Thermodynamics of Natural Systems Theory and Applications in Geochemistry and Environmental Science 3rd edition Anderson Solutions Manual

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Chapter 2

A2.1 Because the reference or standard state of gases in the tables is the ideal gas. In other words, all the properties are those the gas would have if it were ideal. From Appendix A, the molar volume of an ideal gas at 273.15 K, 1 bar is $0.02241410\,\mathrm{m^3 mol^{-1}}$. By the ideal gas law, the volume at 298.15 K is $0.02241410 \times 298.15/273.15 = 0.0244656\,\mathrm{m^3 mol^{-1}}$, or $24465.6\,\mathrm{cm^3 mol^{-1}}$.

A2.2 $\Delta_r V^\circ = 17.3 + 0 - 17.3 = 0\,\mathrm{cm^3}$. The properties of individual ions such as Cl^- cannot be measured. In order to have properties for them, the properties of the hydrogen ion H^+ are defined as zero, and so the properties of Cl^- become the same as the properties of HCl(aq), which can be measured. Now that the properties of Cl^- are known, measuring the properties of NaCl(aq) in the reaction $NaCl = Na^+ + Cl^-$ allows calculation of the properties of Na^+, and similarly for other ions in other reactions.

A2.3 Has no answer without specifying what reaction or process is being considered. Apart from having thermal and mechanical equilibrium but not chemical equilibrium (in a practical sense, ignoring the caveats in Section 2.3.4) the reaction must be specified. If the reaction is

$$CaCO_3(s) = CaCO_3(aq)$$

there is one component. If the reaction is

$$CaCO_3(s) = Ca^{2+} + CO_3^{2-}$$

there is also one component. If the reaction is

$$CaCO_3(s) + H_2O(l) = Ca(OH)_2(s) + CO_2(g)$$

there are two components. Only if H_2O is in the reaction is it a component. This might be happening in a complex environment like a soil with many other compounds present. It makes no difference, except to the activity coefficients.

Chapter 3

A3.1 $12.782/1500 = 0.00852$ days, or about 12 minutes. Unfortunately, humans cannot digest corundum.

A3.2 $\Delta_r H^\circ = H^\circ_{\mathrm{water}} - H^\circ_{\mathrm{ice}} = 6008\,\mathrm{J\,mol^{-1}}$.
$\Delta_r C^\circ_P = C^\circ_{P\mathrm{water}} - C^\circ_{P\mathrm{ice}} = 76.1 - 36.5 = 39.6\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

$$\frac{d\Delta H}{dT} = \Delta C_P$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_P(T_2 - T_1) \quad \text{if } \Delta C_P \text{ is constant.}$$

$$\Delta H_{263.15} - \Delta H_{273.15} = 39.6(263.15 - 273.15)$$
$$= -396\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

so $H^\circ_{\mathrm{water}} - H^\circ_{\mathrm{ice}}$ is $-396\,\mathrm{J\,mol^{-1}}$ less at $-10\,^\circ\mathrm{C}$ than it is at $0\,^\circ\mathrm{C}$, or $6008 - 396 = 5612\,\mathrm{J\,mol^{-1}}$.

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10 Real Solutions

(Chapter 10 from the Second Edition)

10.1 Introduction

We have now considered both ideal solution behavior and deviations from this, but in a rather generalized way, using activity coefficients. We now have to start to consider how to measure these things, and doing this means we have to consider partial molar properties in much more detail.

We start with a fairly detailed look at the volumetric properties of solutions, because these are the most intuitive. Partial molar properties of the other state variables are the same in principle, but become more complicated in the case of enthalpy measurements because of their relative nature. The Gibbs energy is also a relative property, but is treated in quite a different way.

Most of the material in this chapter is quite general, and can be applied to any kind of solution, although most of our examples are for aqueous solutions. The properties of electrolyte solutions introduce complications, discussed in Chapter 15. The properties of real gaseous solutions are often handled by "equations of state," the subject of Chapter 13, and those of solid solutions have some unique aspects, discussed in Chapter 14.

10.2 Solution Volumes

All real solutions are of course non-ideal. Our discussion of their properties will be concerned for the most part with deviations from the properties of ideal solutions, whether Henryan or Raoultian.

10.2.1 Partial and Apparent Properties

The properties of a dissolved substance are described in terms of *partial*, *apparent*, and *excess* total or molar properties, so we begin by discussing these terms, using volume as an example.

The Volume of Mixing

If two substances are immiscible (they do not dissolve into one another to any appreciable extent, like oil and water), obviously the volume of the two together is simply the sum of

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the two volumes separately. But if they are completely miscible (they dissolve into one another completely, forming a solution), this may be more or less true, but probably not exactly true. Why?

If you mix white sand and black sand together, there is no interaction or chemical reaction at all between the two kinds of sand, and the volume of the mixture is the same as the two volumes separately. If the volume of the white sand is $\mathbf{V}_w$ and the volume of the black sand is $\mathbf{V}_b$, the total volume is

$$\mathbf{V} = \mathbf{V}_w + \mathbf{V}_b$$

It's sort of like stacking boxes as in Figure 10.1. There is no change in total volume just because they are together.

However, using total volumes usually turns out to be inconvenient. If the volume per mole of white sand is V_w and that of black sand is V_b, then the total volume is

$$\mathbf{V} = n_w V_w + n_b V_b \tag{10.1}$$

where n_w and n_b are the numbers of moles of white and black sand in the mixture. The molar volume is defined as the total volume divided by the number of moles of all components in the system (i.e., the molar volume of pure white sand is therefore $\mathbf{V}_w/n_w$); so if the mixture contains n_w moles of white sand and n_b moles of black sand, the total number of moles in the mixture is $n_w + n_b$. Dividing both sides of equation (10.1) by $n_w + n_b$, we get

$$V = x_w V_w + x_b V_b \tag{10.2}$$

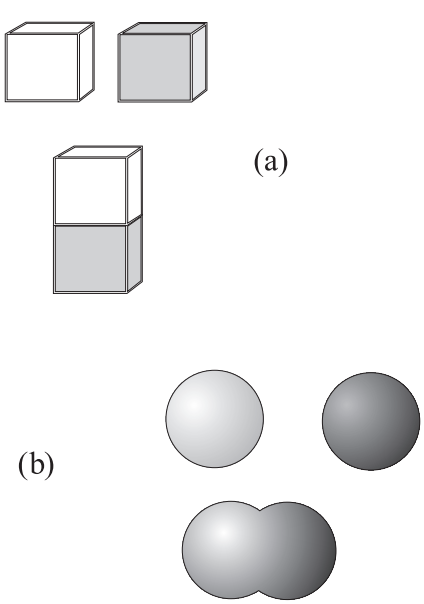

Figure 10.1 (a) There is no volume change when boxes are stacked together – they do not interact. (b) When molecules are mixed together, they may occupy less volume than they did separately.

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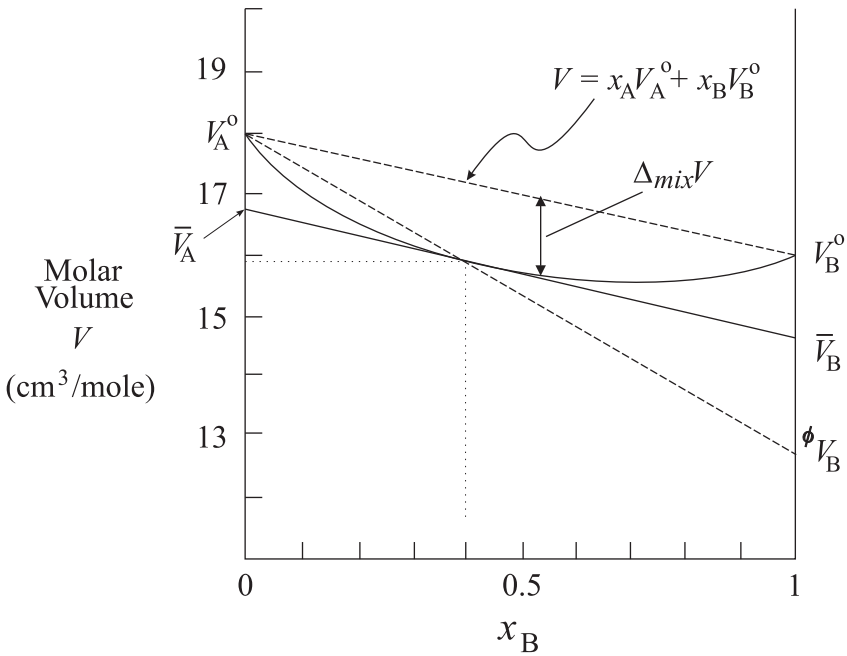

Figure 10.2 The molar volume of solutions of A and B. The molar volume of pure A (V_A°) is $18.0\,\text{cm}^3\,\text{mol}^{-1}$ and that of pure B (V_B°) is $16.0\,\text{cm}^3\,\text{mol}^{-1}$. The molar volume of an ideal solution having $x_B = 0.4$ is $0.6 \times 18.0 + 0.4 \times 16.0 = 17.2\,\text{cm}^3\,\text{mol}^{-1}$. The molar volume of a real solution having $x_B = 0.4$ is actually $15.9\,\text{cm}^3\,\text{mol}^{-1}$. It may be calculated in the same way, but using $\overline{V}_A$ and $\overline{V}_B$ instead of V_A° and V_B°. The difference between the real and the ideal molar volumes is the change in V on mixing $\Delta_{mix}V$. The apparent molar volume of B ($^\phi V$) in a solution is the intercept on the $x_B = 1$ axis of a line joining the molar volume of pure A and the molar volume of the solution. $^\phi V = 12.75\,\text{cm}^3\,\text{mol}^{-1}$ from Equation (10.12)

Here, V is the *molar volume* of the mixture and x is the *mole fraction*, where

$$x_w = \frac{n_w}{\sum n} = \frac{n_w}{n_w + n_b} \tag{10.3}$$

and similarly for x_b. This equation simply says that the volume of the mixture is the same as the volume of the two things separately. The introduction of n and x is just to determine how much of each is used. If we plot molar volume against mole fraction of either component sand, we get a straight line (Figure 10.2), called the *ideal mixing* line.

Clearly these relations do not depend on the grain size of the sands;[1] they depend on the fact that the sands do not react in any way with each other. Each grain of white sand is indifferent to what kind of sand is next to it. Now imagine that the grain size of the sands

[1] Actually, only as long as the grain sizes of the black and white sands are the same.

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gets smaller and smaller. Soon they get so small that you can no longer distinguish the colors – the mixture becomes gray. Imagine the grain size continuing to get smaller and smaller – right down to atomic proportions, so that instead of having a mechanical mixture of black and white sand, we have a true solution of black and white atoms. If the black and white atoms continue to have no attraction, repulsion, or chemical reaction with one another, the volume of the two together will continue to be exactly the same as the sum of the two separately. Actually, we have oversimplified a bit – normally the white molecules interact with each other even in the pure state, and similarly with the black molecules. If these interactions are very similar in nature, then when they are mixed together the molecules will continue to interact with each other in the same way, and the volumes will be additive. In other words, it is not necessary for there to be no molecular interactions for ideal mixing, only that white molecules react with black molecules in exactly the same way that they do with other white molecules.

But suppose that at this molecular size, white (w) and black (b) particles are attracted to one another more than to others of the same kind, perhaps even forming a new kind of particle (wb). Because of this attraction, the particles will be closer together than they would otherwise be, and the total volume of the mixture will be smaller, as shown in Figure 10.1(b), and instead of getting a straight mixing line as in Figure 10.2, the line is curved downward as in Figure 10.2. Alternatively, if the white and black particles repel each other, the total volume will be greater, and in Figure 10.2(b) the curved line for the molar volume of the mixture will lie above the straight line that represents no interaction. The volume change on mixing ($\Delta_{\text{mix}}V$, Figure 10.2) caused by the attraction between A and B is the difference between the straight line and the curved line. The straight line

$$V = x_{\text{A}}\, V_{\text{A}}^{\circ} + x_{\text{B}}\, V_{\text{B}}^{\circ} \tag{10.4}$$

is called *ideal mixing* and is rarely observed.[2] The curved line represents non-ideal mixing, the general case. The difference between the ideal mixing line and the actual molar volume V is called the change in volume on mixing, $\Delta_{\text{mix}}V$. Thus

$$\Delta_{\text{mix}}V = V - (x_{\text{A}}\, V_{\text{A}}^{\circ} + x_{\text{B}}\, V_{\text{B}}^{\circ}) \tag{10.5}$$

10.2.2 Partial Molar Volumes

Now suppose in our mixture of white and black particles that attract each other, that we are not satisfied to have the total volume or the molar volume of the mixture as a whole. We would like to know the volume of each component in the mixture, not just the combined volume. But how can this be done, when each is dispersed at the molecular level and is interacting strongly with another component? Simple. Just draw the tangent to the molar volume curve at the composition you are interested in. The intercepts of this tangent give the volumes of each component in the solution, called *partial molar volumes*, which are combined to give the total molar volume in exactly the same way as the black and white sands in Equation (10.2) and Figure 10.2.

[2] Volumetric ideal mixing (Equation (10.4)) is also called Amagat's law, which we saw was connected to the Lewis fugacity rule in Chapter 8.

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Looking at partial molar volumes in this way, they seem to be just a sort of geometrical construct. They are defined such that they can be substituted for V_A and V_B in Equation (10.2) in cases where mixing results in a curved line for the molar volumes; thus

$$V = x_A \overline{V}_A + x_B \overline{V}_B \qquad \text{(Figure 10.2)} \tag{10.6}$$

or, multiplying both sides by $(n_A + n_B)$,

$$\mathbf{V} = n_A \overline{V}_A + n_B \overline{V}_B \tag{10.7}$$

In Figure 10.2 we have shown a case where A and B are attracted to each other, and their partial molar volumes are both *less* than the volumes of the pure components ($\overline{V}_A < V_A^\circ$). If A and B repelled one another, the mixing line would lie above the straight line and the partial molar volumes would be *larger* than the pure volumes. There is no general rule for the shapes and positions of these mixing curves; they must be measured experimentally. This would be done by density measurements in the case of volume, and calorimetry in the case of enthalpy and entropy. It is quite possible for the mixing curve to be shaped such that in a certain range of composition one of the tangent intercepts is at less than zero volume – a negative partial molar volume. This is why some of the tabulated thermodynamic parameters in Appendix B are negative for some solute components. It is, of course, not possible for pure components to have a negative volume.

The Room Analogy

But there is another way of looking at partial molar volumes which shows that they really are the volume of a mole of each component in solution. Just for a change we will switch from components A and B to a solution of salt (NaCl) in water. Consider an extremely large quantity of water – say enough to fill a large room (Figure 10.3). Now let's add enough salt to make the concentration exactly 1 molal, and adjust the volume of the solution so that the room is full and a little excess solution sticks up into a calibrated tube inserted into the ceiling. By observing changes in the level of solution in the tube, we can accurately record changes in the **V** of the solution in the room.

