

Activity Coefficients of Strong Electrolytes in Aqueous Solution—Effect of Temperature

H. P. MEISSNER

Chemical Engineering Department
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

C. L. KUSIK

Arthur D. Little, Inc.,
Cambridge, Massachusetts 02140

JEFFERSON W. TESTER

Chemical Engineering Department
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

The reduced activity coefficient Γ for an individual strong electrolyte in aqueous solution is defined as γ_{\pm}^{1/z_+z_-} where γ_{\pm} is the mean ionic activity coefficient and z_+ and z_- are the charges on the cations and anions respectively. A generalized relation at 25°C between Γ and μ , the ionic strength, is shown graphically in Figure 1 (Meissner and Tester, 1972). Since there is usually only minor curve cross over in this family of curves, the entire curve for any strong electrolyte can be located on Figure 1 from a single value of Γ at 25°C available at a μ of 2 or higher.

Given the necessary data, a family of curves similar to that of Figure 1 could presumably be constructed at any temperature resulting, however, in a multiplicity of charts. The object here is to propose a general method whereby Figure 1 alone can be used for predicting values of γ_{\pm} for any strong electrolyte in aqueous solution over temperatures ranging from 0° to 150°C and higher.

TEMPERATURE VERSUS Γ

Values of γ_{\pm} at other than 25°C are reported in the literature for few electrolyte solutions. The change of γ_{\pm} with temperature can, of course, be calculated from partial molal enthalpies of solution using the familiar thermodynamic relations (for example, Robinson and Stokes, 1955), but few such enthalpy measurements are reported. Fortunately, abundant data exist on the vapor pressures of water over solutions of many electrolytes at various concentrations and temperatures (International Critical Tables, 1926; Smithsonian Physical Tables, 1954). The quantity γ_{\pm} can be determined from these vapor pressures by use of the familiar Gibbs-Duhem equation, written as follows for aqueous electrolytes of molality m (Pitzer and Brewer, 1961; Harned and Owen, 1958).

$$d \ln \gamma_{\pm} = -d \ln m - \frac{55.5}{\nu m} d \ln a_w \quad (1)$$

Here a_w is the activity of water, namely the ratio of water's vapor pressure over the solution divided by the vapor pressure of pure water at the temperature in question. Similarly, ν is the number of moles of ions formed upon complete dissociation of one mole of the electrolyte in question.

Equation (1) is relatively simple to integrate for any given temperature over the concentration range from 0.01 molal (in the Debye-Huckel region where γ_{\pm} can be directly calculated) to any higher concentration. Examina-

tion of the isothermal curves of Γ versus μ so calculated for solutions of various electrolytes leads to the following observations:

1. As a first approximation, for temperatures from 0°C to over 100°C, isothermal curves of $\log \Gamma$ versus μ for 40 typical strong electrolytes were found to remain members of the curve family of Figure 1. Therefore, to locate a curve for, say CaBr_2 on Figure 1 at a temperature such as 80°C, it is merely necessary to have available a known value of $\log \Gamma$ at 80°C for some value of μ above 2. Locating this point on Figure 1, the entire curve can be drawn in immediately.

2. A change in temperature has no effect upon γ_{\pm} values at any given ionic strength for solutions of those electrolytes represented by the dotted curve of Figure 1. Thus, this dotted curve applies to all temperatures, from the freezing point to the boiling point.

3. For a system whose curve at 25°C of $\log \Gamma$ versus μ lies either above or below the dotted curve on Figure 1, a change in temperature at constant μ in the range of from

