

METHODS OF CALCULATION OF ACTIVITY COEFFICIENTS.

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A large portion of the data from which activity coefficients can be calculated has been studied in this laboratory. The methods of calculation have been gradually developed and modified in such a way that the experimental results from the various sources can be directly compared. Graphical methods in which small experimental differences, especially in the dilute solutions, are made evident have been found to be the most satisfactory, both from the standpoint of rapidity of treatment and the ease with which a weighted mean of all the data can be obtained.

It is the purpose of this paper to present the methods, some of which have not been previously described, which are most used. No attempt will be made to develop the theory, but for the notation and derivation of the fundamental equations the reader is referred to the work of Lewis and Randall.¹

Composition is expressed throughout as molality (mols per 1000 g. of water in vacuum). Although it may appear to be an unimportant detail, the error involved in converting the data, when expressed in mols per litre, is often greater than that of the experiments themselves and prevents the full use of otherwise excellent data. The composition of a solution when expressed as mols per litre changes with the temperature owing to the expansion of the solution when heated. In a few cases the transformation to molalities has been found impossible, and we have used a different activity coefficient referred to mols per litre; but as it is almost impossible to determine the temperature coefficient of such a quantity its use is limited to the temperature at which it was determined.

¹ Lewis and Randall, (a) *J. Amer. Chem. Soc.*, **43**, 233, 1113 (1921); (b) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

The determinations of the activity of the solute may be divided into two classes: first, those which determine the relative activity of the solute and, second, those which determine the activity of the solvent and, by means of the partial molal equations, give the activity of the solute. Simple functions of the experimental results are found and presented in such a form that the results of each class may be compared. Although we shall discuss only the aqueous solution, the procedure may be readily adapted for use with non-aqueous solutions.

Activity Coefficients of Aqueous Solutions from Determinations of the Activity of the Water.

The following experimental methods all give the activity of the water: freezing-point lowering, vapour pressure lowering, boiling-point raising, osmotic pressure, dew-point lowering, distribution ratio of the solvent and, in the case of a few solvents, measurements of the electromotive force in which the solvent is the substance involved in the electrode reactions.

Two of these methods, the freezing-point lowering and the boiling-point raising, give the activity of the water at the freezing- or boiling-point of the solution rather than at a constant temperature, but fortunately the change of the activity with temperature is small and we have methods of accurately estimating this change.²

Freezing-Point Lowering.—For the freezing-point lowering, Lewis and Randall used a divergence function,³

$$j = 1 - (\theta/\nu\lambda m), \quad . \quad . \quad . \quad (1)$$

where θ is the freezing-point lowering, or the boiling-point raising, ν is the number of molecules formed per molecule of solute, λ is a constant = 1.858, and m is the molality (mols per 1000 g. water).

Boiling-Point Raising.—Randall and Adams⁴ have used Equation 1 for all the available data for aqueous solutions of electrolytes. At the boiling-point λ has the value 0.5125, but this value varies slightly with the barometric pressure.

Vapour Pressure Lowering.—For the other experimental methods the divergence function h of Lewis and Randall was generalised by Randall and White,⁵

$$h = 1 + (55.51 \ln a_1)/(\nu m) \quad . \quad . \quad . \quad (2)$$

For vapour pressure lowering we substitute for $\ln a_1$,

$$\ln a_1 = - \frac{p_1^0 - p_1}{p_1^0} - \frac{1}{2} \left(\frac{p_1^0 - p_1}{p_1^0} \right)^2 - \dots, \quad . \quad . \quad (3)$$

where p_1^0 is the vapour pressure of the pure solvent and p_1 is the vapour pressure of the solution.

Osmotic Pressure.—For osmotic pressure we substitute for $\ln a_1$

$$\ln a_1 = - \frac{1}{RT} \int_{P^0}^P \bar{v}_1 dP \quad . \quad . \quad . \quad (4)$$

where R is expressed in c.c. atmos., P^0 is the pressure on the solvent in the standard state, P is the pressure on the solvent in osmotic equilibrium with

² Ref. 1 (b) pp. 288, 348.

³ A quantity Φ identical in value with $1 - j$ was called the osmotic coefficient by Bjerrum (*Z. Elektrochem.*, **24**, 321 (1918)). The function j is a property of the solvent.

⁴ Randall and Adams, unpublished.

