

## 11.4: Enthalpies of Solution and Dilution

The processes of solution (dissolution) and dilution are related. The IUPAC Green Book (E. Richard Cohen et al, *Quantities, Units and Symbols in Physical Chemistry*, 3rd edition, RSC Publishing, Cambridge, 2007, Sec. 2.11.1) recommends the abbreviations sol and dil for these processes.

For an electrolyte solute, a plot of  $\Delta H_m(\text{sol}, m_B)$  versus  $m_B$  has a limiting slope of  $+\infty$  at  $m_B=0$ , whereas the limiting slope of  $\Delta H_m(\text{sol}, m_B)$  versus  $\sqrt{m_B}$  is finite and can be predicted from the Debye–Hückel limiting law. Accordingly, a satisfactory procedure is to plot  $\Delta H_m(\text{sol}, m_B)$  versus  $\sqrt{m_B}$ , perform a linear extrapolation of the experimental points to  $\sqrt{m_B}=0$ , and then shift the origin to the extrapolated intercept. The result is a plot of  $\Phi_L$  versus  $\sqrt{m_B}$ . An example for aqueous NaCl solutions is shown in Fig. 11.10(a).

We can also evaluate  $\Phi_L$  from experimental enthalpies of dilution. From Eqs. 11.4.10 and 11.4.22, we obtain the relation

$$\Phi_L(m_B'') - \Phi_L(m_B') = \Delta H_m(\text{dil}, m_B' \rightarrow m_B'') \quad (11.4.25)$$

We can measure the enthalpy changes for diluting a solution of initial molality  $m_B'$  to various molalities  $m_B''$ , plot the values of  $\Delta H_m(\text{dil}, m_B' \rightarrow m_B'')$  versus  $\sqrt{m_B}$ , extrapolate the curve to  $\sqrt{m_B}=0$ , and shift the origin to the extrapolated intercept, resulting in a plot of  $\Phi_L$  versus  $\sqrt{m_B}$ .

In order to be able to use Eq. 11.4.23, we need to relate the derivative  $d\Phi_L/dm_B$  to the slope of the curve of  $\Phi_L$  versus  $\sqrt{m_B}$ . We write

$$d\sqrt{m_B} = \frac{1}{2\sqrt{m_B}} dm_B \quad dm_B = 2\sqrt{m_B} d\sqrt{m_B} \quad (11.4.26)$$

Substituting this expression for  $dm_B$  into Eq. 11.4.23, we obtain the following operational equation for evaluating  $L_B$  from the plot of  $\Phi_L$  versus  $\sqrt{m_B}$ :

$$L_B = \Phi_L + \frac{\sqrt{m_B}}{2} \frac{d\Phi_L}{d\sqrt{m_B}} \quad (11.4.27)$$

(constant  $T$  and  $p$ )

The value of  $\Phi_L$  goes to zero at infinite dilution. When the solute is an electrolyte, the dependence of  $\Phi_L$  on  $m_B$  in solutions dilute enough for the Debye–Hückel limiting law to apply is given by

$$\Phi_L = C_{\Phi_L} \sqrt{m_B} \quad (11.4.28)$$

(very dilute solution)

For aqueous solutions of a 1:1 electrolyte at 25 °C, the coefficient  $C_{\Phi_L}$  has the value

$$C_{\Phi_L} = 1.988 \times 10^3 \text{ J kg}^{1/2} \text{ mol}^{-3/2} \quad (11.4.29)$$

(The fact that  $C_{\Phi_L}$  is positive means, according to Eq. 11.4.25, that dilution of a very dilute electrolyte solution is an exothermic process.)  $C_{\Phi_L}$  is equal to the limiting slope of  $\Phi_L$  versus  $\sqrt{m_B}$ , of  $\Delta H_m(\text{sol}, m_B)$  versus  $\sqrt{m_B}$ , and of  $\Delta H_m(\text{dil}, m_B' \rightarrow m_B'')$  versus  $\sqrt{m_B}$ . The value given by Eq. 11.4.29 can be used for extrapolation of measurements at 25 °C and low molality to infinite dilution.

