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.
During a solution process, a solute is transferred from a pure solute phase (solid, liquid, or gas) to a solvent or solution phase. During a dilution process, solvent is transferred from a pure solvent phase to a solution phase. We may specify the advancement of these two kinds of processes by \( \xi_{\text{sol}} \) and \( \xi_{\text{dil}} \), respectively. Note that both processes take place in closed systems that (at least initially) have two phases. The total amounts of solvent and solute in the systems do not change, but the amounts in pure phases diminish as the processes advance and \( \xi_{\text{sol}} \) or \( \xi_{\text{dil}} \) increases (Fig. 11.8).

The equations in this section are about enthalpies of solution and dilution, but you can replace \( H \) by any other extensive state function to obtain relations for its solution and dilution properties.

### 11.4.1 Molar enthalpy of solution

First let us consider a solution process in which solute is transferred from a pure solute phase to a solution. The molar differential enthalpy of solution, \( \Delta_{\text{sol}} H \), is the rate of change of \( H \) with the advancement \( \xi_{\text{sol}} \) at constant \( T \) and \( p \), where \( \xi_{\text{sol}} \) is the amount of solute transferred:

\[
\Delta_{\text{sol}} H = \frac{\partial H}{\partial \xi_{\text{sol}}} \tag{11.4.1}
\]

The value of \( \Delta_{\text{sol}} H \) at a given \( T \) and \( p \) depends only on the solution molality and not on the amount of solution.

When we write the solution reaction as \( B(s) \rightarrow B(\text{sln}) \), the general relation \( \Delta_{\text{sol}} H = H(B) - H(B^*) \) (Eq. 11.2.15) becomes:

\[
\Delta_{\text{sol}} H = H(B) - H(B^*) \tag{11.4.2}
\]

where \( H(B) \) is the partial molar enthalpy of the solute in the solution and \( H(B^*) \) is the molar enthalpy of the pure solute at the same \( T \) and \( p \).

The molar enthalpy of solution at infinite dilution, \( \Delta_{\text{sol}} H^\infty \), is the rate of change of \( H \) with \( \xi_{\text{sol}} \) when the solute is transferred to a solution with the thermal properties of an infinitely dilute solution. We can think of \( \Delta_{\text{sol}} H^\infty \) as the enthalpy change per amount of solute transferred to a very large volume of pure solvent. According to Eq. 11.4.2, this quantity is given by:

\[
\Delta_{\text{sol}} H^\infty = H(B^\infty) - H(B^*) \tag{11.4.3}
\]

Note that because the values of \( H(B^\infty) \) and \( H(B^*) \) are independent of the solution composition, the molar differential and integral enthalpies of solution at infinite dilution are the same.

An integral enthalpy of solution, \( \Delta H_{\text{sol}} \), is the enthalpy change for a process in which a finite amount \( \xi_{\text{sol}} \)
subs(sol) of solute is transferred from a pure solute phase to a specified amount of pure solvent to form a homogeneous solution phase with the same temperature and pressure as the initial state. Division by the amount transferred gives the molar integral enthalpy of solution which this e-book will denote by $\Delta H_{\text{solmB}}$, where $m_B$ is the molality of the solution formed:

$$\Delta H_{\text{solmB}} = \frac{\Delta H_{\text{sol}}}{\xi_{\text{sol}}} \tag{11.4.4}$$

An integral enthalpy of solution can be evaluated by carrying out the solution process in a constant-pressure reaction calorimeter, as will be described in Sec. 11.5.1. Experimental values of $\Delta H_{\text{sol}}$ as a function of $\xi_{\text{sol}}$ can be collected by measuring enthalpy changes during a series of successive additions of the solute to a fixed amount of solvent, resulting in a solution whose molality increases in stages. The enthalpy changes are cumulative, so the value of $\Delta H_{\text{sol}}$ after each addition is the sum of the enthalpy changes for this and the previous additions.