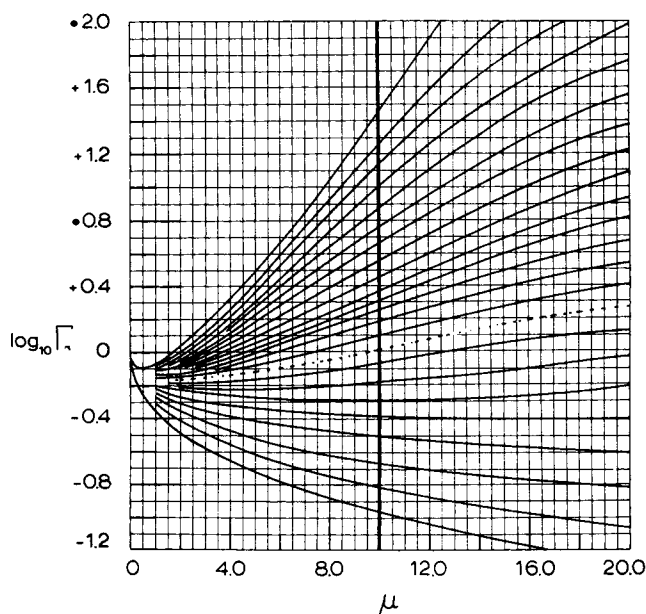


Fig. 1. Generalized isothermal lines of the reduced activity coefficient Γ versus the ionic strength μ . The dotted line, which passes through the point where $\log \Gamma$ is 0 when μ is 10, separates the regions of positive and negative temperature dependence.

0°C to 150°C will cause a shift in Γ . For systems whose curves lie above the dotted curve on Figure 1, an increase in temperature always results in a diminution in Γ . For systems with curves below this dotted curve, an increase in temperature causes an increase in Γ .

For a solution of any given strong electrolyte at a given μ , the quantity $\log \Gamma_T$ is found to be a unique function of $\log \Gamma_{25^\circ\text{C}}$. At a constant μ of 10, this function becomes linear, in that at a fixed temperature T , a plot of $\log \Gamma_T$ versus $\log \Gamma_{25^\circ\text{C}}$ for various electrolytes forms a straight line. This is illustrated by Figure 2, on which points of $\log \Gamma_{100^\circ\text{C}}$ [calculated from Equation (1)] are plotted against $\log \Gamma_{25^\circ\text{C}}$ for selected electrolytes. It was also found that at any fixed μ , the quantity $\log \Gamma_T$ generally varies in a linear fashion with temperature. Thus for HCl in a solution in which μ (and also molality) equals 10, Akerlof and Teare (1937) showed experimentally that $\log \Gamma$ diminishes by (0.059 ± 0.001) for each increase of 10°C in temperatures between 0°C and 50°C.

The following empirical equation, which applies only at a μ value of 10 and temperatures in the range of 0° to 150°C, expresses the foregoing analytically:

$$\log(\Gamma_T)_{\mu=10} = \{1 - 0.0050(T - 25)\} \log(\Gamma_{25^\circ\text{C}})_{\mu=10} \quad (2)$$

Note that $\log \Gamma_{25^\circ\text{C}}$ is zero when μ equals 10 for the dotted curve of Figure 1, and so as expected from Equation (2) any change in temperature leaves Γ_T equal to $\Gamma_{25^\circ\text{C}}$, namely unity. Similarly, for points above the dotted line of Figure 1, by Equation (2), an increase in temperature causes Γ_T to diminish relative to $\Gamma_{25^\circ\text{C}}$. Again for points lying below the dotted line by Equation (2), Γ_T increases relative to $\Gamma_{25^\circ\text{C}}$ as temperature increases. It is therefore obvious that, knowing the curve on Figure 1 which applies to the electrolyte in question at 25°C, the curve for any other temperature can be immediately located by use of Equation (2). To illustrate: $\log \Gamma$ at 25°C for HCl is reported to be 1.6179 at a μ value of 16 (Akerlof and Teare, 1937). Locating this point on Figure 1 and moving down the curve thus identified, $\log \Gamma$ at 25°C and a μ of 10 is found to be 0.96. Substituting into Equation (2) $\log \Gamma$ at 50°C and a μ of 10 is 0.84 compared to an experimental value of 0.8699. Following up the corresponding curve on Figure 1 ($\log \Gamma = 0.84$; $\mu = 10$) to where μ equals 16, $\log \Gamma$ is here shown to be 1.42, versus an experimental value of 1.373.

DISCUSSION

Only limited experimental data are available on activity coefficients of electrolytes in aqueous solutions at higher ionic strengths and temperatures other than 25°C. Few direct tests of these methods for relating γ_{\pm} of an electrolyte to temperature can therefore be made, and other test procedures must be adopted. Thus, the values of $\log \Gamma_{100^\circ\text{C}}$ at an ionic strength of 10 calculated by Equation (1) from isothermal vapor pressure data at 100°C for selected electrolytes, plotted as points on Figure 2, fall reasonably close to the line on this figure for Equation (2). Agreement between the points and the line is usually within 20% of the value calculated by Equation (1), although in some cases as with BeSO_4 the error is as great as 45%. Such errors encountered with Equation (2) tend to diminish at T values below 100°C. This behavior is observed despite the finding that when μ is 10, $\log \Gamma_T$ is often only approximately linear in T , and for some materials, such as NaOH, $\log \Gamma$ shows a shallow maximum between 0° and 100°C. In these latter cases, however, the