Equation 11.4.28 can be derived as follows. For simplicity, we assume the pressure is the standard pressure  $p^\circ$ . At this pressure  $H_B^\infty$  is the same as  $H_B^\circ$ , and Eq. 11.4.17 becomes  $L_B = H_B - H_B^\circ$ . From Eqs. 12.1.3 and 12.1.6 in the next chapter, we can write the relations

$$H_B = -T^2 \left[ \frac{\partial(\mu_B/T)}{\partial T} \right]_{p, \{n_i\}} \quad H_B^\circ = -T^2 \frac{d(\mu_{m,B}^\circ/T)}{dT} \quad (11.4.30)$$

Subtracting the second of these relations from the first, we obtain

$$H_B - H_B^\circ = -T^2 \left[ \frac{\partial(\mu_B - \mu_{m,B}^\circ)/T}{\partial T} \right]_{p, \{n_i\}} \quad (11.4.31)$$

The solute activity on a molality basis,  $a_{m,B}$ , is defined by  $\mu_B - \mu_{m,B}^\circ = RT \ln a_{m,B}$ . The activity of an electrolyte solute at the standard pressure, from Eq. 10.3.10, is given by  $a_{m,B} = (\nu_+^{\nu_+} \nu_-^{\nu_-}) \gamma_{\pm}^\nu (m_B/m^\circ)^\nu$ . Accordingly, the relative partial molar enthalpy of the solute is related to the mean ionic activity coefficient by

$$L_B = -RT^2 \nu \left( \frac{\partial \ln \gamma_{\pm}}{\partial T} \right)_{p, \{n_i\}} \quad (11.4.32)$$

We assume the solution is sufficiently dilute for the mean ionic activity coefficient to be adequately described by the Debye–Hückel limiting law, Eq. 10.4.8:  $\ln \gamma_{\pm} = -A_{DH} |z_+ z_-| \sqrt{I_m}$ , where  $A_{DH}$  is a temperature-dependent quantity defined in Sec. 10.4. Then Eq. 11.4.32 becomes

$$L_B = RT^2 \nu |z_+ z_-| \sqrt{I_m} \left( \frac{\partial A_{DH}}{\partial T} \right)_{p, \{n_i\}} \quad (11.4.33) \quad (\text{very dilute solution})$$

Substitution of the expression given by Eq. 10.4.9 for  $I_m$  in a solution of a single completely-dissociated electrolyte converts Eq. 11.4.33 to

$$L_B = \left[ \frac{RT^2}{\sqrt{2}} \left( \frac{\partial \rho_A^* A_{DH}}{\partial T} \right)_{p, \{n_i\}} (\nu |z_+ z_-|)^{3/2} \right] \sqrt{m_B} = C_{L_B} \sqrt{m_B} \quad (11.4.34) \quad (\text{very dilute solution})$$

The coefficient  $C_{L_B}$  (the quantity in brackets) depends on  $T$ , the kind of solvent, and the ion charges and number of ions per solute formula unit, but not on the solute molality.

Let  $C_{\Phi_L}$  represent the limiting slope of  $\Phi_L$  versus  $\sqrt{m_B}$ . In a very dilute solution we have  $\Phi_L = C_{\Phi_L} \sqrt{m_B}$ , and Eq. 11.4.27 becomes

$$L_B = \Phi_L + \frac{\sqrt{m_B}}{2} \frac{d\Phi_L}{d\sqrt{m_B}} = C_{\Phi_L} \sqrt{m_B} + \frac{\sqrt{m_B}}{2} C_{\Phi_L} \quad (11.4.35)$$

By equating this expression for  $L_B$  with the one given by Eq. 11.4.34 and solving for  $C_{\Phi_L}$ , we obtain  $C_{\Phi_L} = (2/3)C_{L_B}$  and  $\Phi_L = (2/3)C_{L_B} \sqrt{m_B}$ .

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