⁵ Randall and White, *J. Amer. Chem. Soc.* **48**, 2514 (1926).

the solution, $(P - P^0)$ is the osmotic pressure, and \bar{v}_1 is the partial molal volume of the solvent. The value of the integral is found by plotting \bar{v}_1 as ordinate, the osmotic pressure as abscissa, and taking the area under the curve to the pressure measured. Whence,

$$h = 1 - (55.51 \times \text{Area}) / (82.07 \, \nu m T) \quad (5)$$

Or, if the solution is dilute, we may take \bar{v}_1 as constant and equal to the molal volume, whence

$$h = 1 - 12.185 (P - P^0) / (\nu m T). \quad (\text{approx.}) \quad (6)$$

Dew-Point Lowering.—Randall, McBain, and White⁶ reduced the dew point lowering to the equivalent vapour pressure and then used Equation 3.

The distribution and electromotive force measurements give a_1 or $\ln a_1$ which can be substituted directly in Equation 2.

Non-Electrolytes.—In the case of non-electrolytes Lewis and Randall assumed h/m or j/m to approach constancy in the dilute solutions. There are no reliable data to test this assumption. The values of the function are not very large, but within the limits of the experimental error it has been verified by Randall⁷ for the freezing-point data, by Randall and Adams⁷ for the boiling-point data, and by Randall and Batchelder⁷ for the osmotic pressure data. Bury⁸ has deduced the limiting value of j/m at $m = 0$, by showing that it is equal to the negative of the slope of the curve of θ/m plotted against θ (B plot of Lewis and Randall). Bury's device is especially valuable as it uses the data in the more concentrated solutions, which are relatively the most accurate, as an aid in determining the limit at $m = 0$.

Determinations by these methods can be plotted with j/m or h/m against m on the same piece of paper, or they may be plotted on transparent paper and superimposed for the purpose of aiding in the selection of the most probable value.

The value of the activity coefficient is then given by

$$\log \gamma' = - \frac{j}{2.303} - \frac{1}{2.303} \int_0^m \frac{j}{m} dm + 0.00025 \int_0^m \frac{\theta}{m} d\theta - 55.51 \int_0^m \frac{1}{m} dx \quad (7)$$

where the value of the first integral is the area under the curve of j/m against m . The value of the second integral is small except in concentrated solutions. The value of the last integral, which depends upon the heat of dilution, is also small. These are fully discussed by Lewis and Randall. In the case of the h function the second and third integrals do not appear, and the value of the activity coefficient is at the temperature of the measurements.

Dissociable Substances and Electrolytes.—Randall and White⁹ have shown that the values of $j/m^{\frac{1}{2}}$ or of $h/m^{\frac{1}{2}}$ for strong electrolytes when plotted against $m^{\frac{1}{2}}$ will approach limiting values at $m = 0$, which are the same for each valence type. This limit may be obtained empirically or from the Debye and Hückel¹⁰ theory which requires a slightly different limit for each temperature owing to a change in the dielectric constant of the water. For electrolytes, therefore, we plot $j/m^{\frac{1}{2}}$ or $h/m^{\frac{1}{2}}$ against $m^{\frac{1}{2}}$ and obtain the activity coefficient from the equation,

$$\log \gamma' = - \frac{j}{2.303} - \frac{2}{2.303} \int_0^m \frac{j}{m^{\frac{1}{2}}} dm^{\frac{1}{2}} + \frac{0.00025}{\nu} \int_0^m \frac{\theta}{m} d\theta - \frac{55.51}{\nu} \int_0^m - \frac{1}{m} dx \quad (8)$$

⁶ Randall, McBain, and White, *J. Amer. Chem. Soc.*, **48**, 2517 (1926).

⁷ Unpublished. All the available data have been studied.

⁸ Bury, *J. Amer. Chem. Soc.*, **48**, 3123 (1926).

⁹ (a) Randall, *J. Amer. Chem. Soc.*, **48**, 2514 (1926); (b) Randall and White, *Ref. 5*.

¹⁰ Debye and Hückel, *Physikal. Z.*, **24**, 185 (1923).

where the first integral is the area under the curve of $j/m^{\frac{1}{2}}$ and the others are the same as those in Equation 7.