### Figure 11.9
Enthalpy change for the dissolution of NaCH$_3$CO$_2$(s) in one kilogram of water in a closed system at $298.15\, \text{K}$ and $1\, \text{atm}$, as a function of the amount $\xi_{\text{sol}}$ of dissolved solute (data from Donald D. Wagman et al, J. Phys. Chem. Ref. Data, 11, Supplement No. 2, 1982, page 2-315). The open circle at $\xi_{\text{sol}} = 15\, \text{mol}$ indicates the approximate saturation limit; data to the right of this point come from supersaturated solutions. At the composition $m_B = 15\, \text{mol kg}^{-1}$, the value of $\Delta H_{\text{solmB}}$ is the slope of line a and the value of $\Delta H_{\text{sol}}$ is the slope of line b. The value of $\Delta H_{\text{sol}}^\infty$ is the slope of line c.

The relations between $\Delta H_{\text{sol}}$ and the molar integral and differential enthalpies of solution are illustrated in Fig. 11.9 with data for the solution of crystalline sodium acetate in water. The curve shows $\Delta H_{\text{sol}}$ as a function of $\xi_{\text{sol}}$, with $\xi_{\text{sol}}$ defined as the amount of solute dissolved in one kilogram of water. Thus at any point along the curve, the molality is $m_B = \xi_{\text{sol}}/(1\, \text{units kg}^{-1})$, and the ratio $\Delta H_{\text{sol}}/\xi_{\text{sol}}$ is the molar integral enthalpy of solution $\Delta H_{\text{solmB}}$ for the solution process that produces solution of this molality. The slope
of the curve is the molar differential enthalpy of solution: 

\[
\Delta_{sol}H = \frac{\Delta H}{\Delta \xi_{subs}}
\]

(11.4.5) cond{(constant \(T\), \(p\), and \(nA\))} end{gather}

The slope of the curve at \(\xi_{subs} = 0\) is \(\Delta_{sol}H^\infty\), the molar enthalpy of solution at infinite dilution. If the measurements are made at the standard pressure, \(\Delta_{sol}H^\infty\) is the same as the standard molar enthalpy of solution, \(\Delta_{sol}(sol)H^\infty\), because the standard molar enthalpy of a solute is the molar enthalpy at \(p = p^\text{st}\) and infinite dilution.

### 11.4.2 Enthalpy of dilution

Next let us consider a dilution process in which solvent is transferred from a pure solvent phase to a solution phase. The molar differential enthalpy of dilution is the rate of change of \(H\) with the advancement \(\xi_{dil}\) at constant \(T\) and \(p\) of the dilution process, where \(\xi_{dil}\) is the amount of solvent transferred: 

\[
\Delta_{dil}H = \frac{\Delta H}{\Delta \xi_{dil}}
\]

(11.4.6) end{equation}

For the dilution reaction \(A^*_\rightarrow A\text{(sln)}\), the general relation \(\Delta_{r}X = \sum_{i} \nu_i X_i\) becomes 

\[
\Delta_{dil}H = H^\text{A} - H^\text{A^*}
\]

(11.4.7) end{equation}

where \(H^\text{A}\) is the partial molar enthalpy of the solvent in the solution. In the limit of infinite dilution, \(H^\text{A}\) must approach the molar enthalpy of pure solvent, \(H^\text{A^*}\); then Eq. 11.4.7 shows that \(\Delta_{dil}H\) approaches zero in this limit.

An integral enthalpy of dilution, \(\Delta H_{dil}\), refers to the enthalpy change for transfer of a finite amount of solvent from a pure solvent phase to a solution, \(T\) and \(p\) being the same before and after the process. The molar integral enthalpy of dilution is the ratio of \(\Delta H_{dil}\) and the amount of solute in the solution. For a dilution process at constant solute amount \(nB\) in which the molality changes from \(m^\text{B'}\) to \(m^\text{B''}\), this e-book will use the notation 

\[
\Delta H_{\text{dil, } m^\text{B'}\rightarrow m^\text{B''}} = \frac{\Delta H_{\text{dil}}}{nB}
\]

(11.4.8) end{equation} The value of \(\Delta H_{\text{dil}}\) at a given \(T\) and \(p\) depends only on the initial and final molalities \(m^\text{B'}\) and \(m^\text{B''}\).