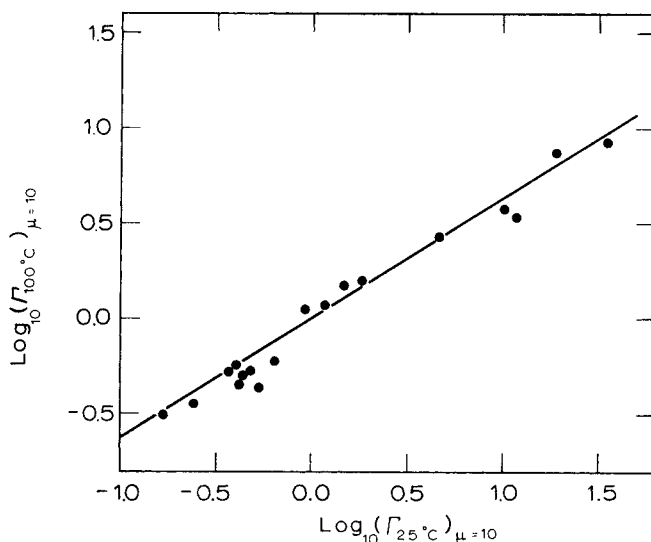


Fig. 2. $\log \Gamma_{100^\circ\text{C}}$ versus $\log \Gamma_{25^\circ\text{C}}$ at a μ value of 10. Moving from left to right, the points are for the following compounds: NH_4NO_3 , PbSO_4 , Na_2SO_4 , K_2CrO_7 , NH_4Cl , MnSO_4 , NiSO_4 , BeSO_4 , $\text{Ca}(\text{NO}_3)_2$, KI , AlCl_3 , NaCl , CaBr_2 , NaI , LiCl , HCl , LiBr .

curves of $\log \Gamma$ versus μ lie relatively close to the dotted curve of Figure 1, so that \log of $\Gamma_T/\Gamma_{25^\circ\text{C}}$ is small at worst. Other sources of error are discussed elsewhere (Meissner and Tester, 1972; Meissner and Kusik, 1972). This method is therefore to be used only when experimental data are not available.

As temperatures increase, isotherms for all electrolytes move towards the dotted line of Figure 1, with some indication that they may all fall together on this dotted line at all temperatures over about 250°C. Equation (2), however, has been tested only up to 150°C and obviously cannot be used much above this temperature.

Mixture rules have been presented (Meissner and Kusik, 1972) for estimating γ_{\pm} values at 25°C of an electrolyte in an aqueous solution containing several other electrolytes. To apply these rules at 25°C, information is required on Γ values of individual electrolytes in "pure" solution at 25°C. These same rules are applicable without modification to any other temperature, given information on Γ for the individual electrolytes in pure solution at this new temperature. Thus, by use of Figure 1 and Equation (2), the mixture rules formulated for 25°C can be extended to other temperatures.

LITERATURE CITED

- Akerlof, G., and J. W. Teare, "Thermodynamics of Concentrated Aqueous Solutions of Hydrochloric Acid," *J. Am. Chem. Soc.*, **59**, 1855 (1937).
- Harned, H. S., and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," 3rd ed., Reinhold, New York (1958).
- International Critical Tables, Vol. 3, pp. 361-380, McGraw-Hill, New York (1926).
- Meissner, H. P., and J. W. Tester, "Activity Coefficients of Strong Electrolytes in Aqueous Solution," *Ind. Eng. Chem. Process Design Develop.*, **11**, 128 (1972).
- Meissner, H. P., and C. L. Kusik, "Activity Coefficients of Strong Electrolytes in Multicomponent Aqueous Solutions," *AIChE J.*, **18**, 294 (1972).
- Pitzer, K. S., and L. Brewer, "Thermodynamics," 2nd ed. McGraw-Hill, New York (1961).
- Robinson, R. A., and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1955).
- Smithsonian Physical Tables, Smithsonian Inst. Publ., pp. 374-5, 9th Rev. ed. Wash. D. C. (1954).