frac{E_1 \vartheta^5}{5} + \dots \right) + 2.3026x \quad (5)$$

$$\log \gamma = - \int_0^m j d \log m - \frac{j}{2.3026} + \frac{1}{\nu} \int_0^m \frac{(B_2 \vartheta + C_2 \vartheta^2 + D_2 \vartheta^3 + E_2 \vartheta^4 + \dots)}{m} d\vartheta - \frac{55.508}{\nu} \int_0^m \frac{dx}{m} \quad (6)$$

$$\log \gamma = - \int_0^m j d \log m - \frac{j}{2.3026} + \frac{B_2}{\nu} \int_0^m \frac{\vartheta}{m} d\vartheta + \frac{C_2}{2\nu} \int_0^m \frac{\vartheta}{m} d(\vartheta^2) + \frac{D_2}{3\nu} \int_0^m \frac{\vartheta}{m} d(\vartheta^3) + \frac{E_2}{4\nu} \int_0^m \frac{\vartheta}{m} d(\vartheta^4) + \dots - \frac{55.508}{\nu} \int_0^m \frac{dx}{m} \quad (7)$$

Values adopted for the various physical constants used in this investigation are given below. The substitution of these data for those used by Lewis and Randall results in a slightly increased discrepancy at 4 molal. The author is indebted for these estimates to a recent study made by Spencer (5).

$$\Theta = 273.18 \text{ degrees,}$$

$$R = 1.9864 \text{ cal. mole}^{-1} \text{ deg.}^{-1},$$

$$\lambda = 1.858_3 \text{ kilogram deg. mole}^{-1},$$

$$\Delta H_\Theta = -1436.7 \text{ cal. mole}^{-1},$$

$$\Delta \Gamma_0 = -9.04_3 \text{ cal. mole}^{-1} \text{ deg.}^{-1},$$

$$\Delta \Gamma_1 = 0.05_{66} \text{ cal. mole}^{-1} \text{ deg.}^{-2}, \dots \Delta \Gamma_2 = \Delta \Gamma_3 = 0.$$

The approximations which Lewis and Randall allowed to enter their calculations may be summarized as follows;—

1. Treatment of ΔC_p as a constant, which implies the omission of all terms after the second in equation 2;
2. Omission of all terms between the third and last of equation 7;
3. Treatment of \bar{L}_1 as a linear function of temperature.

The first two of these may be discussed together, since the terms omitted from equation 2 affect only the C , D , E , (and higher) terms of the series in equation 7. The importance of the C , D , and E terms may be illustrated with a few examples. Table 3 shows the per cent by which the calculated value of γ is reduced by each of the terms. The discrepancy between the freezing point and electromotive force methods is not reduced by the use

of the temperature variation of ΔC_p and the introduction of the extra series terms, but is increased slightly. However, at least the C_2 term must be used for the calculation of γ when a precision of a few tenths of one per cent is required.

In an investigation of the temperature variation of \bar{L}_1 recently conducted in this laboratory (6, 7), measurements were made at 25°, 12.5°, and 0°C. Values read from three plots of \bar{L}_1 versus molality are shown in figure 1. They are connected by solid lines, corresponding to quadratic equations derived to represent the data. Dotted lines represent extrapolations of these equations to the freezing points of the respective solutions.

TABLE 3
Effect of terms on calculated values of γ

TERM CONTAINING	4.0 MOLAL NaCl	5.2 MOLAL NaCl
C_2	0.28 per cent	0.58 per cent
D_2	0.02 per cent	0.06 per cent
E_2	0.001 per cent	0.006 per cent

The determination of x from these data is illustrated by the following example for a 4.45_s molal solution.

$$\bar{L}_1 = 21.1_s - 1.02_s (t - 25) + 0.008_{ss} (t - 25)^2 \quad (8)$$

$$\log \frac{a_1''}{a_1'} = x = -21.1_s y - 1.02_s z - .017_s \Omega \quad (9)$$

The terms y and z are defined by Lewis and Randall (p. 349) and

$$\Omega = 298.18 \left(z + \frac{t' - 25}{2} y \right) \quad (10)$$

According to equation 9, $x = -.00603$. If the last term is neglected, $-.00534$ is obtained for x .

In the fifth column of table 1 is $\gamma/\gamma_{0.1}$ derived from these x values and the j values of Lewis and Randall. In the sixth column are activity coefficient data determined from these same x values, and from the freezing point data listed in International Critical Tables (8). Spencer's constants and the C_2 term of

equation 7 were employed in this calculation, though the discrepancy was thus increased. For the 4 molal solution the difference between the electromotive force data and the freezing point method has been reduced from nearly 6 per cent to about 3 per cent.