There is a simple relation between molar integral enthalpies of solution and dilution, as the following derivation demonstrates. Consider the following two ways of preparing a solution of molality \(m^\text{B''}\) from pure solvent and solute phases. Both paths are at constant \(T\) and \(p\) in a closed system.

- **Path 1**: The solution forms directly by dissolution of the solute in the solvent. The enthalpy change is \(nB\Delta H_{\text{sol, } m^\text{B''}}\), where the molality of the solution is indicated in parentheses.
- **Path 2**: Starting with the unmixed solvent and solute, the solute dissolves in a portion of the solvent to form a solution of composition \(m^\text{B'}\) (more concentrated than \(m^\text{B''}\)). The enthalpy change is \(nB\Delta H_{\text{sol, } m^\text{B'}}\). In a second step of this path, the remaining pure solvent mixes with the solution to dilute it from \(m^\text{B'}\) to \(m^\text{B''}\). The enthalpy change of the second step is \(nB\Delta H_{\text{dil, } m^\text{B'}\rightarrow m^\text{B''}}\).

Since both paths have the same initial states and the same final states, both have the same overall enthalpy change: 

\[
\begin{align*}
\Delta H_{\text{sol, } m^\text{B''}} &= nB\Delta H_{\text{sol, } m^\text{B'}} + nB\Delta H_{\text{dil, } m^\text{B'}\rightarrow m^\text{B''}} \\
&= H_{\text{sol, } m^\text{B''}} - H_{\text{sol, } m^\text{B'}} + H_{\text{dil, } m^\text{B'}\rightarrow m^\text{B''}}
\end{align*}
\]

(11.4.9) end{equation} or \(\Delta H_{\text{sol, } m^\text{B''}} = H_{\text{sol, } m^\text{B''}} - H_{\text{sol, } m^\text{B'}} + \Delta H_{\text{dil, } m^\text{B'}\rightarrow m^\text{B''}}\)

(11.4.10) end{equation} Equation 11.4.10 is the desired relation. It shows how a measurement of the molar integral enthalpy change for a solution process that produces solution of a certain molality can be combined with dilution measurements in order to calculate molar integral enthalpies of solution for more dilute solutions.

Experimentally, it is sometimes more convenient to carry out the dilution process than the solution process, especially when the pure solute is a gas or solid.
11.4.3 Molar enthalpies of solute formation

Molar integral enthalpies of solution and dilution are conveniently expressed in terms of molar enthalpies of formation. The molar enthalpy of formation of a solute in solution is the enthalpy change per amount of solute for a process at constant \(T\) and \(p\) in which the solute, in a solution of a given molality, is formed from its constituent elements in their reference states. The molar enthalpy of formation of solute B in solution of molality \(m_B\) will be denoted by \(\Delta f H^\text{(B, } m_B)\).

As explained in Sec. 11.3.2, the formation reaction of a solute in solution does not include the formation of the solvent from its elements. For example, the formation reaction for NaOH in an aqueous solution that has \(50\) moles of water for each mole of NaOH is:

\[
\text{Na(s)} + \frac{1}{2}\text{O}_2(g) + \frac{1}{2}\text{H}_2(g) + 50 \text{H}_2\text{O(l)} \rightarrow \text{NaOH in 50 H}_2\text{O}.
\]

Consider a solution process at constant \(T\) and \(p\) in which an amount \(n_B\) of pure solute (solid, liquid, or gas) is mixed with an amount \(n_A\) of pure solvent, resulting in solution of molality \(m_B\). We may equate the enthalpy change of this process to the sum of the enthalpy changes for the following two hypothetical steps:

1. An amount \(n_B\) of the pure solute decomposes to the constituent elements in their reference states. This is the reverse of the formation reaction of the pure solute.
2. The solution is formed from these elements and an amount \(n_A\) of the solvent.