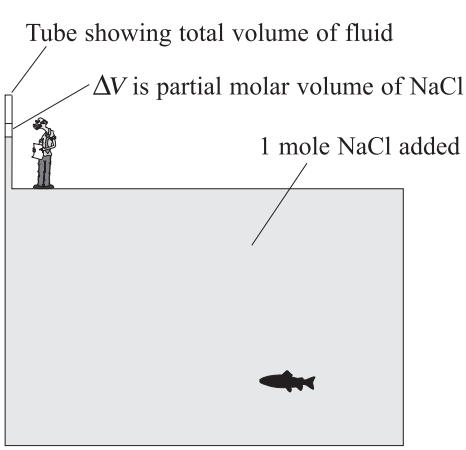

Figure 10.3 A roomful of 1 molal salt solution. The observer sees the change in volume caused by adding one mole of salt, which is the partial molar volume of salt in the 1 molal solution.

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Now, when we add a mole of NaCl (58.5 g of NaCl occupying 27 cm^3) to the solution, the change in concentration is very small. In fact, if we can detect *any* change in concentration by the finest analytical techniques available, then our room is too small, and we must find and inundate a larger one. Eventually, we will fill a sufficiently large room with salt solution that on adding 58.5 g of NaCl we are unable to detect any change in concentration – it remains at 1.000 mole NaCl/kg H_2O. But although the concentration remains unchanged, the volume of course does not. The salt added cannot disappear without a trace. The level in the tube in the ceiling changes, and the $\Delta\mathbf{V}$ seen there is evidently the volume occupied by 1 mole of NaCl in a 1 molal NaCl solution, in this case about 19.47 $cm^3\ mol^{-1}$ of NaCl. This is, in quite a real sense, the volume occupied by a mole of salt in that salt solution and has a right to be thought of as a *molar volume* (just as much as 27 $cm^3\ mol^{-1}$ is the molar volume of crystalline salt) rather than as an arbitrary mathematical construct. It is referred to as the *partial* molar volume of NaCl in the salt solution, $\overline{V}_{NaCl}$.

Some readers will have difficulty in seeing how, on adding our salt, the concentration does not change but the total volume does. If this is the case, think of the room as containing not a solution, but nine million white tennis balls and one million black tennis balls, all mixed together. The room is full, the balls are arranged so that no space is available for another ball, and a few balls overflow into the tube in the ceiling. The total volume is the volume of ten million tennis balls. Now we add one more black tennis ball, somewhere in the middle of the room. The fractional concentration of black balls changes from $10^6/10^7$ to $(10^6 + 1)/(10^7 + 1)$, or from 0.1 to 0.10000009, a change so small it is completely negligible.[3] But the total volume has changed by the volume of one tennis ball, and this change must be reflected by the level of the balls in the tube, which will rise by the volume of one ball. We can even extend the analogy by imagining that the balls in the room are compressed by the pressure, so that when we add another ball, it becomes compressed too, and the level in the tube rises by the volume of a compressed tennis ball, not a normal (standard state) tennis ball.

The Formula for Partial Molar Properties

The partial molar concept is applied to most thermodynamic properties, not just volume. The mathematical expression, introduced in Section 2.4.1, is

$$\left(\frac{\partial \mathbf{Z}}{\partial n_i}\right)_{\hat{n}_i} = \overline{Z}_i \tag{10.8}$$

where $\mathbf{Z}$ is a thermodynamic parameter such as $\mathbf{V}$, $\mathbf{S}$, $\mathbf{G}$, etc., n_i is the moles of component i, and $\hat{n}_i$ is the moles of all solution components *except* i. It is important to note that the derivative is taken of the *total* quantity, $\mathbf{Z}$, not the molar property, Z. It is the change in the *total* volume of the solution in the room that is measured, not the molar volume.

Put in this partial differential form, partial molar properties look somewhat obscure. However, it is important to have an intuitive grasp of their meaning, and you will be well advised to think of them in the sense of the room analogy, as *molar* properties of solutes in solutions of particular compositions, rather than in terms of Equation (10.8).

[3] If you don't find it negligible, just imagine a bigger room and more tennis balls, until the change *is* negligible.

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10.2.3 Apparent Molar Volume

The first thing we come across when looking at real data is that quite often the data are reported as "apparent" molar volumes, enthalpies, entropies or heat capacities. If we call component 1 the solvent (usually water in our cases), component 2 the solute (say, NaCl), **Z** and Z the total and molar forms of any of these properties, then apparent molar properties are defined as

$$^{\phi}Z = \frac{\mathbf{Z} - n_1 Z_1^{\circ}}{n_2} \tag{10.9}$$

or, in the case of volume,

$$^{\phi}V = \frac{\mathbf{V} - n_1 V_1^{\circ}}{n_2} \tag{10.10}$$

where V_1° is the molar volume of the pure phase. Thus the apparent molar volume is the volume that should be attributed to a mole of solute, if one assumes that the solvent contributes the same volume it has in its pure state (Figure 10.2). Alternatively,

$$\mathbf{V} = n_1 V_1^{\circ} + n_2 {}^{\phi}V \tag{10.11}$$

or, dividing by $(n_1 + n_2)$,

$$V = x_1 V_1^{\circ} + x_2 \cdot {}^{\phi}V \tag{10.12}$$

The apparent molar volume is known as accurately and as easily as the molar volume or the total volume of a solution whose composition is known, whereas finding the partial molar volume always involves some manipulation of the raw data (such as determining a tangent) and requires a knowledge of a range of compositions, not just a single one. Therefore measurement of the density of a solution (Section 5.8.1), enables you to calculate **V**, the total volume of the solution. Then because you know the molar volume of the pure solvent V_1°, Equation (10.10) gives you the apparent molar volume of the solute in the solution you measured.

To obtain partial molar volumes from measurements of apparent molar volumes, differentiate Equation (10.11),

$$\left(\frac{\partial \mathbf{V}}{\partial n_2}\right)_{T,P,n_1} = \overline{V}_2 \tag{10.13}$$

$$= n_2 \left(\frac{\partial {}^{\phi}V}{\partial n_2}\right)_{T,P,n_1} + {}^{\phi}V \tag{10.14}$$

$$= m \left(\frac{\partial {}^{\phi}V}{\partial m}\right) + {}^{\phi}V \quad \text{if } n_1 = 55.51 \tag{10.15}$$

so that evidently we need an equation to represent ${}^{\phi}V$ as a function of m, in order to calculate $(\partial {}^{\phi}V/\partial m)$. For electrolytes, it is found that using $\sqrt{m}$ rather than m gives a more linear plot, so that Equation (10.15) becomes

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$$\overline{V}_2 = m\left(\frac{\partial {}^{\phi}V}{\partial m^{1/2}}\right)\left(\frac{\partial m^{1/2}}{\partial m}\right) + {}^{\phi}V$$
$$= \tfrac{1}{2}m^{1/2}\left(\frac{\partial {}^{\phi}V}{\partial m^{1/2}}\right) + {}^{\phi}V \qquad (10.16)$$

Extrapolating values of ${}^{\phi}V$ back to $m = 0$ will therefore provide a value of $\overline{V}_2^{\circ}$, the partial molar volume at infinite dilution, which is the standard state value.

10.2.4 An Example from NaCl–H_2O

As an example of the various terms we have defined, consider the system NaCl–H_2O. This system differs from the system A–B in Figure 10.2 only in the sense that A and B are completely miscible (they dissolve in each other in all proportions), while in NaCl–H_2O water becomes saturated with NaCl at a concentration which depends on P and T. This is 6.1 molal at 25 °C, 10.4 molal at 300 °C, so we can only look at concentrations below this value.

Partial Molar Volume

Apparent molar volumes at concentrations up to 5 molal are shown in Table 10.1 and Figure 10.4. If the mass of solvent, water, is 1 kg, then n_1 is $1000/18.0154 = 55.51$, and n_2 is the NaCl molality, m. The volume of the pure solvent V_1° is $18.068\,\text{cm}^3\,\text{mol}^{-1}$, so measurements of the total volume of the solution **V** give molar volumes (from $\mathbf{V}/(55.51 + m)$) and apparent molar volumes from Equation (10.11).

Table 10.1. Volumetric data for NaCl–H_2O at 25 °C, 1 bar. From the equation of state of Archer (1992).

Molality m (mol kg^{-1})	Mole fraction	Apparent molar volume ${}^{\phi}V$ (cm^3 mol^{-1})	Molar volume V (cm^3 mol^{-1})	Total volume V (cm^3)	Partial molar volume $\overline{V}$ (cm^3 mol^{-1})
0.0	0.0000	16.62	18.068	1002.95	16.62
0.2	0.0036	17.43	18.066	1006.44	17.85
0.4	0.0072	17.78	18.066	1010.07	18.39
0.6	0.0107	18.05	18.068	1013.79	18.80
0.8	0.0142	18.28	18.071	1017.59	19.15
1.0	0.0177	18.49	18.076	1021.45	19.47
1.5	0.0263	18.94	18.091	1031.37	20.15
2.0	0.0348	19.33	18.112	1041.59	20.75
2.5	0.0431	19.67	18.136	1052.09	21.27
3.0	0.0513	19.98	18.165	1062.84	21.75
3.5	0.0593	20.27	18.197	1073.81	22.19
4.0	0.0672	20.52	18.232	1085.00	22.59
4.5	0.0750	20.76	18.270	1096.39	22.97
5.0	0.0826	20.97	18.311	1107.97	23.31

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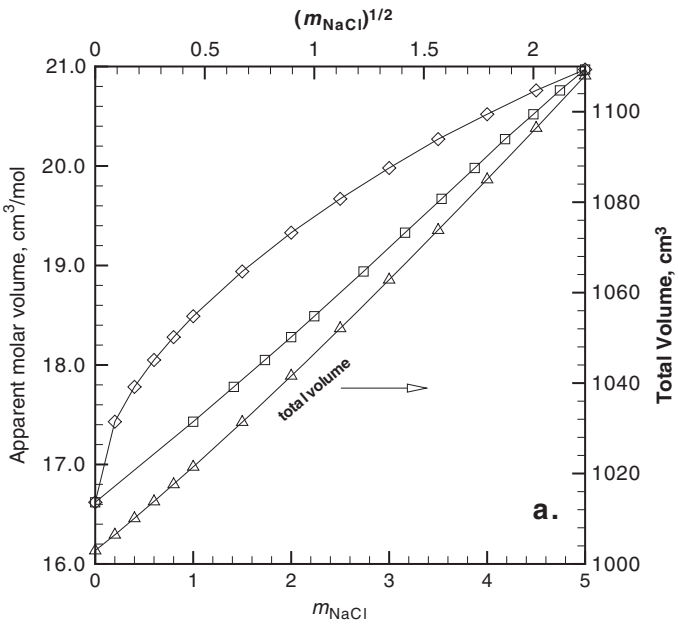

Figure 10.4 Apparent molar volume of NaCl ($^{\phi}V$) in water, and the total volume of solution, as a function of NaCl molality. Top curve: $^{\phi}V$ vs. m_{NaCl}; middle curve: $^{\phi}V$ vs. $m_{NaCl}^{1/2}$; bottom curve: total volume of NaCl solution.

Apparent molar volumes $^{\phi}V$ can be converted into partial molar volumes in several ways. One way would be to actually do the operation illustrated in Figure 10.2, that is, construct the tangent to the molar volume curve, and determine the intercept on the $x_{NaCl} = 1$ axis.[4] The tangent at 3 molal is shown in Figure 10.5. Note that the intercept at $x_{NaCl} = 1$, which is 21.67 $cm^3\ mol^{-1}$, is a bit different from the value in Table 10.1, 21.75 $cm^3\ mol^{-1}$. This is because the tangent method involves differentiation plus a very long distance from $x_{NaCl} = 0.0513$ (the value at 3 molal) to $x_{NaCl} = 1$.

Another way would be to determine the slope of the total volume curve (Equation (10.13)), which gives another slightly different value. But the commonest method has been to fit an equation to $^{\phi}V$ data. If we use a linear equation and $m^{1/2}$ in place of m, we get

$$^{\phi}V = \overline{V}^{\infty} + S_V^* m^{1/2} \tag{10.17}$$

known as the Masson equation, where the slope is S_V^* and the intercept at $m = 0$ is the partial molar volume at infinite dilution, $\overline{V}^{\infty}$. Using the data in Table 10.1, S_V^* is 1.978, and $\overline{V}^{\infty}$ is 16.54 $cm^3\ mol^{-1}$. However, Millero (1971) shows that despite the fact that this equation has the correct theoretical slope at infinite dilution, and was used extensively for many years, it often gives incorrect values of $\overline{V}^{\infty}$.

[4] The mole fractions in Table 10.1 and Figure 10.5 are calculated using $\nu = 1$ rather than $\nu = 2$ as defined in Equation (7.2). Extrapolating a tangent to $x_{NaCl} = 1$ using $\nu = 2$ results in a value of $\frac{1}{2}\overline{V}_{NaCl}$, and the diagram is less intuitive.

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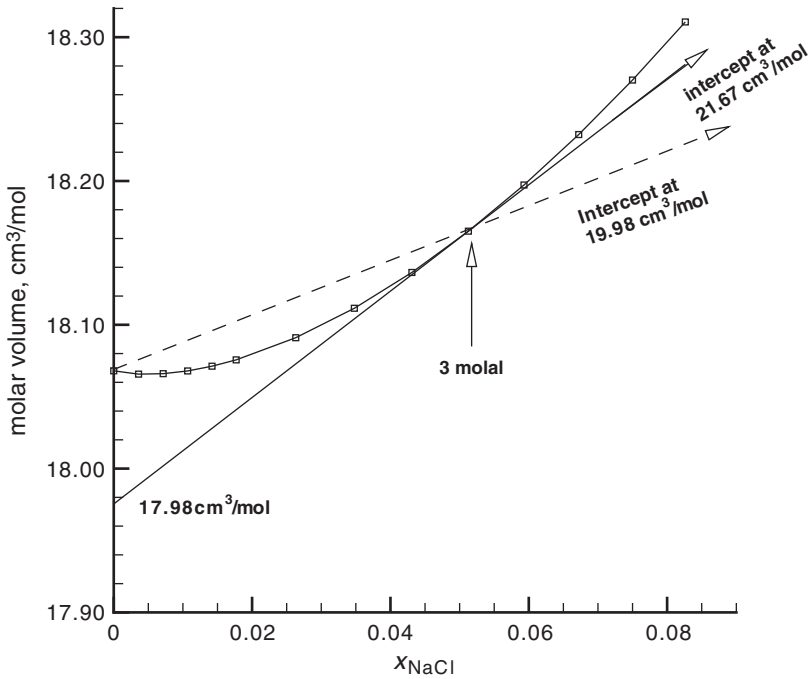

Figure 10.5 Molar volume of NaCl solutions vs. mole fraction NaCl. The tangent to the curve at 3 molal intercepts the $x_{NaCl} = 1$ axis at $\overline{V}^{\circ}_{NaCl}$ and the $x_{NaCl} = 0$ axis at $\overline{V}^{\circ}_{H_2O}$. The dashed line intercepts the $x_{NaCl} = 1$ axis at the apparent molar volume ${}^{\phi}V$. The tangent to the curve at $x_{NaCl} = 0$ intercepts the $x_{NaCl} = 1$ axis at $\overline{V}^{\infty}_{NaCl}$.