We are thus able to use the same plot to obtain the activity coefficient from measurements by any of the methods which measure the activity of the solvent. We may also compare this plot with that of similar salts by superimposition. If the substance is not a typical strong electrolyte, as an alkali nitrate, or barium nitrate or sulphuric acid,¹¹ then the plot of $j/m^{\frac{1}{2}}$ will rise above the curve of other salts of the same type in dilute solution, but the curve will approach the same limit, at $m = 0$. If the electrolyte is only moderately strong, as in the case of cadmium chloride, the rise in the dilute end may amount to a decided peak in the curve. In general, if the salt is highly hydrated in solution then the $j/m^{\frac{1}{2}}$ curve is low and the values of the activity coefficient are high. For salts of about the same degree of hydration, the weaker salts, or those having an ionic diameter less than the distance of nearest approach of the ions,¹² will have curves lying above the curves of the stronger salt.

Activity Coefficients of Aqueous Solutions from Determinations of the Activity of the Solute.

The activity coefficient as determined from the activity of the solvent at various temperatures may be corrected to any other temperature by aid of the values of the partial molal heat content and capacity, and the results shown by a plot of $\log \gamma$ against the square root of the ionic strength, $\mu^{\frac{1}{2}}$. We shall show that the results of the measurements by all other methods may be transformed so that $\log \gamma$ plus a constant may be plotted on the same scale against the square root of the ionic strength. Then by superimposing all the curves the best value of the constant in each case can be determined and the several curves averaged.

Electromotive Force.—From the electromotive force of cells without liquid junctions in which the electrodes react in such a way as to form in solution the substance whose activity is desired, we may write

$$\log \gamma - \frac{E^0}{(0.00019844 \nu T)/N} = - \frac{E}{(0.00019844 \nu T)/N} - \log m_{\pm} \quad (9)$$

where E is the measured electromotive force, ν the number of ions formed from each molecule of dissolved substance, N the number of equivalents of electricity per molecule of solute formed, m_{\pm} the stoichiometric mean molality, and E^0 is the standard *E.M.F.*, or the *E.M.F.* when the ions of the solute are at unit activity. The value of the constant is to be obtained by reference to the $\log \gamma$ vs. $\mu^{\frac{1}{2}}$ plot. Of course, a primary extrapolation to $m = 0$ can be made, using the theoretically required slope at the axis as an aid. The standard *E.M.F.*, E^0 , equals $\text{const.} \times (0.00019844 \nu T)/N$.

In concentration cells without liquid junctions the following equation is used:

$$\log \gamma + \text{const.} = - \frac{E}{(0.00019844 \nu T)/N} - \log m_{\pm} \quad (10)$$

where m_{\pm} is the mean molality of the ions at the varied concentrations. In making the plot against $\mu^{\frac{1}{2}}$, $\log \gamma + \text{const.} = - \log m_{\pm}'$, where m_{\pm}' is the fixed concentration, is also used as one of the points. The constant when found is really $-(\log m_{\pm}' + \log \gamma')$.

¹¹ Randall and Scott, *J. Amer. Chem. Soc.*, **49**, 647 (1927).

¹² See Bjerrum, *Det. Kgl. Danske Videnskab Selskab Math.-fys. Medd.*, **7**, No. 9 (1926).

Vapour Pressure of the Solute.—The activity of the solute is proportional to the fugacity of the solute in the gas, or, as a first approximation, proportional to the partial pressure of the solute. Hence we find $\log a_2 = \log p + \text{const.}$, or

$$\log \gamma + \text{const.} = (1/\nu) \log p - \log m_{\pm} \quad (11)$$

Distribution Ratios.—If the activity of the solute is proportional to the mol fraction of the solute in a second solvent, then

$$\log \gamma + \text{const.} = (1/\nu) \log N_2 - \log m_{\pm} \quad (12)$$

or, in general, if γ_u is the activity coefficient of the solute in the second phase, then

$$\log \gamma + \text{const.} = (1/\nu) \log (\gamma_u N_2) - \log m_{\pm} \quad (13)$$

The constant is the logarithm of the distribution ratio at infinite dilution.