The total enthalpy change is then

\[
\Delta H_{\text{sol}} = \Delta f H^\text{(B\(^*\))} + \Delta f H^\text{(B, } m_B)\). Dividing by \(n_B\), we obtain the molar integral enthalpy of solution:

\[
\Delta H_{\text{sol}} = \Delta f H^\text{(B, } m_B)\) - \Delta f H^\text{(B\(^*\))} \tag{11.4.11}
\]

By combining Eqs. 11.4.10 and 11.4.11, we obtain the following expression for a molar integral enthalpy of dilution in terms of molar enthalpies of formation:

\[
\Delta H_{\text{dil}} = \Delta f H^\text{(B, } m_B\) - \Delta f H^\text{(B\(^*\))} \tag{11.4.12}
\]

From tabulated values of molar enthalpies of formation, we can calculate molar integral enthalpies of solution with Eq. 11.4.11 and molar integral enthalpies of dilution with Eq. 11.4.12. Conversely, calorimetric measurements of these molar integral enthalpies can be combined with the value of \(\Delta f H^\text{(B\(^*\))}\) to establish the values of molar enthalpies of solute formation in solutions of various molalities.

11.4.4 Evaluation of relative partial molar enthalpies

Although it is not possible to determine absolute values of partial molar enthalpies, we can evaluate \(\frac{\Delta H}{n_A}\) and \(\frac{\Delta H}{n_B}\) relative to appropriate solvent and solute reference states.

The relative partial molar enthalpy of the solvent is defined by:

\[
\Delta A^\text{H} \defeq \Delta A^\text{H} - \Delta A^\text{H}^* \tag{11.4.13}
\]

This is the partial molar enthalpy of the solvent in a solution of given composition relative to pure solvent at the same temperature and pressure.

\(\Delta A^\text{H}\) can be related to molar differential and integral enthalpies of solution as follows. The enthalpy change to form a solution from amounts \(n_A\) and \(n_B\) of pure solvent and solute is given, from the additivity rule, by:

\[
\Delta H = n_A \Delta A^\text{H} + n_B \Delta A^\text{H}^* \tag{11.4.14}
\]

This equation is derived from the additivity rule by taking the difference between the total molar enthalpy of solution and the molar enthalpy of solute formation.

By combining Eqs. 11.4.11 and 11.4.14, we obtain:

\[
\Delta A^\text{H} = \frac{\Delta H - n_B \Delta A^\text{H}^*}{n_A} \tag{11.4.15}
\]

From Eq. 11.4.15, we can calculate the relative partial molar enthalpy of the solvent in any molality of solution for a given solute.

The relative partial molar enthalpy of the solute is defined by:

\[
\Delta B^\text{H} \defeq \Delta B^\text{H} - \Delta B^\text{H}^* \tag{11.4.16}
\]

This is the partial molar enthalpy of the solute in a solution of given composition relative to pure solute at the same temperature and pressure.

By combining Eqs. 11.4.12 and 11.4.16, we obtain:

\[
\Delta B^\text{H} = \frac{\Delta H - n_B \Delta A^\text{H}^*}{n_B} \tag{11.4.17}
\]

From Eq. 11.4.17, we can calculate the relative partial molar enthalpy of the solute in any molality of solution for a given solvent.

11.4.5 Evaluation of relative molar enthalpies

Although it is not possible to determine absolute values of molar enthalpies, we can evaluate \(\frac{\Delta H}{n_A}\) and \(\frac{\Delta H}{n_B}\) relative to appropriate solvent and solute reference states.

The relative partial molar enthalpy of the solvent is defined by:

\[
\Delta A^\text{H} \defeq \Delta A^\text{H} - \Delta A^\text{H}^* \tag{11.4.18}
\]

This is the partial molar enthalpy of the solvent in a solution of given composition relative to pure solvent at the same temperature and pressure.

\(\Delta A^\text{H}\) can be related to molar differential and integral enthalpies of solution as follows. The enthalpy change to form a solution from amounts \(n_A\) and \(n_B\) of pure solvent and solute is given, from the additivity rule, by:

\[
\Delta H = n_A \Delta A^\text{H} + n_B \Delta A^\text{H}^* \tag{11.4.19}
\]

This equation is derived from the additivity rule by taking the difference between the total molar enthalpy of solution and the molar enthalpy of solute formation.