Other approaches can be used based on corrections to this equation (e.g., Helgeson and Kirkham (1976)), but in recent years the tendency has been to use the Pitzer equations (Chapter 15). Determining the intercept of this equation, or any nonlinear equation, at $m = 0$ places great emphasis on measurements of very dilute solutions, where they are most difficult. Clearly, some theoretical knowledge of what the slope at the intercept (the "limiting slope") should be is important, and all modern treatments of data of this type use the limiting slopes predicted from Debye–Hückel theory, which will be discussed in Chapter 15. The values in Table 10.1 from Archer (1992) are from an equation of state which uses the theoretical limiting slopes, and in addition involves not just the data at 25 °C, 1 bar, but a great many other data as well.

Electrostriction

Millero (1971) provides an interesting history of ideas on the volume occupied by dissolved electrolytes. Before 1770, a salt was thought to dissolve in water simply by filling up void spaces, thereby not changing the water volume. The experimental evidence used to support this idea was that a glass of water did not overflow when a spoonful of salt was added. In 1770 Watson (reference in Millero (1971)) showed that the volume definitely decreases when various salts are added to water, showing that the prevailing theory of the "porous"

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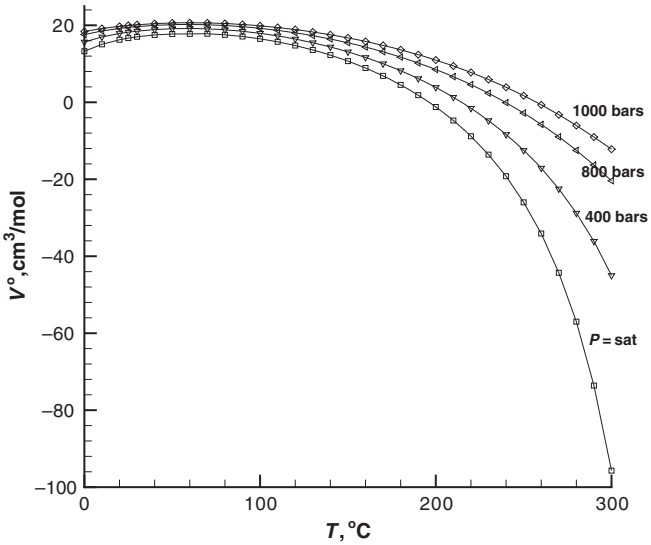

Figure 10.6 The partial molar volume of NaCl at infinite dilution as a function of temperature and pressure. P = sat is 1 bar up to 100 °C, and the saturation pressure of water above 100 °C. Data from Pitzer *et al.* (1984).

nature of water was incorrect. However, his work was soon forgotten, and the older ideas prevailed for another 70 years. Millero reports that Watson tired of chemistry and entered the ministry.

These days we look at the partial molar volume of salts. The molar volume of pure crystalline NaCl is 27.015 $cm^3\,mol^{-1}$, so you see from the values of the partial molar volume in Table 10.1 that NaCl occupies less volume per mole in solution than it does in the solid form, at all concentrations. This fact is even more striking if you look at the partial molar volume at infinite dilution at high temperatures, as shown in Figure 10.6. At every pressure up to 1000 bars, $\overline{V}_{NaCl}$ becomes negative, reaching almost $-100\,cm^3\,mol^{-1}$ at 300 °C, saturation vapor pressure (which is 86 bars). This means that if you were the observer on top of the room full of pure water in Figure 10.3, and if the water was at 300 °C, you would observe the volume of water in the room to *decrease* by almost 100 cm^3 when 58 grams of NaCl was added to the water. The volume of water is so large that after adding the salt, its presence is undetectable, i.e., it is at infinite dilution.

Figure 10.1 suggests that this effect is due to attraction between the NaCl and the H_2O. This is true, but in the case of electrolytes in water, it is somewhat oversimplified. Water is not gas-like, with a complete absence of structure, but largely due to its polar nature and hydrogen bonding, it has some kind of structure which has been the subject of much debate. Addition of charged particles in the form of a dissociated electrolyte disrupts and "collapses" this structure, and the resulting ion–water interactions of several types usually results in an overall decrease in volume, known as "electrostriction," despite the additional volume of the electrolyte. These interactions form the basis of the HKF model embedded in SUPCRT92, to be discussed in Chapter 15.

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10.3 The Infinite Dilution Standard State

So far we have just assumed that the standard state for our mixing components is the pure phase, just as it was in Chapter 3. This presents no problem for water and NaCl – the standard states are, or could be, pure water and pure halite at the T and P of interest. But this doesn't work in the many cases where the solute does not exist as a pure liquid or solid phase, such as any gaseous solute. An alternative is the "infinitely dilute solution," which is always available by extrapolation, and has the advantage that in the standard state the solute particles interact only with the solvent, not with other solute particles. Deviations from the standard state value are then some measure of solute–solute (or solute–affected solvent-solute) interactions. So infinite dilution is the standard state chosen for enthalpy. It is also the standard state for volume and heat capacity.

A Final Reminder about Standard States. Standard states are necessary because G, A, H, and their partial derivatives, as well as the activity (functionally related to a difference in Gibbs energies), can only express the energy difference between a state of interest and some other state. The standard state is used to answer the question, the difference from what other state? Once this state is defined, it of course also has values of V° and C_P°, which don't really require standard states, because their absolute values are (or can be) known.

10.3.1 The Entropy Standard State

In summary, then, for dissolved substances we use the ideal one molal standard state for Gibbs energy, and the infinite dilution standard state for enthalpy, volume and heat capacity. What about entropy?

By looking at one of our Equations (7.26)

$$\mu_A - G_A^\circ = RT \ln x_A$$

it is easy to see why we cannot use infinite dilution for Gibbs energy. G_A° is a constant, so $\mu_A \to -\infty$ as $x_A \to 0$. So infinite dilution is hard to deal with. Equation (7.28) is

$$\overline{S}_i - \overline{S}_i^\circ = -R \ln x_i$$

so the same problem arises for entropy. Now we can write

$$G = H - TS \quad \text{and}$$

$$G^\circ = H^\circ - TS^\circ$$

and

$$G - G^\circ = (H - H^\circ) - T(S - S^\circ)$$

where G° is for an ideal one molal solution and H° is for infinite dilution, and the question is, to what does S° refer?

It happens that for H (and V, C_P), the value at infinite dilution is equal to the value in an ideal one molal solution (and anywhere else on the Henryan tangent), so if G, H, and S

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refer to an ideal one molal solution, then $G - G^\circ$ and $H - H^\circ$ are both zero, and $S - S^\circ$ is zero only if S° also refers to an ideal one molal solution. Because entropy is calculated from other measurements (e.g., $\overline{S} = (\overline{H} - \overline{G})/T$) rather than being measured directly, this fact is perhaps not as useful as the others we have been discussing.

10.3.2 The Reference State

Because partial molar volume, enthalpy, and heat capacity are the same anywhere on the Henry's law tangent, including both the state of infinite dilution and the ideal one molal solution, either of these states can serve as the standard state for these properties. We have chosen to say that the infinitely dilute solution is the standard state, but many treatments prefer to say that the standard state for these properties, as well as for the Gibbs energy and entropy, is the ideal one molal solution. For some reason, these treatments (e.g., Klotz (1964, p. 361)) then define the "reference state" for enthalpy, volume and heat capacity as the state of infinite dilution. This appears to have little usefulness, whatever standard state definition is used.

If the standard state is defined as having a fixed pressure of 1 bar, the reference state is also sometimes referred to as a state reached from the standard state by a change in pressure (Pitzer and Brewer, 1961, p. 249). Because in this text we use a variable pressure standard state, we have no need of the reference state in this sense either.

10.3.3 Symbols for the Standard State

Superscript $^\circ$, as in V°, indicates the standard state. Up to this point, this has generally been synonymous with the pure state (pure solid, liquid, or gas), so one might get the impression that $^\circ$ indicates the pure phase. However, with solutions, we must be more careful, because the pure phase is not always the standard state.

In solutions, particularly electrolyte solutions, the standard state for the solvent is always the pure phase (pure water), so that, for example, V_1° refers to the molar volume of pure component 1, that is, pure water. For the solute, the standard state for most properties is, as just mentioned, the state of infinite dilution, so we could use $\overline{V}_2^\circ$ for the partial molar volume of the solute in the standard state. However, this proves a bit confusing, so for clarity we introduce superscript $^\infty$ to indicate the infinite dilution state ($\overline{V}_2^\infty$), and we understand that this is also the standard state for volume, enthalpy, and heat capacity. This raises the question of what symbol to use for the solute in its pure state. The IUPAC recommends the use of * for pure substances, but our examples involve only minerals so we will just use the mineral name. Thus we use V^{halite} for the molar volume of pure NaCl. In the case of the Gibbs energy (Section 8.2.3) and entropy the standard state is *neither* the pure phase nor the infinitely dilute state, and the usual $^\circ$ symbol is appropriate, as in G° and μ°.

10.4 Excess Properties

In this section we extend our discussion of solution volumes (Section 10.2) to other properties, and introduce the excess properties. The difference between the property

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(V, H, etc.) of a real solution, and what that property would be if the solution was ideal, is called an *excess* property.

Thus, from Equations (7.9), (7.10), and (7.11),

$$V^{\mathrm{EX}} = V_{\text{real solution}} - V_{\text{ideal solution}}$$

$$= V_{\text{real solution}} - \sum_i x_i V_i^\circ \tag{10.18}$$

$$= \Delta_{\mathrm{mix}} V \tag{10.19}$$

and similarly

$$H^{\mathrm{EX}} = \Delta_{\mathrm{mix}} H \tag{10.20}$$

$$C_P{}^{\mathrm{EX}} = \Delta_{\mathrm{mix}} C_P \tag{10.21}$$

For ideal solutions, these quantities are of course all zero (Equations (7.12), (7.13), and (7.14)). They are also true for the total properties, so that for ideal solutions

$$\mathbf{V}^{\mathrm{EX}} = 0 \tag{10.22}$$

$$\mathbf{H}^{\mathrm{EX}} = 0 \tag{10.23}$$

$$\mathbf{C}_P^{\mathrm{EX}} = 0 \tag{10.24}$$

Relations between excess properties are the same as between their parent properties. For example,

$$\left(\frac{\partial G^{\mathrm{EX}}}{\partial P}\right)_T = \left(\frac{\partial G_{\mathrm{real}}}{\partial P}\right) - \left(\frac{\partial G_{\mathrm{ideal}}}{\partial P}\right) \tag{10.25}$$

$$= V_{\mathrm{real}} - V_{\mathrm{ideal}} \tag{10.26}$$

$$= V^{\mathrm{EX}} \tag{10.27}$$

so that in addition,

$$\left(\frac{\partial G^{\mathrm{EX}}}{\partial T}\right)_P = -S^{\mathrm{EX}} \tag{10.28}$$

$$\left(\frac{\partial H^{\mathrm{EX}}}{\partial T}\right)_P = C_P{}^{\mathrm{EX}} \tag{10.29}$$

and so on.

The total excess enthalpy is also called the *relative enthalpy*, $\mathbf{L}$, and is related to the excess total Gibbs energy by

$$\mathbf{L} = \mathbf{H}^{\mathrm{EX}}$$

$$= \mathbf{G}^{\mathrm{EX}} + T\,\mathbf{S}^{\mathrm{EX}}$$

$$= \mathbf{G}^{\mathrm{EX}} - T\left(\frac{\partial \mathbf{G}^{\mathrm{EX}}}{\partial T}\right)_{P,m} \tag{10.30}$$

$$= -T^2\left(\frac{\partial \mathbf{G}^{\mathrm{EX}}/T}{\partial T}\right)_{P,m} \tag{10.31}$$

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The total excess heat capacity, the *relative heat capacity*, also gets its own symbol

$$\mathbf{J} = \mathbf{C}_P^{\mathrm{EX}} \tag{10.32}$$

$$= \left(\frac{\partial \mathbf{H}^{\mathrm{EX}}}{\partial T}\right)_{P,m} \tag{10.33}$$

For entropy,

$$S^{\mathrm{EX}} = S_{\text{real solution}} - S_{\text{ideal solution}} \tag{10.34}$$

$$= \Delta_{\mathrm{mix}} S_{\text{real solution}} - \Delta_{\mathrm{mix}} S_{\text{ideal solution}}$$

$$= \Delta_{\mathrm{mix}} S_{\text{real solution}} + R \sum_i x_i \ln x_i \tag{10.35}$$

Excess total entropy is also related to the relative enthalpy and excess total Gibbs energy as

$$\mathbf{S}^{\mathrm{EX}} = (\mathbf{L} - \mathbf{G}^{\mathrm{EX}})/T \tag{10.36}$$

For Gibbs energy,

$$G^{\mathrm{EX}} = G_{\text{real solution}} - G_{\text{ideal solution}}$$

$$= \Delta_{\mathrm{mix}} G_{\text{real solution}} - \Delta_{\mathrm{mix}} G_{\text{ideal solution}}$$

$$= \Delta_{\mathrm{mix}} G_{\text{real solution}} - RT \sum_i x_i \ln x_i \tag{10.37}$$

Partial Molar Excess Properties

These have the same meaning as other partial molar properties. The general formulation then is

$$\left(\frac{\partial \mathbf{Z}^{\mathrm{EX}}}{\partial n_i}\right)_{\hat{n}_i} = \overline{Z}_i^{\mathrm{EX}}$$

$$= \left(\frac{\partial \mathbf{Z}^{\mathrm{real}}}{\partial n_i}\right) - \left(\frac{\partial \mathbf{Z}^{\mathrm{ideal}}}{\partial n_i}\right)$$

$$= \overline{Z}_i^{\mathrm{real}} - \overline{Z}_i^{\mathrm{ideal}}$$

For volume, using $i = 2$ to indicate the solute, this becomes

$$\overline{V}_2^{\mathrm{EX}} = \overline{V}_2^{\mathrm{real}} - \overline{V}_2^{\mathrm{ideal}}$$

$$= \overline{V}_2^{\mathrm{real}} - \overline{V}_2^{\infty}$$

The superscript *real* is not generally needed, so we have

$$\overline{V}_2^{\mathrm{EX}} = \overline{V}_2 - \overline{V}_2^{\infty} \tag{10.38}$$

where the substitution $\overline{V}_2^{\mathrm{ideal}} = \overline{V}_2^{\infty}$ means that we are using the infinitely dilute solution of the solute as the ideal solution. It is therefore a Henryan sort of ideal solution.