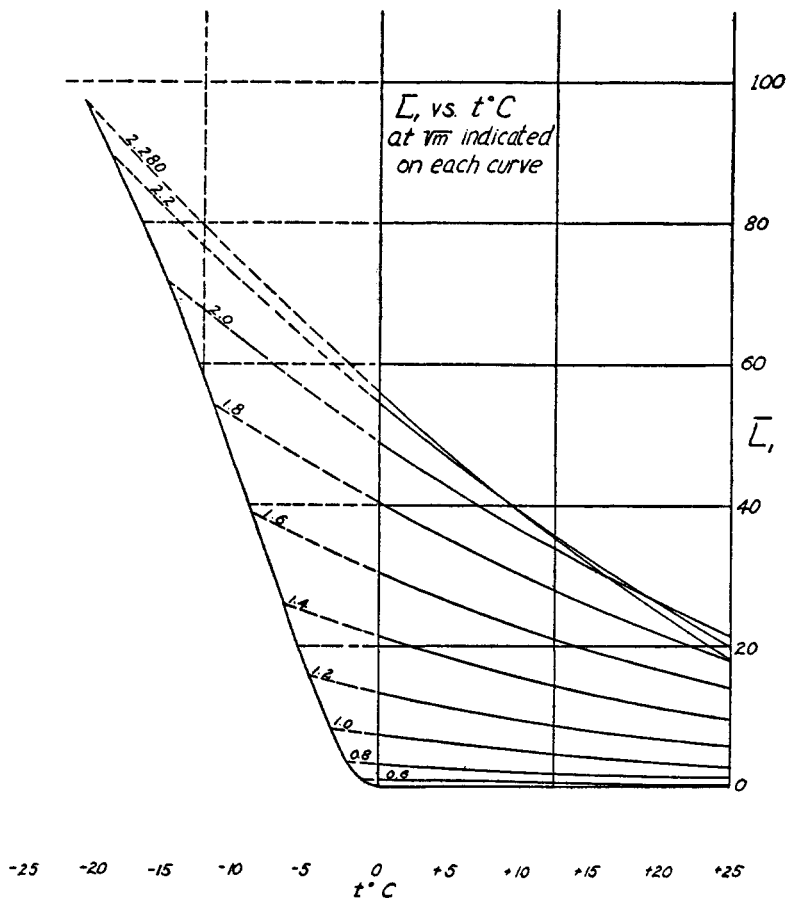


FIG. 1. RELATIVE PARTIAL MOLAL HEAT CONTENTS

The discrepancy is still larger than it should be, and the data must be examined to reveal the cause. For this purpose, the following equation is useful.

$$\log \left[\left(\frac{\gamma'}{\gamma_{0.1}} \right) \left(\frac{m}{0.1} \right) \right] = - \frac{55.508}{2.3026 \nu R} \int_{0.1}^m \frac{\Delta H}{mT^2} d\vartheta \quad (11)$$

According to table 1, column 2, the logarithm in the left side of this equation is about 1.5 for a 4 molal solution. An error of 0.1 per cent in R , or an average 0.1 per cent error in ΔH or T^2 would produce the same per cent error in this logarithm, i.e., an error of 0.0015. $\log (\gamma/\gamma_{0.1})$ would be affected by the same amount and an error of 0.3₅ per cent would therefore be introduced into $\gamma/\gamma_{0.1}$.

The probable error in ΔH_{θ} according to the estimate in International Critical Tables (9) is 0.10 per cent. An error of this magnitude would introduce into ΔH an error varying from 0.10 per cent to 0.12 per cent and, therefore, one of about 0.4 per cent into $\gamma/\gamma_{0.1}$ at 4 molal. The error in ΔC_p is not likely to be important in comparison with this hypothetical error in ΔH_{θ} ; a change in $\Delta \Gamma_0$ greater than 1 per cent would be required to affect the B_2 term and higher terms sufficiently to produce a variation of 0.1 per cent in γ at 4 molal.

The probable error in R , according to Birge (10), is too small to affect materially the precision of the activity coefficient calculation. The probable error in Θ^2 , Birge estimates, is about 0.022 per cent, which produces a probable error in T^2 of 0.022 per cent to 0.024 per cent. This also would add very little to the uncertainty in $\gamma/\gamma_{0.1}$. Further errors in T^2 are caused by errors in ϑ , which are discussed below.

A thoroughly satisfactory calculation requires measurements of \bar{L}_1 below 0°C. Such data might be introduced into the calculation by the incorporation of a fourth term in equations of the type of 8 and 9. The third term introduced a correction into γ at 4 molal of only 2.1 per cent. Probably the three terms represent the \bar{L}_1 curve so well that a fourth term would have little further effect.

The greatest uncertainty in the calculation seems to lie in the freezing point data. A systematic error of 1 per cent in ϑ would imply a constant error of 1 per cent in $d\vartheta$ of equation 11 together with a small additional error (always less than 0.2 per cent) in

T^2 . The remaining discrepancy of about 3 per cent could be caused therefore by an average error of about 0.8 per cent in ϑ .

An example of existing discrepancies in freezing point data is shown in the following values of ϑ for a 1 molal solution.

ϑ used by Lewis and Randall	= 3.33
ϑ of International Critical Tables	= 3.37
ϑ Scatchard (3)	= 3.39

In International Critical Tables (8) only one investigation of freezing points of sodium chloride solutions more concentrated than 1.2 molal is listed. The data of this series were adopted for concentrated solutions, although the value of ϑ given for a 1 molal solution is 1.2 per cent smaller than that selected for the Tables to represent all of the significant data in this region. New measurements of freezing points of concentrated solutions will probably reduce much further the discrepancy between the freezing point calculations and the electromotive force data of Harned and Nims (4). These measurements with further investigations of \bar{L}_1 at low temperatures may soon reduce the uncertainty in $\gamma/\gamma_{0.1}$ close to the 0.4 per cent due to the probable error in ΔH_e .

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