By combining Eqs. 11.4.11 and 11.4.19, we obtain:

\[
\Delta A^\text{H} = \frac{\Delta H - n_B \Delta A^\text{H}^*}{n_A} \tag{11.4.20}
\]

From Eq. 11.4.20, we can calculate the relative partial molar enthalpy of the solvent in any molality of solution for a given solute.

The relative partial molar enthalpy of the solute is defined by:

\[
\Delta B^\text{H} \defeq \Delta B^\text{H} - \Delta B^\text{H}^* \tag{11.4.21}
\]

This is the partial molar enthalpy of the solute in a solution of given composition relative to pure solute at the same temperature and pressure.

By combining Eqs. 11.4.12 and 11.4.21, we obtain:

\[
\Delta B^\text{H} = \frac{\Delta H - n_B \Delta A^\text{H}^*}{n_B} \tag{11.4.22}
\]

From Eq. 11.4.22, we can calculate the relative partial molar enthalpy of the solute in any molality of solution for a given solvent.

11.4.6 Evaluation of relative molar enthalpies

Although it is not possible to determine absolute values of molar enthalpies, we can evaluate \(\frac{\Delta H}{n_A}\) and \(\frac{\Delta H}{n_B}\) relative to appropriate solvent and solute reference states.

The relative partial molar enthalpy of the solvent is defined by:

\[
\Delta A^\text{H} \defeq \Delta A^\text{H} - \Delta A^\text{H}^* \tag{11.4.23}
\]

This is the partial molar enthalpy of the solvent in a solution of given composition relative to pure solvent at the same temperature and pressure.

\(\Delta A^\text{H}\) can be related to molar differential and integral enthalpies of solution as follows. The enthalpy change to form a solution from amounts \(n_A\) and \(n_B\) of pure solvent and solute is given, from the additivity rule, by:

\[
\Delta H = n_A \Delta A^\text{H} + n_B \Delta A^\text{H}^* \tag{11.4.24}
\]

This equation is derived from the additivity rule by taking the difference between the total molar enthalpy of solution and the molar enthalpy of solute formation.

By combining Eqs. 11.4.11 and 11.4.24, we obtain:

\[
\Delta A^\text{H} = \frac{\Delta H - n_B \Delta A^\text{H}^*}{n_A} \tag{11.4.25}
\]

From Eq. 11.4.25, we can calculate the relative partial molar enthalpy of the solvent in any molality of solution for a given solute.

The relative partial molar enthalpy of the solute is defined by:

\[
\Delta B^\text{H} \defeq \Delta B^\text{H} - \Delta B^\text{H}^* \tag{11.4.26}
\]

This is the partial molar enthalpy of the solute in a solution of given composition relative to pure solute at the same temperature and pressure.

By combining Eqs. 11.4.12 and 11.4.26, we obtain:

\[
\Delta B^\text{H} = \frac{\Delta H - n_B \Delta A^\text{H}^*}{n_B} \tag{11.4.27}
\]

From Eq. 11.4.27, we can calculate the relative partial molar enthalpy of the solute in any molality of solution for a given solvent.
A \( H_A + n_B \cdot H_B \) - (n\( A \cdot \Delta H_A \cdot A^* + n_B \cdot \Delta H_B \cdot B^* \)). We rearrange and make substitutions from Eqs. 11.4.2 and 11.4.13:

\[
\begin{split}
\Delta H_{\text{sol}} &= n_A (H_A - H_A^*) + n_B (H_B - H_B^*) \\
&= n_A L_A + n_B \Delta H_{\text{sol}} \tag{11.4.14}
\end{split}
\]

Equating both expressions for \( \Delta H_{\text{sol}} \)

\[
\Delta H_{\text{sol}} = n_B \Delta H_{\text{sol}} \tag{11.4.15}
\]

Solving for \( L_A \), we obtain:

\[
L_A = \frac{M_A m_B \Delta H_{\text{sol}}}{\Delta H_{\text{sol}} - \Delta H_{\text{sol}}^*} \tag{11.4.16}
\]

Thus \( (L_A) \) depends on the difference between the molar integral and differential enthalpies of solution.