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Similarly for enthalpy and heat capacity, the only difference being that they get special symbols,

$$\overline{H}_2^{\mathrm{EX}} = \overline{H}_2 - \overline{H}_2^{\infty} \tag{10.39}$$

$$= \overline{L}_2 \tag{10.40}$$

$$\overline{C_{P2}}^{\mathrm{EX}} = \overline{C_{P2}} - \overline{C_{P2}}^{\infty} \tag{10.41}$$

$$= \overline{J}_2 \tag{10.42}$$

The meanings of these terms are illustrated in Figures 10.7 and 10.8. In Figure 10.5 we see that in a 3 molal solution of NaCl in water, $\overline{V}_{\mathrm{NaCl}} = 21.67\,\mathrm{cm^3\,mol^{-1}}$, and $\overline{V}^{\infty} = 16.62\,\mathrm{cm^3\,mol^{-1}}$, so that in Figure 10.7, $\overline{V} - \overline{V}^{\infty} = 5.05\,\mathrm{cm^3\,mol^{-1}}$, but note that we know this difference because we know both $\overline{V}$ and $\overline{V}^{\infty}$.

In Figure 10.8, on the other hand, we know that $\overline{L}_{\mathrm{NaCl}} = \overline{H} - \overline{H}^{\infty} = 45\,\mathrm{J\,mol^{-1}}$, but although we can measure $\overline{L}$ (see below), we don't know either $\overline{H}$ or $\overline{H}^{\infty}$. When we can only measure differences, the standard state becomes important. As shown, $\overline{H} - \overline{H}^{\infty}$ is negative, meaning that $\Delta_{\mathrm{mix}}H$ is positive (H of the solution is greater than the combined H of the pure phases), and so dissolution of NaCl is endothermic (absorbs heat). Entropy and Gibbs energy on the other hand do not get special symbols.

$$\overline{S}^{\mathrm{EX}} = \overline{S} - \overline{S}^{\mathrm{ideal}} \tag{10.43}$$

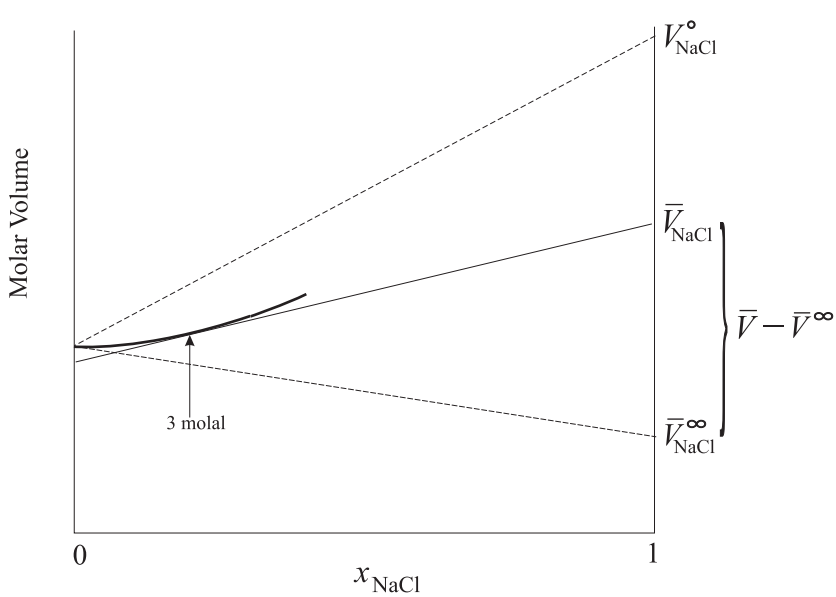

Figure 10.7 Schematic illustration of the meaning of $\overline{V}^{\mathrm{EX}}$. The diagram is a modification of Figure 10.5 but with the dilute region of the x_{NaCl} scale greatly exaggerated and not to scale.

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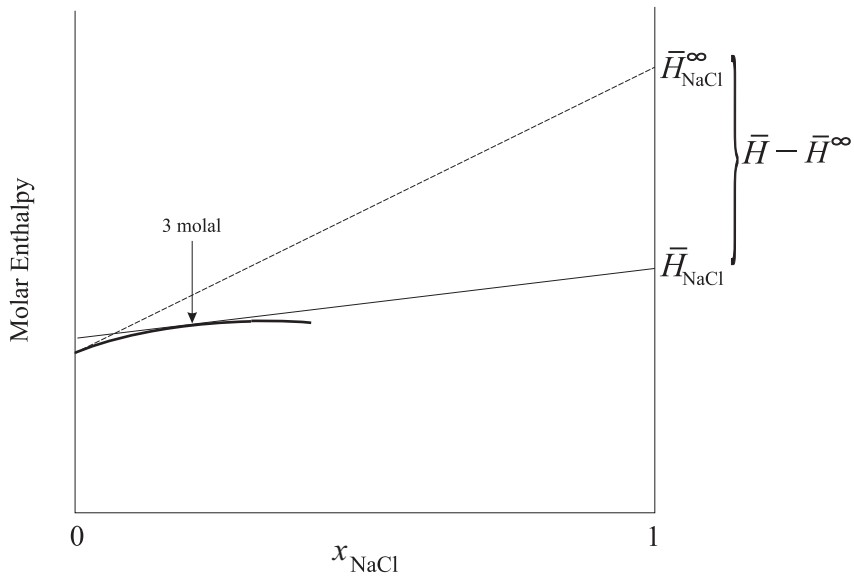

Figure 10.8 Schematic illustration of the meaning of $\overline{H}^{\mathrm{EX}}$.

and is not measured but calculated from other quantities, and

$$\begin{aligned}\overline{G}^{\mathrm{EX}} &= \mu^{\mathrm{EX}} \\ &= \overline{G} - \overline{G}^{\mathrm{ideal}} \\ &= \mu - \mu^{\mathrm{ideal}}\end{aligned} \tag{10.44}$$

But there are some important differences besides the lack of special symbols.

1. We write superscript $^{\circ}$ rather than $^{\infty}$ because the standard state for these quantities is not the infinitely dilute solution, and it is not always the pure phase.
2. Gibbs energy has a completely different functional relationship to concentration than do the other properties. They all use the *apparent* properties, which we defined in Section 10.2.3, whereas with Gibbs energy we use Equations (8.30).

For aqueous solutions, it is more useful to write

$$\begin{aligned}\overline{G}_i^{\mathrm{EX}} &= \mu_i^{\mathrm{EX}} \\ &= \mu_i - \mu_i^{\mathrm{ideal}} \\ &= [\mu_i^{\circ} + RT \ln (m_i \gamma_i)] - [\mu_i^{\circ} + RT \ln m_i] \\ &= RT \ln \gamma_i\end{aligned} \tag{10.45}$$

or

$$\frac{\mu_i^{\mathrm{EX}}}{RT} = \ln \gamma_i \tag{10.46}$$

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or, as it often appears,

$$\frac{\partial \mathbf{G}^{\mathrm{EX}}/RT}{\partial n_i} = \ln \gamma_i \tag{10.47}$$

Another Expression for Excess Gibbs Energies

The molar Gibbs energy of ideal mixing was given as in Chapter 7 as

$$\Delta_{\mathrm{mix}} G_{\text{ideal solution}} = RT \sum_i x_i \ln x_i \tag{7.20}$$

It will be useful to have an expression for the Gibbs energy of mixing of real solutions. This is a bit more complicated for aqueous systems which are "unsymmetrical," that is, which have different standard states for the solvent and solute, and a completely different method of expressing deviations from ideality – osmotic coefficients for the solvent, and Henryan activity coefficients for the solutes. This development follows Pitzer (1991).

To start, think about Figure 7.4, but instead of ideal mixing, the mixing is for a real case, and the curve has any shape. Whatever the shape of the mixing curve, the chemical potentials of the two components are still given by the tangent intercepts, and the molar Gibbs energy of mixing of a real solution can be expressed as

$$\Delta_{\mathrm{mix}} G = x_{\mathrm{A}}(\mu_{\mathrm{A}} - \mu_{\mathrm{A}}^{\circ}) + x_{\mathrm{B}}(\mu_{\mathrm{B}} - \mu_{\mathrm{B}}^{\circ})$$

Because we will need excess chemical potentials as well, we change to the total form of the Gibbs energy (recall that chemical potentials are derivatives of the total Gibbs energy $\mathbf{G}$, not of the molar Gibbs energy G). Multiplying both sides by $(n_{\mathrm{A}} + n_{\mathrm{B}})$, we get

$$\Delta_{\mathrm{mix}} \mathbf{G} = n_{\mathrm{A}}(\mu_{\mathrm{A}} - \mu_{\mathrm{A}}^{\circ}) + n_{\mathrm{B}}(\mu_{\mathrm{B}} - \mu_{\mathrm{B}}^{\circ})$$

or, where component A is H_2O and there are several solutes B,

$$\begin{aligned}\Delta_{\mathrm{mix}} \mathbf{G} &= n_{\mathrm{H_2O}}(\mu_{\mathrm{H_2O}} - \mu_{\mathrm{H_2O}}^{\circ}) + \sum_i n_i(\mu_i - \mu_i^{\circ}) \\ &= RT\left(n_{\mathrm{H_2O}} \ln a_{\mathrm{H_2O}} + \sum_i n_i \ln a_i\right)\end{aligned} \tag{10.48}$$

If the number of moles of water in a system is $n_{\mathrm{H_2O}}$, the number of kilograms of water is

$$\mathrm{kg_w} = \frac{n_{\mathrm{H_2O}}}{55.51}$$

and for n_i moles of solute i, $n_i/\mathrm{kg_w}$ is the number of moles of i per kg of water, i.e., the molality, m_i. Substituting this relation, the relation $a_i = m_i\gamma_i$, and Equation (8.37)

$$\phi = -\frac{55.51}{\sum_i m_i} \ln a_{\mathrm{H_2O}} \tag{8.37}$$

into (10.48), we get

$$\Delta_{\mathrm{mix}} \mathbf{G} = RT \sum_i n_i[-\phi + \ln(m_i\gamma_i)] \tag{10.49}$$

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Next we divide this into an ideal part containing only concentration terms and another part containing the correction terms ϕ and γ,

$$\Delta_{\text{mix}}\mathbf{G} = \underbrace{-RT\sum_i n_i(1-\ln m_i)}_{\textit{ideal part}} + \underbrace{RT\sum_i n_i(1-\phi+\ln\gamma_i)}_{\textit{corrective part}}$$

The "corrective part" is evidently the excess Gibbs energy, so

$$\mathbf{G}^{\text{EX}} = \Delta_{\text{mix}}\mathbf{G} + RT\sum_i n_i(1-\ln m_i) \tag{10.50}$$

$$= RT\sum_i n_i(1-\phi+\ln\gamma_i) \tag{10.51}$$

and

$$\mathbf{G}^{\text{EX}}/\text{kg}_{\text{w}} = RT\sum_i m_i(1-\phi+\ln\gamma_i) \tag{10.52}$$

and, as in (10.47),

$$\left[\frac{\partial\mathbf{G}^{\text{EX}}/(\text{kg}_{\text{w}}RT)}{\partial m_i}\right]_{n_{\text{H}_2\text{O}}} = \ln\gamma_i \tag{10.53}$$

(Pitzer (1973, Equation 23) or Pitzer (1991, Equation 34)) but now we also have an expression for ϕ in terms of $\mathbf{G}^{\text{EX}}$,

$$\phi - 1 = -\frac{(\partial\mathbf{G}^{\text{EX}}/\partial\text{kg}_{\text{w}})_{n_i}}{RT\sum_i m_i} \tag{10.54}$$

(Pitzer (1973, Equation 22) or Pitzer (1991, Equation 35)).

Because Gibbs energy as a function of T and P is a fundamental equation (Section 4.12.1), excess Gibbs energies can be used to calculate not only activity coefficients but all other deviations from ideal behavior, such as osmotic coefficients, excess enthalpies, excess heat capacities, excess volumes, and so on (Section 10.4), so it is potentially quite informative. Also, properties calculated from $\mathbf{G}^{\text{EX}}$ in this way will be entirely self-consistent, which might not be the case if each property was determined separately.

However, determining $\mathbf{G}^{\text{EX}}$ for multicomponent electrolyte aqueous solutions has proved to be a difficult task. Virtually all applications these days use the formulation of K. S. Pitzer and his colleagues, developed during the 1970s and 1980s, which we discuss in Chapter 13. Equation (10.52) and its derivatives are the essential first step in the development of the Pitzer equations.

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10.5 Enthalpy and Heat Capacity

Starting with Equation (10.7) as applied to enthalpy rather than volume, and adopting the usual convention where component 1 is the solvent and component 2 the solute,[5]

$$\mathbf{H} = n_1 \overline{H}_1 + n_2 \overline{H}_2 \tag{10.55}$$

where the partial molar enthalpies are of course

$$\overline{H}_1 = \left(\frac{\partial \mathbf{H}}{\partial n_1}\right)_{T,P,n_2}$$

$$\overline{H}_2 = \left(\frac{\partial \mathbf{H}}{\partial n_2}\right)_{T,P,n_1}$$

And, as with the other partial molar properties (except μ), it is convenient to use apparent properties, so from Equation (10.9),

$$^{\phi}H_2 = \frac{\mathbf{H} - n_1 H_1^{\circ}}{n_2} \tag{10.56}$$

and

$$^{\phi}H_2^{\infty} = \frac{\mathbf{H}^{\infty} - n_1 H_1^{\circ}}{n_2} \tag{10.57}$$

where H_1° is the molar enthalpy of pure water. As before, the apparent and partial molar enthalpies are related by

$$\overline{H}_2 = n_2 \left(\frac{\partial {}^{\phi}H_2}{\partial n_2}\right)_{T,P,n_1} + {}^{\phi}H_2 \tag{10.58}$$

Equation (10.55) remains true as $n_2 \to 0$, so we can write

$$\begin{aligned} \mathbf{H}^{\infty} &= n_1 \overline{H}_1^{\infty} + n_2 \overline{H}_2^{\infty} \\ &= n_1 H_1^{\circ} + n_2 \overline{H}_2^{\infty} \end{aligned} \tag{10.59}$$

where we can write H_1° in place of $\overline{H}_1^{\infty}$ because infinitely dilute component 1 is just pure water, and partial molar properties are the same as molar properties for pure phases.

Subtracting (10.59) from (10.55),

$$\mathbf{H} - \mathbf{H}^{\infty} = n_1(\overline{H}_1 - H_1^{\circ}) + n_2(\overline{H}_2 - \overline{H}_2^{\infty}) \tag{10.60}$$

$$= n_2({}^{\phi}H_2 - {}^{\phi}H_2^{\infty}) \tag{10.61}$$

Now if we define

$$\mathbf{L} = \mathbf{H} - \mathbf{H}^{\infty} \tag{10.62}$$

$$\overline{L}_1 = \overline{H}_1 - H_1^{\circ} \tag{10.63}$$

$$\overline{L}_2 = \overline{H}_2 - \overline{H}_2^{\infty} \tag{10.64}$$

$$^{\phi}L_2 = {}^{\phi}H_2 - {}^{\phi}H_2^{\infty} \tag{10.65}$$

[5] Equation (10.55) is self-evident to someone familiar with Euler's theorem (Section C.7).