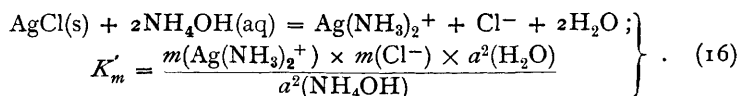
Solubility of Salt in a Mixture of Electrolytes.—The activity coefficient is proportional to the reciprocal of the mean molality of the ions of a saturated solution of a moderately soluble salt in water, for since a_2 , the activity of the salt, is constant (solid phase present),

$$\log a_2 = \log (m_{\pm} \gamma)^{\nu} \quad (14)$$

$$\text{and} \quad \log \gamma + \text{const.} = \log (1/m_{\pm}) \quad (15)$$

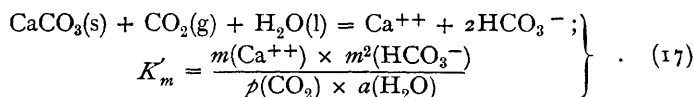
If the salt whose ions are added have the same characteristics, *i.e.* activity coefficient, as the saturating salt the activity coefficient curve of the saturating salt would be continued without a break, but if the added salt has different characteristics there will be a break. We therefore plot the reciprocal of the mean molality against the square root of the ionic strength. By comparison of the curves obtained with the curves for various electrolytes which we would expect to have activity coefficients of about the same values as those of the saturating salt, we are able to obtain the value of the proportionality factor or constant.¹³

The Equilibrium Constant of a Reaction.—If we consider a reaction in which only pure solids, liquids, gases or weak electrolytes and equivalent amounts of positive and negative ions are formed from solids, liquids, gases or weak electrolytes, we may obtain the activity coefficient of the dissolved salt in a way similar to that of moderately soluble salts. Consider a reaction such as



which has been studied by Randall and Halford¹⁴

or



which has been studied by Randall and Tamele.¹⁵ The equilibrium constant is written so that only one mol of the salt being considered is formed. The activities of the solids are constant; those of the weak electrolytes can

¹³ Randall and Vietti (unpublished) have examined all the available measurements.

¹⁴ Randall and Halford, unpublished.

¹⁵ Randall and Tamele, unpublished.

be determined from their vapour pressure, distribution ratio, or, as a first approximation, may be taken equal to the molality, if the solution is dilute. The activities of the gases are approximately equal to their pressure in atmospheres, or the fugacity can be found. The activity of the water is easily estimated to within a few tenths of a per cent. The activities of the ions are equal to the activity coefficient times their molality. If the stoichiometric molality of the ions and the activity of the other substances are substituted in the equilibrium expression it is seen that the activity coefficient is given by the equation,

$$\log \gamma + \text{const.} = (1/\nu) \log K'_m \quad . \quad . \quad . \quad (18)$$

The plots of $\log \gamma + \text{const.}$ and of $\log \gamma$ against $\mu^{\frac{1}{2}}$ are now superimposed, and by the aid of similar plots of the activity coefficients of other salts of similar type the best values are selected. We have thus been able to compare data determined by the various methods. Some of these methods give data that are more reliable in one range than in another, but the average result obtained by this procedure is the best that can be obtained.

Interpolation of Activity Coefficients.—A modification of an equation of Brönsted's¹⁶ has been suggested by Randall and Breckenridge¹⁷

$$(\log \gamma)/\mu^{\frac{1}{2}} = A + B\mu^{\frac{1}{2}} + C\mu + \dots \quad . \quad . \quad . \quad (19)$$

in which A, B and C are constants. A plot of $(\log \gamma)/\mu^{\frac{1}{2}}$ against $\mu^{\frac{1}{2}}$ is nearly a straight line for strong electrolytes, but for moderately strong electrolytes there is a minimum near the dilute end corresponding to the maximum referred to in discussing the $j/m^{\frac{1}{2}}$ against $m^{\frac{1}{2}}$ curves. The intersection on the axis is at A, which corresponds to the slope of the $\log \gamma$ against $\mu^{\frac{1}{2}}$ curve near $m = 0$.

Summary.

Methods of calculating the activity coefficient of the solute from that of the solvent are suggested in which the results from all the different methods are brought into the same plot. (j/m vs. m and $h/m^{\frac{1}{2}}$ vs. $m^{\frac{1}{2}}$ plots.)

The results of the previous methods and those from measurements which give the activity of the solute are correlated in such a way that the plots may be superimposed and the best average values selected. ($\log \gamma + \text{const.}$ vs. $\mu^{\frac{1}{2}}$ plots.)

A method of interpolating the activity coefficients of strong electrolytes is suggested. ($\log \gamma)/\mu^{\frac{1}{2}}$ vs. $\mu^{\frac{1}{2}}$ plots.)

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¹⁶ Brönsted, *Z. Amer. Chem. Soc.*, **45**, 2998 (1923)

¹⁷ Randall and Breckenridge, *ibid.*, **49** (1927).