The relative partial molar enthalpy of a solute is defined by

\[
L_B \defeq H_B - H_B^\infty \tag{11.4.17}
\]

The reference state for the solute is the solute at infinite dilution. To relate \( (L_B) \) to molar enthalpies of solution, we write the identity

\[
L_B = H_B - H_B^\infty = (H_B - H_B^*) - (H_B^\infty - H_B^*) \tag{11.4.18}
\]

From Eqs. 11.4.2 and 11.4.3, this becomes

\[
L_B = \Delta H_{\text{sol}} - \Delta H_{\text{sol}}^\infty \tag{11.4.19}
\]

We see that \( (L_B) \) is equal to the difference between the molar differential enthalpies of solution at the molality of interest and at infinite dilution.

For a solution of a given molality, \( (L_A) \) and \( (L_B) \) can be evaluated from calorimetric measurements of \( \Delta H_{\text{sol}} \) by various methods. Three general methods are as follows. The descriptions refer to graphical plots with smoothed curves drawn through experimental points. A plot can be replaced by an algebraic function (e.g., a power series) fitted to the points, and slopes and intercepts can then be evaluated by numerical methods.

1. \( (L_A) \) and \( (L_B) \) can be evaluated by the variant of the method of intercepts described in Sec. 9.2.3. The molar integral enthalpy of mixing, \( (\Delta H_{\text{mix}} = \Delta H_{\text{sol}}/(n_A + n_B)) \), is plotted versus \( (x_B) \). The tangent to the curve at a given value of \( (x_B) \) has intercepts \( (L_A) \) at \( (x_B = 0) \) and \( (H_B - H_B^* = \Delta H_{\text{sol}} H) \) at \( (x_B = 1) \), where the values of \( (L_A) \) and \( (\Delta H_{\text{sol}} H) \) are for the solution of composition \( (x_B) \). The tangent to the curve at \( (x_B = 0) \) has intercept \( (\Delta H_{\text{sol}} H^\infty) \) at \( (x_B = 1) \). \( (L_B) \) is equal to the difference of these values of \( (\Delta H_{\text{sol}} H) \) and \( (\Delta H_{\text{sol}} H^\infty) \) (Eq. 11.4.19).

2. Values of \( (\Delta H_{\text{sol}} H) \) for a constant amount of solvent can be plotted as a function of \( (\xi_{\text{sol}}) \), as in Fig. 11.9. The slope of the tangent to the curve at any point on the curve is equal to \( (\Delta H_{\text{sol}} H) \) for the molality \( (m_B) \) at that point, and the initial slope at \( (\xi_{\text{sol}}) = 0) \) is equal to \( (\Delta H_{\text{sol}} H^\infty) \). \( (L_B) \) at molality \( (m_B) \) is equal to the difference of these two values, and \( (L_A) \) can be calculated from Eq. 11.4.16.

3. A third method for the evaluation of \( (L_A) \) and \( (L_B) \) is especially useful for solutions of an electrolyte solute. This method takes advantage of the fact that a plot of \( (\Delta H_{\text{mix}}) \) versus \( (\xi_{\text{sol}}) \) has a finite limiting slope at \( (\xi_{\text{sol}}) = 0) \) whose value for an electrolyte can be predicted from the Debye–Hückel limiting law, providing a useful guide for the extrapolation of \( (\Delta H_{\text{mix}}) \) to its limiting value \( (\Delta H_{\text{sol}} H^\infty) \). The remainder of this section describes this third method.

The third method assumes we measure the integral enthalpy of solution \( (\Delta H_{\text{sol}}) \) for varying amounts \( (\xi_{\text{sol}}) \) of solute transferred at constant \( (T) \) and \( (p) \) from a pure solute phase to a fixed amount of solvent. From Eq. 11.4.5, the molar differential enthalpy of solution is given by

\[
(\Delta H_{\text{sol}} H) = \frac{\Delta H_{\text{sol}}}{n_A} \tag{11.4.20}
\]

where \( (n_A) \) is held constant. We make the substitution \( (\Delta H_{\text{sol}} H) = \xi_{\text{sol}} \Delta H_{\text{mix}}(\xi_{\text{sol}}) \) and take the derivative of the expression with respect to \( (\xi_{\text{sol}}) \):

\[
\Delta H_{\text{sol}} = \frac{\Delta H_{\text{mix}}}{\xi_{\text{sol}}} \tag{11.4.19}
\]