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we have

$$\mathbf{L} = n_1 \overline{L}_1 + n_2 \overline{L}_2 \tag{10.66}$$

$$= n_2 {}^{\phi}L_2 \tag{10.67}$$

so

$${}^{\phi}L_2 = \frac{\mathbf{L}}{n_2} \tag{10.68}$$

where $\mathbf{L}$ is called the *relative enthalpy* of the solution, $\overline{L}_2$ is the *relative partial molar enthalpy* and ${}^{\phi}L_2$ is the *apparent relative molar enthalpy* of component 2. Equation (10.66) is clearly analogous to (10.7) and (10.55). At infinite dilution, both $\overline{L}_1$ and $\overline{L}_2$ are zero. Equation (10.62) can also be written

$$\mathbf{L} = \mathbf{H} - \mathbf{H}_1^{\circ}$$

$$= \mathbf{H} - n_1 H_1^{\circ} \tag{10.69}$$

In other words $\mathbf{L}$ is the difference between the total enthalpy of a solution and the total enthalpy of the same amount of pure water. Differentiating Equation (10.67) with respect to n_2 we get a familiar expression for $\overline{L}_2$,

$$\overline{L}_2 = \frac{\partial \mathbf{L}}{\partial n_2}$$

$$= n_2 \left(\frac{\partial {}^{\phi}L_2}{\partial n_2} \right)_{T,P,n_1} + {}^{\phi}L_2 \tag{10.70}$$

and, as with volume, using $\sqrt{m}$ is often advantageous, so Equation (10.70) becomes

$$\overline{L}_2 = \tfrac{1}{2} m^{1/2} \left(\frac{\partial {}^{\phi}L_2}{\partial m^{1/2}} \right) + {}^{\phi}L_2 \tag{10.71}$$

An expression for $\overline{L}_1$ can be obtained by substituting Equations (10.70) and (10.67) into (10.66),

$$n_1 \overline{L}_1 = n_2 {}^{\phi}L_2 - n_2 \overline{L}_2$$

$$= n_2 {}^{\phi}L_2 - n_2 \left[{}^{\phi}L_2 + n_2 \left(\frac{\partial {}^{\phi}L_2}{\partial n_2} \right)_{n_1} \right]$$

$$\overline{L}_1 = -\frac{n_2^2}{n_1} \left(\frac{\partial {}^{\phi}L_2}{\partial n_2} \right) \tag{10.72}$$

Values of $\overline{L}_2$ can be obtained by measuring heats of dilution. The meaning of some of these terms is illustrated in Figure 10.9.

10.5.1 Heat of Dilution

When a solution of initial molality m_{i} is diluted to a final molality m_{f}, the observed heat effect is

$$\Delta_{\mathrm{dilution}} H = {}^{\phi}L_2(m_{\mathrm{f}}) - {}^{\phi}L_2(m_{\mathrm{i}})$$

$$= \Delta {}^{\phi}L_2 \tag{10.73}$$

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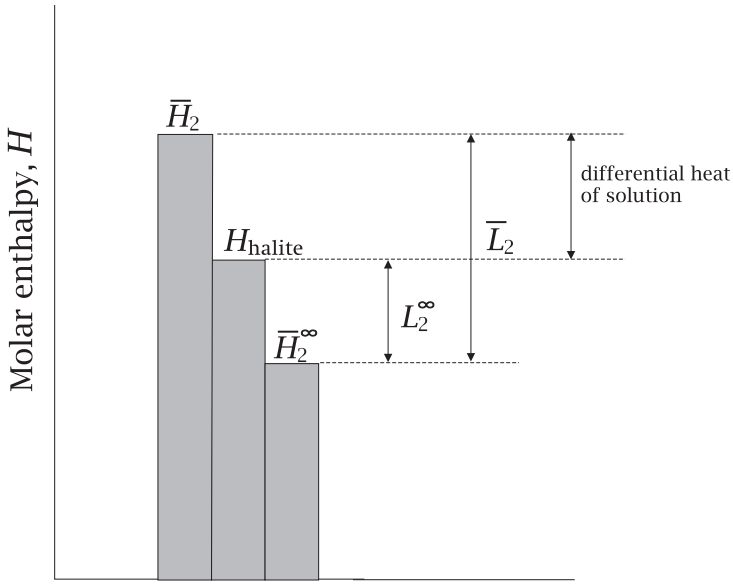

Figure 10.9 Schematic illustration of the meaning of some enthalpy terms.

which, if you insert the definitions of ${}^{\phi}L_2$ and ${}^{\phi}H_2$ means that

$$\Delta_{\text{dilution}}H = \frac{\mathbf{H}_{\text{f}} - \mathbf{H}_{\text{i}}}{n_2}$$

or, if you prefer,

$$\Delta_{\text{dilution}}\mathbf{H} = \mathbf{H}_{\text{f}} - \mathbf{H}_{\text{i}} \tag{10.74}$$

Some experimental heat of dilution data for NaCl are shown in Figure 10.10. The negative values show that the enthalpy of a dilute NaCl solution is less than that of a more concentrated one. The data in this diagram are an answer to the question "what is the (non-ideal) heat of mixing of NaCl and water?" In this case the NaCl is at two different concentrations – one is 1.0 molal, and the other is as shown on the x-axis.

After adjusting to a common pressure, the data were fitted with a Pitzer equation, the slopes determined, and Equation (10.71) used to calculate values of $\overline{L}_2$, which are shown in Figure 10.11.

Another question would be "what is the heat of mixing of water and solid halite?"

10.5.2 Integral Heat of Solution

The dissolution of halite in water can be written as

$$n_2\,\text{NaCl(s)} + n_1\,\text{H}_2\text{O(l)} = [\text{solution of } n_2 \text{ moles of NaCl and } n_1 \text{ moles of H}_2\text{O}] \tag{10.75}$$

or alternatively

$$n_2\,\text{NaCl(s)} + 55.51\,\text{H}_2\text{O(l)} = n_2\,\text{NaCl(aq}, m) \tag{10.76}$$

where (aq, m) signifies an aqueous solution of concentration m.

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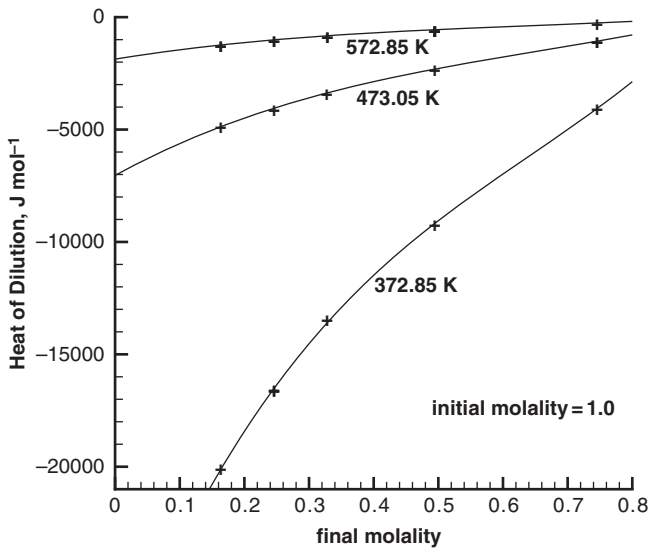

Figure 10.10 The heat of dilution of NaCl from 1 molal to the final molality shown, at the indicated temperatures. Data from Busey *et al.* (1984).

This process of forming a solution from pure solvent and pure solute is called the *integral heat of solution*, and the heat effect in this process is

$$\begin{aligned}\Delta_{\text{integral}}\mathbf{H} &= \Delta_{\text{mix}}\mathbf{H}\\ &= \underbrace{(n_1\overline{H}_1 + n_2\overline{H}_2)}_{\mathbf{H}\ \textit{solution}} - \underbrace{(n_1H_1^\circ + n_2H^{\text{halite}})}_{\mathbf{H}\ \textit{pure phases}}\\ &= n_1(\overline{H}_1 - H_1^\circ) + n_2(\overline{H}_2 - H^{\text{halite}}) \qquad (10.77)\\ &= n_1\overline{L}_1 + n_2(\overline{H}_2 - \overline{H}_2^\infty) - n_2(H^{\text{halite}} - \overline{H}_2^\infty)\\ &= \underbrace{n_1\overline{L}_1 + n_2\overline{L}_2}_{\mathbf{L}} - n_2(H^{\text{halite}} - \overline{H}_2^\infty) \qquad (10.78)\end{aligned}$$

where $(n_1\overline{H}_1 + n_2\overline{H}_2)$ is the absolute enthalpy of the solution itself (Equation (10.55)), $\mathbf{H}^{\text{solution}}$, and $(n_1H_1^\circ + n_2H^{\text{halite}})$ is the absolute enthalpy of the pure starting materials, water and halite. It is actually a form of Equation (7.13), except that we write $\mathbf{H}^{\text{solution}}$ and mole numbers rather than $H^{\text{ideal solution}}$ and mole fractions, and it is a form of Equation (10.60) but using a different standard state for component 2. Many sources introduce another symbol for $(H^{\text{halite}} - \overline{H}_2^\infty)$, such as $\overline{L}^{\text{halite}}$, or $\overline{L}(s)$, but we will retain $(H^{\text{halite}} - \overline{H}_2^\infty)$ in a small and perhaps futile attempt to lessen confusion.

Integral heats of solution cannot be obtained directly from heat of dilution measurements, because they do not include the energy required to break the solid into its constituent ions, and then hydrate them. This is shown by the fact that a term for H^{halite} appears in our equations.

Dividing through by n_2 in Equation (10.78) we get a more intuitive expression for the integral heat of solution.

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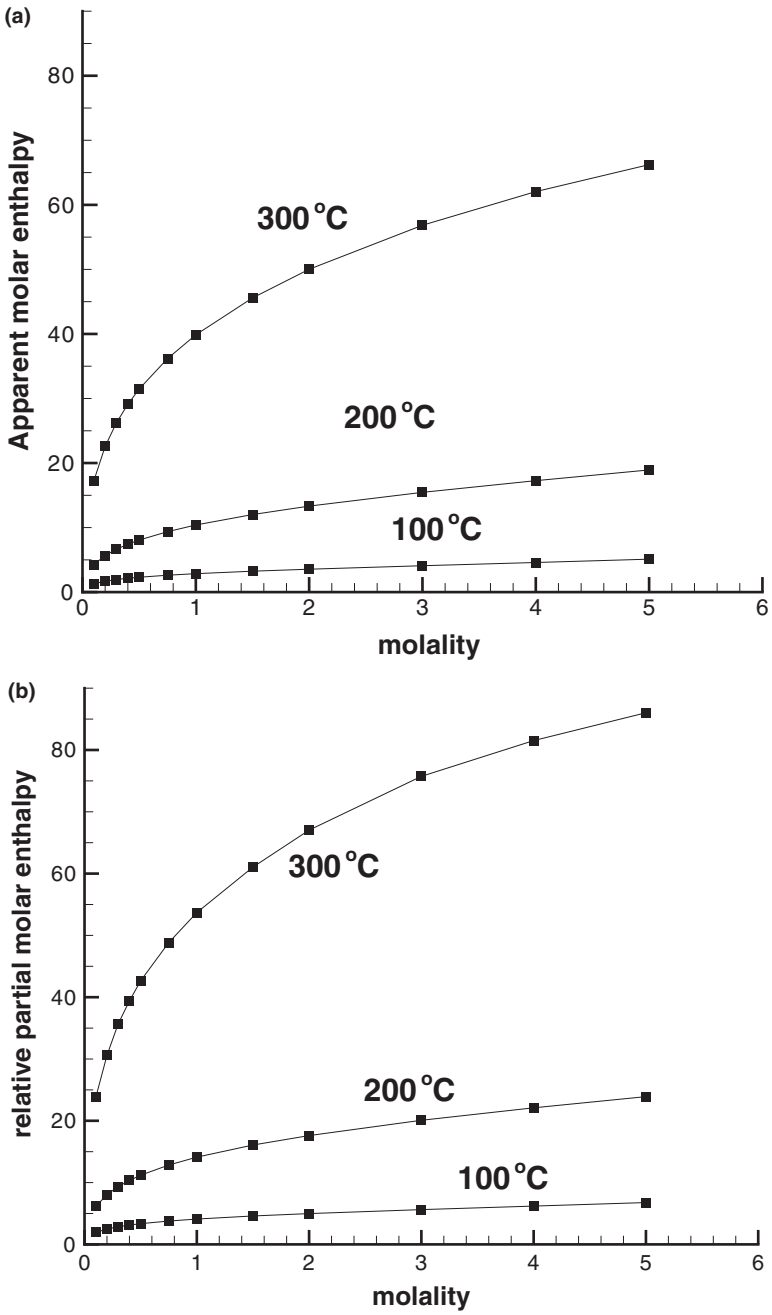

Figure 10.11 (a) The apparent relative molar enthalpy of NaCl ($^{\phi}L_2$), from the data in Figure 10.10. (b) The relative partial molar enthalpy ($\overline{L}_2$) of NaCl from the data in Figure 10.10. Data from Busey *et al.* (1984).

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$$\frac{\Delta_{\text{integral}}\mathbf{H}}{n_2} = \frac{\mathbf{L}}{n_2} - (H^{\text{halite}} - \overline{H}_2^{\infty})$$

or

$$\Delta_{\text{integral}}H = {}^{\phi}L_2 + (\overline{H}_2^{\infty} - H^{\text{halite}}) \tag{10.79}$$

In this equation $(\overline{H}_2^{\infty} - H^{\text{halite}})$ is the heat of solution of halite into an infinite amount of water, and ${}^{\phi}L_2$ is the heat difference between this infinitely dilute solution (which is pure water) and the solution at whatever concentration we wish. When the concentration of interest is 1 molal, ${}^{\phi}L_2$ is given by the intercept of the curves in Figure 10.10 at $m = 0$, and because ${}^{\phi}L_2$ at infinite dilution is zero, it is shown for all concentrations in Figure 10.11(a).

Box 10.1 Integral Heat of Solution of NaCl

How much heat is absorbed (or evolved?) when 1 mole of halite is dissolved in 1 kg of water at 100, 150, and 200 °C?

To calculate this we need to know

1. the enthalpy change when a mole of halite is dissolved in an infinite amount of water, and
2. the enthalpy change between this solution and the 1 molal solution, which is the negative of the heat of dilution from 1 m to infinite dilution.

This is summed up in Equation (10.79).