At constant \( (n_A) \), \( (m_B) \) is proportional to \( (\xi_{\text{sol}}) \), so that \( (\xi_{\text{sol}}) \) can be replaced by \( (m_B m_B) \). When we combine the resulting expression for

\[
(\Delta H_{\text{mix}}) \] with Eq. 11.4.19, we get the following expression for the relative partial molar enthalpy of the solute:
\begin{equation}
L = \Delta H_{\text{solm}} + m \frac{\text{dif} \Delta H_{\text{solm}}}{\text{dif} m} - \Delta H^\infty_{\text{sol}} \tag{11.4.21}
\end{equation}

It is convenient to define the quantity \(\varPhi_L\) \begin{equation}
\varPhi_L \defn \Delta H_{\text{solm}} - \Delta H^\infty_{\text{sol}} \tag{11.4.22}
\end{equation}
known as the relative apparent molar enthalpy of the solute. Because \(\Delta H^\infty_{\text{sol}}\) is independent of \(m\), the derivative \(\frac{\text{dif} \varPhi_L}{\text{dif} m}\) is equal to \(\frac{\text{dif} \Delta H_{\text{solm}}}{\text{dif} m}\). We can therefore write Eq. 11.4.21 in the compact form \begin{gather}
L = \varPhi_L + m \frac{\text{dif} \varPhi_L}{\text{dif} m} \tag{11.4.23}
\end{gather} \(\text{constant} (T, p)\). Equation 11.4.23 allows us to evaluate \(L\) at any molality from the dependence of \(\varPhi_L\) on \(m\), with \(\varPhi_L\) obtained from experimental molar integral enthalpies of solution according to Eq. 11.4.22.

Once \(\varPhi_L\) and \(L\) have been evaluated for a given molality, it is a simple matter to calculate \(L'\) at that molality. By combining Eqs. 11.4.16 and 11.4.22, we obtain the relation \begin{equation}
L' = M_A m \frac{\varPhi_L - L}{L} \tag{11.4.24}
\end{equation}

For an electrolyte solute, a plot of \(\Delta H_{\text{solm}}\) versus \(m\) has a limiting slope of \(+\infty\) at \(m=0\), whereas the limiting slope of \(\Delta H_{\text{solm}}\) versus \(\sqrt{m}\) is finite and can be predicted from the Debye–Hückel limiting law. Accordingly, a satisfactory procedure is to plot \(\Delta H_{\text{solm}}\) versus \(\sqrt{m}\), perform a linear extrapolation of the experimental points to \(\sqrt{m}=0\), and then shift the origin to the extrapolated

**Figure 11.10** Thermal properties of aqueous NaCl at \(25.00\text{ degC}\).

(a) Left axis: molar integral enthalpy of solution to produce solution of molality \(m\) (calculated from molar enthalpy of formation values in Donald D. Wagman et al., *J. Phys. Chem. Ref. Data*, 11, Supplement No. 2, 1982, p. 2-301). The dashed line has a slope equal to the theoretical limiting value of the slope of the curve. Right axis: relative apparent molar enthalpy of the solute.

intercept. The result is a plot of \( \varPhi_L \) versus \( \sqrt{m_B} \). An example for aqueous NaCl solutions is shown in Fig. 11.10(a).

We can also evaluate \( \varPhi_L \) from experimental enthalpies of dilution. From Eqs. 11.4.10 and 11.4.22, we obtain the relation
\[
\varPhi_L(m_B'') - \varPhi_L(m_B') = \Delta H_{m}^{\text{dil, } m_B' \rightarrow m_B''}
\tag{11.4.25}
\]
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 \( \varPhi_L \) versus \( \sqrt{m_B} \).