Criss and Cobble (1961), 0 to 95 °C and Gardner *et al.* (1969), 100 to 200 °C, report values of the heat of solution of halite in dilute NaCl solutions, extrapolated to $m_{\text{NaCl}} = 0$, thus giving values of $\overline{H}_2^{\infty} - H^{\text{halite}}$. If we combine these data we find they are fit very well by a cubic polynomial, which is

$$\overline{H}_2^{\infty} - H^{\text{halite}} = 1833.66 - 38.8870\,T + 0.161221\,T^2 - 0.000803184\,T^3 \tag{10.80}$$

where T is in °C.

From the tabulated values in Busey *et al.* (1984) which were used to plot Figure 10.11(a), we find values of ${}^{\phi}L_{\text{NaCl}}$. Combining these data we get

T (°C)	$\overline{H}_2^{\infty} - H^{\text{halite}}$ (J mol^{-1})	${}^{\phi}L_{\text{NaCl}}$ (J mol^{-1})	$\Delta_{\text{integral}}H$ (J mol^{-1})
25	+914	⇐ from Criss and Cobble (1961)	
100	−5213	2861	−2352
150	−12898	5731	−7167
200	−24771	10400	−14371

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The remarkable decrease in both $\overline{H}_2^{\infty} - H^{\text{halite}}$ and $\Delta_{\text{integral}}H$ with temperature, including a change from endothermic to exothermic in $\overline{H}_2^{\infty} - H^{\text{halite}}$ between 25 and 100 °C, is but one of many indications that there is a great increase in energy liberating processes (hydration, solvent collapse, ion-pair formation) as T is increased.

10.5.3 Differential Heat of Solution

The differential heat of solution is another name for the partial molar enthalpy of solution, i.e., the heat effect of dissolving a mole of solute in an infinite amount of solution of some particular concentration. It's like measuring the heat effect instead of the volume effect in Figure 10.3, and it's just the slope of the integral heat effect. The integral and differential heats of solution become identical at infinite dilution. According to the definition of partial molar properties (Equation (10.8)), differentiation of an equation for the integral heat should give us the differential heat, so

$$\left(\frac{\partial \Delta_{\text{integral}}\mathbf{H}}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial \mathbf{L}}{\partial n_2}\right)_{T,P,n_1} + \left(\frac{\partial\, n_2(H^{\text{halite}} - \overline{H}_2^{\infty})}{\partial n_2}\right)_{T,P,n_1}$$

$$= \overline{L}_2 + (H^{\text{halite}} - \overline{H}_2^{\infty}) \tag{10.81}$$

$$= \overline{H}_2 - H^{\text{halite}} \tag{10.82}$$

Klotz and Rosenberg (1994, p. 394) give the following expression for the heat absorbed (in cal mol^{-1}) when m moles of halite are dissolved in 1000 g of H_2O (the integral heat of solution of halite in water) at 25 °C

$$\Delta_{\text{integral}}H = 923\,m + 476.1\,m^{3/2} - 726.1\,m^2 + 243.5\,m^{5/2} \tag{10.83}$$

so the differential heat is

$$\left(\frac{\partial \Delta_{\text{integral}}H}{\partial m}\right)_{T,P} = 923 + 714.15\,m^{1/2} - 1452.2\,m + 608.75\,m^{3/2} \tag{10.84}$$

10.5.4 Heat Capacity

Heat capacities can be measured directly in twin tube flow calorimeters (Section 5.8.2) or by manipulation of other measurements. For example, Criss and Cobble (1961) and Gardner *et al.* (1969) measured the heat of solution of halite in water at various temperatures, extrapolated to standard state conditions (infinite dilution), then determined the temperature derivative of the heat of solution measurements. At infinite dilution, because $\overline{H}_1 = H_1^{\circ}$, Equation (10.77) becomes

$$\Delta_{\text{integral}}\mathbf{H} = n_2(\overline{H}_2^{\infty} - H^{\text{halite}})$$

or

$$\Delta_{\text{integral}}H = (\overline{H}_2^{\infty} - H^{\text{halite}}) \tag{10.85}$$

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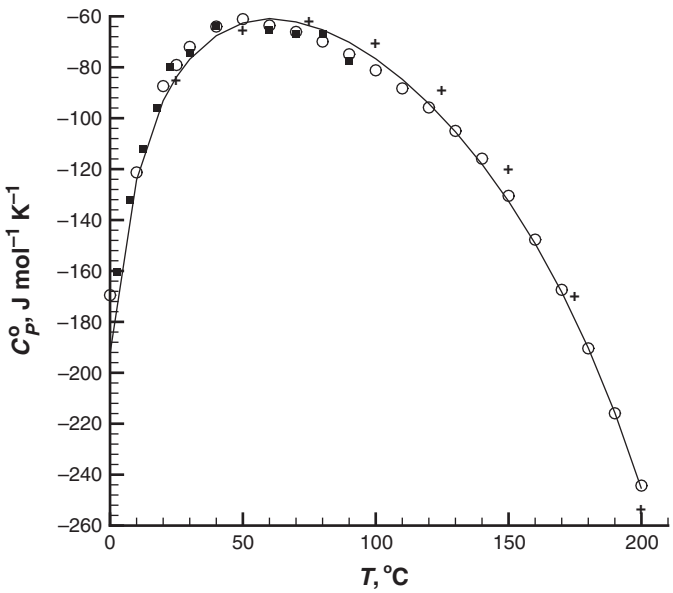

Figure 10.12 Standard state heat capacity of aqueous NaCl as a function of temperature. Squares, Criss and Cobble (1961). Open circles, Gardner *et al.* (1969). Crosses, Helgeson (1981). Line, Pitzer *et al.* (1984).

and the temperature derivative is

$$\left(\frac{\partial(\overline{H}_2^{\infty} - H^{\text{halite}})}{\partial T}\right)_P = \overline{C}_P^{\infty} - C_P{}^{\text{halite}} \tag{10.86}$$

where C_P^{∞} is the heat capacity of aqueous NaCl at infinite dilution, and is normally called C_P°. The heat capacity of halite ($C_P{}^{\text{halite}}$) as a function of temperature is well known, so this is added to the result to obtain C_P^{∞}. Figure 10.12 shows their results, compared with a more recent compilation by Pitzer *et al.* (1984).

Box 10.2 Heat Capacity from Integral Heat of Solution

As shown in Equation (10.86), the temperature derivative of an equation for $\overline{H}_2^{\infty} - H^{\text{halite}}$ will give $\overline{C}_P^{\infty} - C_P^{\text{halite}}$, and adding C_P^{halite} to this will give $\overline{C}_P^{\infty}$.

The temperature derivative of Equation (10.80) is

$$\overline{C}_P^{\infty} - C_P^{\text{halite}} = -38.8870 + 0.0322442\,T - 0.002409552\,T^3$$

where T is in °C and $\overline{C}_P^{\infty} - C_P^{\text{halite}}$ is in cal mol^{-1} K^{-1}. The heat capacity of halite is given by (NIST web site, Shomate equation)

$$C_P^{\text{halite}} = 50.72389 + 6.672267(T/1000) - 2.517167(T/1000)^2 + 10.15934(T/1000)^3 - 0.200675/(T1000)^2$$

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where T is in kelvins and C_P^{halite} is in J mol^{-1} K^{-1}. Converting calories to Joules and combining these data, we get

T (°C)	$\overline{C}_P^{\infty} - C_P^{\text{halite}}$ (J mol^{-1} K^{-1})	C_P^{halite} (J mol^{-1} K^{-1})	$\overline{C}_P^{\infty}$ (J mol^{-1} K^{-1})
25	−135.28	50.50	−84.78
50	−120.45	51.04	−69.41
75	−118.23	51.51	−66.71
100	−128.61	51.95	−76.66
125	−151.59	52.36	−99.23
150	−187.17	52.75	−134.43
175	−235.36	53.12	−182.24
200	−296.15	53.50	−242.65

These values of $\overline{C}_P^{\infty}$ are almost identical to those plotted in Figure 10.12. The inverted-U shape of the C_P curve as a function of T is typical of all electrolytes.

The heat capacity of solution at finite concentrations is analogous to volume, in that they can be measured directly in calorimeters, so that $(\overline{C_P} - \overline{C_P}^{\infty})$ can be evaluated by knowing both quantities, not just the difference. Like volume, $\overline{C_P}^{\infty}$ is evaluated by extrapolating measurements of $\overline{C_P}$ to infinite dilution, or, as above, by manipulating other infinite dilution quantities.

10.6 Gibbs Energies

At this point we have a fundamental problem. Given the relationship between Gibbs energies and compositions for ideal solutions we have developed, how do we handle deviations from this behavior? What mathematical form should our equations for non-ideality take? There is a variety of approaches for this. The most general is to develop an equation of state, and there are a variety of types of those (Chapter 13). Then there are different approaches for dilute and concentrated solutions, and for electrolytes and non-electrolytes. In this section we look at some fairly general methods which have been applied to many solid and liquid solutions.

10.6.1 Regular Solutions

The simplest form of excess Gibbs energy (Equation (10.44)) is illustrated in Figure 10.13. This is a completely symmetrical G^{EX}. The ideal $\Delta_{\text{mix}}G$ curve from Figure 7.4 is shown as a dashed line. The "real" $\Delta_{\text{mix}}G$ curve is the sum of this and G^{EX}, and is therefore also symmetrical. Of course in real solutions both $\Delta_{\text{mix}}G$ and G^{EX} will generally have more complicated shapes, but we can use this simple form of non-ideal solution behavior to examine the relationship between G^{EX} and several other features of non-ideal solutions.

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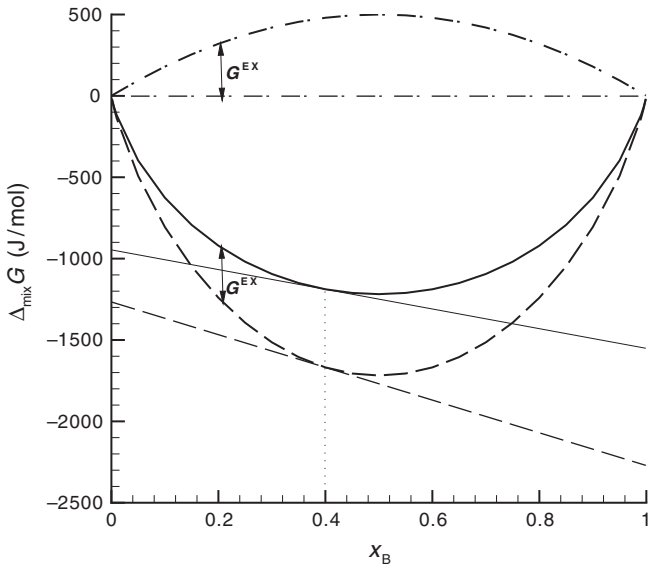

Figure 10.13 The excess Gibbs energy of mixing. The dashed curve is the ideal mixing line from Figure 7.4. The dash–dot curve shows values of G^{EX} for $w_G = 2000\,\mathrm{J\,mol^{-1}}$ which are added to the ideal mixing values.

How should we define the simplest possible deviation from ideal solution behavior? It should evidently have about the same parabolic shape as the ideal mixing curve, which means we need some kind of $y \propto x^2$ function. Then because excess properties are zero for pure components, this function should approach zero as the mole fraction, x_A or x_B of either of the two components, approaches 1.0. Finally, in a solution of two similar components such as benzene and toluene, we might expect the solution to be most non-ideal when the components are mixed in equal proportions (because that's when non-uniform interactions between the two species are maximized). That means the equation should have a maximum or minimum at the 1:1 composition. The simplest equation which satisfies all these conditions is

$$G^{EX} = w_G x_A x_B \tag{10.87}$$

where w_G is a constant with units of energy which is independent of composition, but varies with T and P. If w_G is positive, then molecules A and B repel each other (or prefer energetically to be with molecules of the same type); this can lead to immiscibility and exsolution. If w_G is negative, there is an energy preference for A and B to associate in the solution, and this can produce intermediate compounds. Equation (10.87) is also called a *one-parameter Margules equation*. The equation for the mixing curve in Figure 10.13 is therefore

$$\Delta_{mix}G = RT\,(x_A \ln x_A + x_B \ln x_B) + w_G x_A x_B \tag{10.88}$$

Hildebrand and Scott (1964) discuss many (mostly binary) systems which can be conveniently treated with this formalism. It has been applied to ternary systems, but

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beyond that it gets quite cumbersome. Although not many real systems show such behavior (examples are systems like argon–oxygen; benzene–cyclohexane; Au–Cu), we can easily imagine adding more terms involving adjustable constants and mole fractions to account for more complex non-ideality, and this approach has in fact been pursued extensively.

In Figure 10.13 we have assumed $w_G = 2000\,\mathrm{J\,mol^{-1}}$, so that at $x_B = 0.4$, $w_G x_A x_B = 480.0\,\mathrm{J\,mol^{-1}}$, and $\Delta_{mix}G$ from Equation (10.88) is $-1668.4 + 480.0 = -1188.4\,\mathrm{J\,mol^{-1}}$.

Box 10.3 Solution Theories

There are literally thousands of articles on the theory of solutions, going back to the origins of physical chemistry itself, yet, as pointed out by Prausnitz *et al.* (1999, Chapter 7) after an extensive survey of the subject, "...we are still far from an adequate theory of liquid mixtures." Traditionally, and for good reason, theories on electrolyte and non-electrolyte solutions are treated separately, but there is of course some common ground such as the laws of Raoult and Henry. Theories of the two types of solutions also have an interesting similarity in that they have generally been developed emphasizing either the "physical" or the "chemical" approach.

In non-electrolyte theory, the physical approach goes back to van der Waals, and develops theories which deal with particle arrangements and generalized intermolecular forces, but nothing about the specific nature of any new particles formed due to these forces. The chemical approach concentrates on identifying these new particles, and in the extreme form, begun by Dolezalek in 1908, suggests that if all molecular species are correctly identified, with their respective equilibrium constants, Raoultian mixing is sufficient to account for the solution properties. The physical approach can be traced from van der Waals through van Laar, Scatchard and Hildebrand, resulting in regular solution theory (references in Prausnitz *et al.*, 1999), which turns out to have some overlap with the equations proposed by Margules in 1895.

In electrolyte theory, so different in most respects because of the electrically charged nature of the particles, the same distinction between physical and chemical approaches can be seen. We will present more detail in Chapter 15, but basically the Pitzer equations represent the physical approach, having no reference to individual ionic species, and the HKF model of Helgeson (1981) represents the chemical approach, in which the standard state properties of individual species are defined.

Modern theories of solutions combine aspects of both approaches, and the theories of Pitzer and Helgeson *et al.* are no different in this respect. The Pitzer approach must take into account strong complex formation, and the HKF approach uses activity coefficients, based on generalized electrostatic considerations, in addition to species information.

Corrections to ΔH and ΔS

Because $\Delta G = \Delta H - T\Delta S$, applying a correction to ΔG raises the question as to how this correction is divided between ΔH and ΔS. The two extreme cases would be

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(1) that it all appears as a correction to ΔH with ΔS remaining ideal, or
(2) it all appears as a correction to ΔS, with ΔH remaining zero.

and, of course, there could be some adjustment in both terms. The original definition of *regular solutions* by Hildebrand in 1927 was case 1, with an ideal entropy of mixing and a non-ideal enthalpy of mixing. The other case, retaining $\Delta H = 0$, produces *athermal solutions*. Many other descriptive terms have been used by other authors, and the term "regular solution" now covers both these cases, as well as some extensions.

Because $G^{\mathrm{EX}} = H^{\mathrm{EX}} - TS^{\mathrm{EX}}$, then

$$\begin{aligned} S^{\mathrm{EX}} &= -\frac{\partial G^{\mathrm{EX}}}{\partial T} \\ &= -\frac{\partial}{\partial T}\left(w_G\, x_{\mathrm{A}} x_{\mathrm{B}}\right) \\ &= x_{\mathrm{A}} x_{\mathrm{B}}\, w_S \end{aligned} \tag{10.89}$$

where $(\partial\, w_G/\partial T) = -w_S$, and H^{EX} is

$$\begin{aligned} H^{\mathrm{EX}} &= G^{\mathrm{EX}} + T\, S^{\mathrm{EX}} \\ &= x_{\mathrm{A}} x_{\mathrm{B}} (w_G + T\, w_S) \\ &= x_{\mathrm{A}} x_{\mathrm{B}}\, w_H \end{aligned} \tag{10.90}$$

Similarly, $(\partial\, w_G/\partial P) = w_V$, $V^{\mathrm{EX}} = x_{\mathrm{A}} x_{\mathrm{B}} w_V$, and

$$w_G = w_H - T w_S + P w_V \tag{10.91}$$

Measurements of any of these excess quantities could then contribute to a knowledge of a system's non-ideality as a function of T and P. We give some examples of how this is done in Chapter 13.

$\mu - \mu^\circ$ From Tangent

The slope of the tangent to the mixing curve is

$$\begin{aligned} \left(\frac{d\Delta_{\mathrm{mix}} G}{dx_B}\right) &= \frac{d}{dx_{\mathrm{B}}}\left[RT\left(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right) + w_G x_{\mathrm{A}} x_{\mathrm{B}}\right] \\ &= RT \ln\left(\frac{x_{\mathrm{B}}}{x_{\mathrm{A}}}\right) + w_G\left(1 - 2x_{\mathrm{B}}\right) \end{aligned} \tag{10.92}$$

and the equation for the tangent line itself is, as before,

$$\mu_{\mathrm{A}} = \Delta_{\mathrm{mix}} G - x_{\mathrm{B}}\left(\frac{d\Delta_{\mathrm{mix}} G}{dx_{\mathrm{B}}}\right) \tag{10.93}$$

Calculating the intercept on the x_{A} axis of the tangent at $x_{\mathrm{B}} = 0.4$ with these equations, we get $\mu - \mu^\circ = -946\,\mathrm{J\,mol^{-1}}$.

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$\mu - \mu^\circ$ From Equation

Substitution of Equation (10.92) into Equation (10.93), remembering that $\Delta_{\text{mix}}G$ is now Equation (10.88), we find that

$$\mu_A = RT \ln x_A + w_G x_B^2$$

but we know that here μ_A is really $\mu_A - \mu^\circ$, because we have implicitly assumed that $\mu^\circ = 0$. In other words, the intercept we calculated is the numerical value on the x_B axis, but that numerical value is a ΔG of mixing, a difference, so our μ_A is also a difference. What we have calculated is in fact

$$\mu_A - \mu_A^\circ = RT \ln x_A + w_G x_B^2 \tag{10.94}$$

and at $x_A = 0.6$, $x_B = 0.4$, $w_G = 2000\,\text{J mol}^{-1}$, Equation (10.94) gives $\mu_A - \mu_A^\circ = -946\,\text{J mol}^{-1}$, in agreement (of course) with the tangent method.

If in Equation (7.34) we change μ_i to μ_A^{ideal}, and we compare this with Equation (10.94), we see that

$$\begin{aligned}
\mu_A - \mu_A^{\text{ideal}} &= \mu^{\text{EX}} \\
&= w_G x_B^2 && (10.95)\\
&= 2000 \times (0.4)^2 \\
&= 320\,\text{J mol}^{-1} && (10.96)\\
&= -946 + 1266\,\text{J mol}^{-1}
\end{aligned}$$

(1266 is $RT \ln x_A$ from page 195).

$\mu - \mu^\circ$ From Activity Coefficient

Also, it proves very convenient to define a correction factor for the mole fraction term in Equation (7.34), such that the non-ideal effects are taken into account. In other words, instead of correcting the ΔG or $\mu - \mu^\circ$ side of the equation with G^{EX}, we correct the mole fraction on the other side of the equation to give the same effect (we looked at this approach in more detail in Chapter 8). So we define a factor γ_R such that

$$\begin{aligned}
\mu_A - \mu_A^\circ &= RT \ln (x_A \gamma_{R_A}) && (10.97)\\
&= RT \ln x_A + RT \ln \gamma_{R_A}
\end{aligned}$$

and comparing this with Equation (10.94) we see that

$$\left.\begin{aligned}
RT \ln \gamma_{R_A} &= w_G x_B^2 \\
RT \ln \gamma_{R_B} &= w_G x_A^2
\end{aligned}\right\} \tag{10.98}$$

At $x_B = 0.4$ and $w_G = 2000\,\text{J mol}^{-1}$, $\gamma_{R_A} = 1.1378$ and $\mu_A - \mu_A^\circ = RT \ln (0.6 \times 1.1378) = 946\,\text{J mol}^{-1}$ again.

So there is complete equivalence between the use of the activity coefficient and the excess Gibbs energy. In a sense there is hardly any difference at all. If the correction for non-ideality is in a logarithmic form ($RT \ln \gamma$) it can be combined with the ideal term

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($RT \ln x$) as a correction to x. If it does not have a logarithmic form (wx^2) it becomes a correction to the ΔG or $\Delta\mu$ term.

CO_2 Solubility in NaCl Solutions

An interesting application of regular solution theory is presented by Nesbitt (1984). He shows that activity coefficients for CO_2 in aqueous NaCl solutions to quite high temperatures ($\approx 500\,°C$) and NaCl concentrations ($\approx\ 6\,m$) can be fit very well by a slight modification of (10.98). As written, the activity coefficients in (10.98) are based on Raoultian activities; that is, $\gamma_B \rightarrow 1$ as $x_B \rightarrow 1$. Solubility studies on the other hand normally use Henryan coefficients, where $\gamma_B \rightarrow 1$ as $m_B \rightarrow 0$, where m_B is the molality of the solute.

Following Robinson and Stokes (1959), Nesbitt plots $\ln \gamma_{CO_2}$ vs. $-(x_2^2 - 1)$ instead of x_2^2, where x_2 is the mole fraction of H_2O in the system. This has the desired effect of having $\gamma_{CO_2} \rightarrow 1$ as $x_2 \rightarrow 0$. Nesbitt calculates values of w_G and discusses applications to boiling hydrothermal solutions.

Unmixing

As w_G becomes larger, the mixing curve develops a flat portion, and eventually splits into two separate parabolic curves, one on each side of the diagram, as shown in Figure 10.14. In a real system this means that "unmixing" occurs. Instead of one homogeneous solution, two solutions form at equilibrium, the compositions of which are at the minima in the mixing curve. The chemical potentials in each of the two solutions are given by the tangent common to the two minima, showing that μ_A and μ_B are the same in each solution. Generally, the two compositions converge as temperature increases, generating a

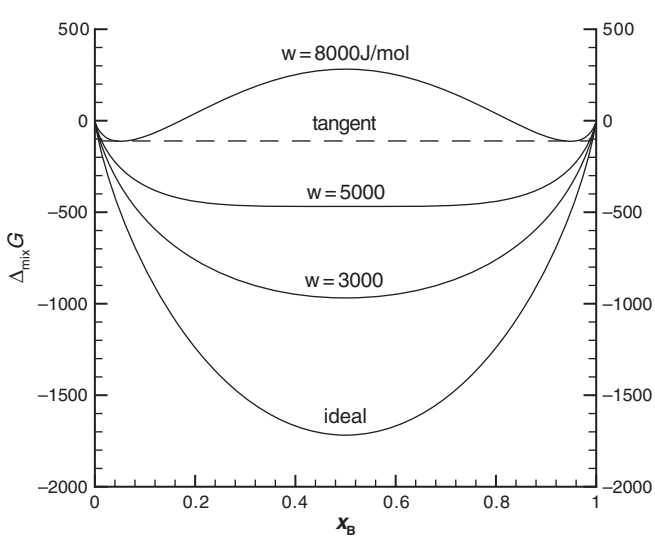

Figure 10.14 The excess Gibbs energy of mixing with various values of w_G, showing unmixing into two separate solutions when $w_G = 8000\,J\,mol^{-1}$. The dashed line is a tangent common to both minima in this curve.

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solvus (a subject continued in Chapter 17). The mixing curve and the solvus are not usually symmetrical as in this simple model. Somewhat more complex equations are required to generate asymmetry (Section 10.7).

10.6.2 The Raoultian Activity

The activities of A ($a_A = x_A \gamma_{R_A}$) and B ($a_B = x_B \gamma_{R_B}$) as a function of mole fraction are shown in Figure 10.15 and Table 10.2. At $x_B = 0.4$ and $w_G = 2000\,\mathrm{J\,mol^{-1}}$, $\gamma_{R_B} = 1.337$ (Equation (10.98)), so the activity of B is $0.4 \times 1.337 = 0.5348$, as shown.

Table 10.2. Activities and activity coefficients in a binary regular solution having $w_G = 2000\,\mathrm{J\,mol^{-1}}$.

x_A	x_B	γ_{R_A}	γ_{R_B}	a_A	a_B
0.9	0.1	1.008	1.922	0.907	0.192
0.8	0.2	1.033	1.676	0.826	0.335
0.7	0.3	1.075	1.485	0.753	0.445
0.6	0.4	1.138	1.337	0.683	0.535
0.5	0.5	1.223	1.223	0.612	0.612
0.4	0.6	1.337	1.138	0.535	0.683
0.3	0.7	1.485	1.075	0.445	0.753
0.2	0.8	1.676	1.033	0.335	0.826
0.1	0.9	1.922	1.008	0.192	0.907

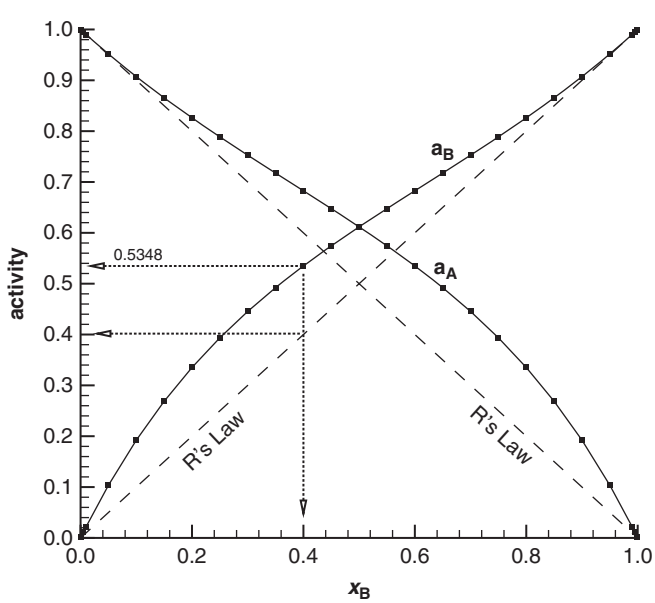

Figure 10.15 The activities of A and B as a function of x_B from Equations (10.98), with $w_G = 2000\,\mathrm{J\,mol^{-1}}$. The same data are shown in Figure 8.2.

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The standard state we have just used is pure substance A, because our values of μ_A are measured on the $x_A = 1$ axis, and our values of $(\mu_A - \mu^\circ)$ refer to the difference between the chemical potential of A in the solution and A in its pure form, whatever that is (solid or liquid A). Standard states in other cases, where we will be dealing with gases or electrolytes in solution, may not always be so obvious.

It is important to realize that all the features we have discussed – the tangent intercepts, activity coefficients, etc. – operate just the same no matter how complex the mixing curve becomes. They are just easier to discuss with a simple model.

10.7 Margules Equations

Because most real solutions do not follow the parabolic, symmetrical form of the one-parameter Margules equations, it is necessary to add more flexibility to the equations by adding more coefficients and more terms. One way to do this is to simply define a second w_G term of the type in (10.87), then combine the two w_G terms in a linear equation in x. This can be imagined as the "mixing" of two solutions, each symmetrical but having different values of w_G:

$$G^{\mathrm{EX}}_{\text{solution 1}} = w_{G_1} x_1 x_2 \tag{10.99}$$

$$G^{\mathrm{EX}}_{\text{solution 2}} = w_{G_2} x_1 x_2 \tag{10.100}$$

Now mix x_2 moles of the first solution with $x_1 (= 1 - x_2)$ moles of the second, stir well, and make a new solution, which is described by the sum of (10.99) and (10.100):

$$G^{\mathrm{EX}}_{\text{solution}} = x_1 (w_{G_2} x_1 x_2) + x_2 (w_{G_1} x_1 x_2) \tag{10.101}$$

or if you want to carry this process further, to m terms, the general expression is

$$G^{\mathrm{EX}}_{\text{solution}} = x_1 x_2 \sum_{i=1}^{m} w_{G_i} x_2^{i-1} \tag{10.102}$$

What we have now is the (weighted) sum of two (or more) parabolic equations to describe a non-ideal, asymmetric solution. Because of the second parameter, (10.101) is frequently called a two-parameter Margules equation, and (10.102) can be called the generalized Margules equation. It seems reasonable that this might have an appropriate form because (10.101) still goes to zero as either x_1 or x_2 approaches 1.0 (the excess Gibbs energy must be zero for pure substances); also with two parameters and two parabolas we should be able to fit a distorted parabolic shape, and that's what we might expect the excess Gibbs energy to look like for many real systems. In fact, two-parameter equations of this type do fit experimental data on real systems quite closely, and even work well with minerals that are sufficiently non-ideal that they have miscibility gaps (a solvus region).

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Box 10.4 The Margules Equations

Margules (1895) suggested an equation for the vapor pressures of solution components (partial pressures) in the form of a series expansion, using the systems ethyl alcohol–water and methyl alcohol–water as examples. Using our notation, his equation was

$$P_i = P_i^\circ x_i^{\alpha_0} e^{[\alpha_1(1-x_i)+\frac{\alpha_2}{2}(1-x_i)^2+\frac{\alpha_3}{3}(1-x_i)^3+\cdots]} \tag{10.103}$$

where i is 1 or 2 (binary solutions, so $x_2 = 1-x_1$), and where, to have the limiting condition that Henry's law is followed as $x_2 \to 0$, $\alpha_0 = 1$ and $\alpha_1 = 0$. This gives, as $(1 - x_1) \to 0$,

$$P_i = P_i^\circ x_i$$

or

$$P_i = \text{constant} \cdot x_i$$

which is Henry's law (Section 7.4.2).