In order to be able to use Eq. 11.4.23, we need to relate the derivative \( \frac{\mathrm{d}\varPhi_L}{\mathrm{d}m_B} \) to the slope of the curve of \( \varPhi_L \) versus \( \sqrt{m_B} \). We write
\[
\frac{\mathrm{d}\sqrt{m_B}}{2\sqrt{m_B}} \frac{\mathrm{d}m_B}{\mathrm{d}\sqrt{m_B}} = \frac{1}{2\sqrt{m_B}} \frac{\mathrm{d}m_B}{\mathrm{d}\sqrt{m_B}} = \frac{\sqrt{m_B}}{2}\frac{\mathrm{d}\varPhi_L}{\mathrm{d}\sqrt{m_B}}
\tag{11.4.26}
\]
Substituting this expression for \( \frac{\mathrm{d}m_B}{\mathrm{d}\sqrt{m_B}} \) into Eq. 11.4.23, we obtain the following operational equation for evaluating \( L_B \) from the plot of \( \varPhi_L \) versus \( \sqrt{m_B} \):
\[
L_B = \varPhi_L + \frac{\sqrt{m_B}}{2} \frac{\mathrm{d}\varPhi_L}{\mathrm{d}\sqrt{m_B}} \tag{11.4.27}
\]
\[(\text{constant } T \text{ and } p)\]

The value of \( \varPhi_L \) goes to zero at infinite dilution. When the solute is an electrolyte, the dependence of \( \varPhi_L \) on \( m_B \) in solutions dilute enough for the Debye–Hückel limiting law to apply is given by
\[
\varPhi_L = C_{\varPhi_L} \sqrt{m_B} \tag{11.4.28}
\]
\[(\text{very dilute solution)}\]

Equation 11.4.28 can be derived as follows. For simplicity, we assume the pressure is the standard pressure \( p(\text{st}) \). At this pressure \( H_B^\infty \) is the same as \( H_B^{\text{st}} \), and Eq. 11.4.17 becomes
\[
L_B = H_B - H_B^{\text{st}}
\]
\[(\text{at standard pressure)}\]

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:
\[
\ln \gamma_i = -A_{\text{sub}(DH)} \left[ z_i^+ z_i^- \sqrt{I_m} \right], \text{ where } A_{\text{sub}(DH)} \text{ is a temperature-dependent quantity defined in Sec. 10.4. Then Eq. 11.4.33 becomes}\]
\[
L_B = RT^2 \nu \left[ z_i^+ z_i^- \sqrt{I_m} \right] A_{\text{sub}(DH)} \left[ \ln \gamma_i \left( m_B / m_B^{\text{st}} \right) / \ln \gamma_i (m_B) \right]
\tag{11.4.33}
\]
\[(\text{very dilute solution)}\]
converts Eq. 11.4.33 to \[ L\mathcal{B} = \left\{ \frac{RT^2}{\sqrt{2}} \right\} \rho \Delta A^* \rho \left( z_+ z_- \right)^{3/2} \sqrt{m\mathcal{B}} = C_{\Delta L\mathcal{B}} \sqrt{m\mathcal{B}} \] \[ \tag{11.4.34} \] \text{(very dilute solution)} \]

The coefficient \( C_{\Delta L\mathcal{B}} \) (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 \( C_{\varPhi_L} \) represent the limiting slope of \( \varPhi_L \) versus \( \sqrt{m\mathcal{B}} \). In a very dilute solution we have \( \varPhi_L = C_{\varPhi_L} \sqrt{m\mathcal{B}} \), and Eq. 11.4.27 becomes \[ L\mathcal{B} = \varPhi_L + \frac{\sqrt{m\mathcal{B}}}{2} \frac{\text{d} \varPhi_L}{\text{d} \sqrt{m\mathcal{B}} \mathcal{B}} \]
\[ = C_{\varPhi_L} \sqrt{m\mathcal{B}} + \frac{\sqrt{m\mathcal{B}}}{2} C_{\varPhi_L} \] \[ \tag{11.4.35} \]
By equating this expression for \( L\mathcal{B} \) with the one given by Eq. 11.4.34 and solving for \( C_{\varPhi_L} \), we obtain \( C_{\varPhi_L} = (2/3) C_{\Delta L\mathcal{B}} \) and \( \varPhi_L = (2/3) C_{\Delta L\mathcal{B}} \sqrt{m\mathcal{B}} \).

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