If we assume that the partial pressures are in fact fugacities ($f_i = P_i$), then, using $a_i = f_i/f_i^\circ$,

$$\ln \gamma_i = \ln\left(\frac{a_i}{x_i}\right)$$

$$= \sum_{j=2}^{n} \frac{1}{j}[\alpha_j(1 - x_i)^j] \tag{10.104}$$

which, for a binary solution and $n = 3$ is

$$\ln \gamma_1 = \tfrac{1}{2}\alpha_2 x_2^2 + \tfrac{1}{3}\alpha_3 x_2^3$$

and so

$$RT \ln \gamma_1 = \text{constant}_1 \cdot x_2^2 + \text{constant}_2 \cdot x_2^3$$

which is the same in form as Equations (10.105) and (10.107), and if truncated to the first term on the right, is the same as the regular solution expression, Equations (10.98).

There is an extensive literature in both chemistry and geochemistry on these and other similar equations and their interrelations. Useful guides are Grover (1977) and Thompson (1967). They apply to any solutions, solid, liquid, or gaseous. Thompson points out that the Margules equations bear the same relationship to Henry's law that the Virial equation (Section 13.5) has to the ideal gas law, in that the first term in the Virial series (in the form of (13.26)) is the ideal gas law, and the Margules equation condenses to Henry's law, as shown above.

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Activity coefficients can also of course be written in terms of the two-parameter equations. Without derivation, they are

$$\left.\begin{aligned} RT\ln\gamma_1 &= \overline{G}_1^{\mathrm{EX}} \\ &= (2w_{G_2} - w_{G_1})x_2^2 + 2(w_{G_1} - w_{G_2})x_2^3 \\ RT\ln\gamma_2 &= \overline{G}_2^{\mathrm{EX}} \\ &= (2w_{G_1} - w_{G_2})x_1^2 + 2(w_{G_2} - w_{G_1})x_1^3 \end{aligned}\right\} \tag{10.105}$$

A different extension of Equation (10.87) is the Redlich–Kister equation,

$$G^{\mathrm{EX}} = x_1x_2\left[A + B(x_1 - x_2) + C(x_2 - x_2)^2 + D(x_1 - x_2)^3 + \cdots\right] \tag{10.106}$$

which has the activity coefficients

$$\left.\begin{aligned} RT\ln\gamma_1 &= a^{(1)}x_2^2 + b^{(1)}x_2^3 + c^{(1)}x_2^4 + \cdots \\ RT\ln\gamma_2 &= a^{(2)}x_1^2 + b^{(2)}x_1^3 + c^{(2)}x_1^4 + \cdots \end{aligned}\right\} \tag{10.107}$$

in which the $a, b, c, \ldots$ parameters are simple combinations of the $A, B, C, \ldots$ parameters in (10.106) (see Prausnitz *et al.*, 1999, p. 228).

These equations ((10.101) and (10.106)) are just a small sample of the many that have been proposed and used in the chemistry and chemical engineering literature.

10.7.1 Margules Equations and Virial Equations

It seems likely that various forms of the Margules equations work well in modeling solutions because they are actually forms of the virial equation (Section 13.5), which, as we said, has a secure theoretical foundation. To show that the Margules equations have the form of a virial equation, rearrange (10.101) for the total excess free energy of a real, asymmetric solution, remembering that $x_1 = 1 - x_2$, giving

$$G^{\mathrm{EX}} = 0 + w_{G_2}x_2 + (w_{G_1} - 2w_{G_2})x_2^2 + (w_{G_2} - w_{G_1})x_2^3 \tag{10.108}$$

Because excess Gibbs energy is zero for ideal solutions, this has exactly the required form – the first term on the right-hand side (zero) is the value of G^{EX} for an ideal solution, and the remaining terms are an ascending polynomial in the variable x_2. Assuming that we can substitute mole fraction for volume ((13.24)) or pressure ((13.26)) by virtue of Henry's law, this has the form of a virial equation carried to the fourth coefficient. For symmetric solutions, $w_{G_2} = w_{G_1}$ and (10.108) reduces to

$$G^{\mathrm{EX}} = w_G x_2 - w_G x_2^2 \tag{10.109}$$

This has the form of a virial equation carried only to the third coefficient (which is why it doesn't fit more general, asymmetric solutions).

10.7.2 Margules Equations for Ternary and Higher-Order Systems

In the examples so far, we have used binary (two-component) solutions exclusively. Exactly the same reasoning may be used to derive equations for ternary, quaternary, and even more

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complex solutions. The equations become more unwieldy with each added component, and the properties they represent cannot be illustrated in two-dimensional graphs. However, the equations can be used in computer programs to generate properties of multicomponent systems for given conditions, and they should continue to fit real solutions adequately for the same reasons discussed above. The main problem with these higher-order systems is not in using the Margules equations, but that a lot of experimental data are required if the fit is to be useful, and rather few solid solutions have been sufficiently investigated in this respect.

Rather than writing out all equations for all properties, we will save space by deriving only the Gibbs energy equations for ternary systems. The same approach can then be used to derive equations for other properties or for solutions containing more than three components. First, for a *ternary symmetric solution*, we can follow the analogous procedure used to derive (10.101) and imagine three regular binary solutions with a total of three components (1+2; 1+3; 2+3) being mixed to form a single ternary regular solution (1+2+3). The total excess Gibbs energy is the sum of the one-parameter equations (10.99) for each of these three solutions:

$$G^{\mathrm{EX}}_{\mathrm{solution}} = w_{G_{12}} x_1 x_2 + w_{G_{23}} x_2 x_3 + w_{G_{13}} x_1 x_3 \tag{10.110}$$

Similarly, we can derive the analogous equation for a *ternary asymmetric solution* by summing expressions (10.101) for a mixture of three asymmetric binary solutions of the same three components:

$$\begin{aligned} G^{\mathrm{EX}}_{\mathrm{solution}} = {} & \left(w_{G_{23}} x_2^2 x_3 + w_{G_{32}} x_3^2 x_2\right) + \left(w_{G_{13}} x_1^2 x_3 + w_{G_{31}} x_3^2 x_1\right) \\ & + \left(w_{G_{12}} x_1^2 x_2 + w_{G_{21}} x_2^2 x_1\right) \end{aligned} \tag{10.111}$$

The brackets here show the original three asymmetric binary solutions we have "mixed." Derivation of Equation (10.111) by series expansion shows that there is actually a seventh term on the right side, a constant, which is often arbitrarily set to zero.

Notice that (10.111) reduces to (10.110) by setting $w_{G_{ij}} = w_{G_{ji}}$ and that symmetric models therefore have half the number of w coefficients. A slightly more complex version of this equation, where the three terms are weighted in proportion to molar composition, is proposed by Grover (1977, p. 81); this is similar to the weighting technique used to derive the binary, asymmetric equation (10.101) above. Notice that the number of Margules w parameters increases three times relative to a binary system for both the symmetric and asymmetric equations. For a quaternary system they would increase four times, and so on. This means that we are going to need a great many data points in multicomponent systems so as not to over-fit the data. For example, you would not want to fit 7 data points in a quaternary system with an 8-parameter Margules equation analogous to (10.111). In practice, this imposes an upper limit on the number of components one might wish to consider if the amount of data for a system is limited.

Fortunately, it is not often necessary to consider solid solutions of more than three or four components. Many minerals have fewer than four major components. Minor components do not have a very significant effect on excess properties of the overall solution, as you can see from Equations (10.110) and (10.111) for ternary systems above. For more detail, see Guggenheim (1952), Prigogine and Defay (1954), Saxena (1973), Thompson (1967),

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and Grover (1977). An algorithm for computer calculation of Margules equations based on higher-degree virial equations and applicable to multicomponent systems is given by Berman and Brown (1984).

10.8 Beyond Margules

As useful and as influential as they have been, series expansions like the Margules, regular and virial equations can really only deal effectively with smooth, continuous curves. A high degree of molecular association, leading eventually to compound formation, as well as or combined with order–disorder effects, results in more complex types of curves which cannot be represented by series expansions without carrying the expansion to unmanageably high orders.

Kress (2003) uses the system CO–O_2 to illustrate the problem in a striking fashion. A naive consideration of the energetics of mixing of these two gases would result in a near-zero enthalpy of mixing and an entropy of mixing based on Equation (7.15)

$$\Delta_{\text{mix}} S_{\text{ideal solution}} = -R(x_1 \ln x_1 + x_2 \ln x_2) \tag{7.15}$$

or some slight variation, resulting in a smooth curve of positive $\Delta_{\text{mix}} S$ values. In reality, the reaction

$$\text{CO(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$$

occurs to a very great extent, and the entropy curve between CO and O_2 is curved downward with a cusp at the CO_2 composition, and the enthalpy and Gibbs energy variations are similarly totally different from ideal mixing.

This problem has long been recognized. Kress presents a useful short summary of the many approaches that have been suggested, beginning with Guggenheim's (1952) "quasi-chemical" approach, as well as algorithms allowing computation of species standard state and mixing properties in non-ideal associated solutions. The problem extends beyond aqueous solutions to fused salts and silicate melts, and represents a research area that will be active for some time to come.

10.9 The Gibbs–Duhem Equation

We must be aware of one very important relationship between solution components, which is that they are not all independent of one another. This seems reasonable enough qualitatively. You can well imagine that changing the concentration, say, of one component of a binary system would have some effect on the activities and activity coefficients of both components, not just one. These changes can be quantified, and this is a highly useful device, because it is very common to measure the activity of only one component in a binary system as a function of concentration, and then calculate the activity of the other component, instead of measuring it too. We mentioned one way of doing this in Section 5.8.4, the isopiestic method.

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This relationship was introduced in Section 4.14.2. Equation (4.72) from that section is

$$d\mu_1 = -\frac{x_2}{x_1}\, d\mu_2 \tag{4.72}$$

showing the interdependence of the chemical potentials in a binary system, but the equation is not used in this form. Now that we have the activity, in the form of Equation (8.19), which is

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

we can substitute this into (4.72) (μ_i° is a constant so $d\mu_i^\circ = 0$, and RT cancels out), obtaining

$$d \ln a_1 = -\frac{x_2}{x_1}\, d \ln a_2 \tag{10.112}$$

This looks more useful, but it is difficult to integrate because a plot of x_2/x_1 vs. $-\ln a_2$ is asymptotic to both axes. If we rewrite the equation with $x_i\gamma_i$ instead of a_i, and note that

$$\begin{aligned} x_1\, d \ln x_1 + x_2\, d \ln x_2 &= x_1 \frac{dx_1}{x_1} + x_2 \frac{dx_2}{x_2} \\ &= dx_1 + dx_2 \\ &= 0 \end{aligned}$$

it becomes

$$d \ln \gamma_1 = -\frac{x_2}{x_1}\, d \ln \gamma_2 \tag{10.113}$$

and a plot of x_2/x_1 vs. $-\ln \gamma_2$ has only one asymptotic branch (for $x_1 \to 0$). Integrating,

$$\ln \gamma_1'' - \ln \gamma_1' = -\int_{x_1'}^{x_1''} \frac{x_2}{x_1}\, d \ln \gamma_2 \tag{10.114}$$

or, if x_1' is pure phase 1 (Raoultian standard state), $\ln \gamma_1' = 0$, and

$$\ln \gamma_1 = -\int_{x_1=1}^{x_1} \frac{x_2}{x_1}\, d \ln \gamma_2 \tag{10.115}$$

showing that if you know $\ln \gamma_2$ over a range of compositions, you can calculate $\ln \gamma_1$ over the same range.

There is a rather large literature on how to perform this integration graphically and analytically. We will show just one very effective method, introduced by Darken and Gurry (1953, Chapter 10), see also Lupis (1983, Chapter 5). If we define

$$\alpha_i = \frac{\ln \gamma_i}{(1 - x_i)^2} \quad (i = 1 \text{ or } 2) \tag{10.116}$$

then

$$\begin{aligned} d \ln \gamma_2 &= d(\alpha_2 x_1^2) \\ &= 2\, \alpha_2 x_1\, dx_1 + x_1^2\, d\alpha_2 \end{aligned}$$

and Equation (10.115) becomes

$$\ln \gamma_1 = -\int_{x_1=1}^{x_1} 2\, \alpha_2 x_2\, dx_1 - \int_{x_1=1}^{x_1} x_1 x_2\, d\alpha_2 \tag{10.117}$$

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Integrating the second integral by parts[6] gives

$$\int_{x_1=1}^{x_1} x_1 x_2 \, d\alpha_2 = \alpha_2 x_1 x_2 - \int_{x_1=1}^{x_1} \alpha_2 \, d(x_1 x_2) \tag{10.118}$$

Combining this with (10.117) then gives, after some manipulation,

$$\ln \gamma_1 = -\alpha_2 x_1 x_2 - \int_{x_1=1}^{x_1} \alpha_2 \, dx_1 \tag{10.119}$$

The last term is quite easy to integrate, because the α function is always finite, even as $x_i \to 0$. That is,

$$\lim_{x_i \to 1} \left[\frac{\ln \gamma_i}{(1 - x_i)^2} \right]$$

is finite, despite the zero squared term in the denominator.

Function α_i in Equation (10.116) looks a lot like our use of w_G in Equation (10.98). In fact, if the solution is strictly regular, in which $\alpha_1 = \alpha_2 =$ a constant, then $\alpha = w_G/RT$, and Equation (10.119) becomes

$$\ln \gamma_1 = -\frac{w_G}{RT} x_1 x_2 - \frac{w_G}{RT}(x_1 - 1) \tag{10.120}$$

and similarly for $\ln \gamma_2$.

10.10 Summary

In previous chapters we have built an impressive theoretical structure, and seen how it could be applied to idealized systems, especially solutions, with a mention of real systems here and there. Eventually, of course, we have to take measurements on real solutions and somehow fit these into our theoretical structure. In this chapter, we start to do that.

We discussed solution volumes at length, because this seems to be the most intuitive way to understand partial molar quantities, and other solution properties. We then broadened the discussion to include enthalpies, heat capacities, and Gibbs energies. A persistent theme is the attempt to find equations that will not only fit real data, but which have some relationship to our theory, so that we can extract thermodynamic data from them.

We found that equations for the Gibbs energy have a different form than equations for the other properties, basically because of its pressure derivative relationship to volume, and hence fugacity and activity. We introduced regular solution theory as the simplest way of dealing with deviations from ideal behavior, and then saw that the basic structure could be expanded to more complex solutions in the form of the Margules equations. Regular, Margules, and virial equations have proven extremely useful, but they are inadequate in solutions with a high degree of association.

Finally we looked at the Gibbs–Duhem equation, and how it is used in binary systems. We will see some applications of this in Chapter 14.

[6] How to integrate by parts is shown in Section 5.6.4, except that here $u = \alpha_2$ and $v = x_1 x_2$.

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