

## **Chap. 8 Mixtures and Solutions**

8.1	<i>Mixtures and Solutions defined; measures of composition</i>	1
8.2	<i>Ideal mixtures and ideal solutions</i>	2
	<i>Ideal gas</i>	3
	<i>Entropy of mixing</i>	4
8.3	<i>Gas-vapor mixtures</i>	8
8.4	<i>Nonideal Liquid and Solid Solutions: Partial Molar Properties</i>	12
8.5	<i>Nonideal Solutions: Excess Properties</i>	14
8.6	<i>The Chemical Potential</i>	15
8.7	<i>Activity and Activity Coefficient</i>	17
8.8	<i>Excess Gibbs Free Energy</i>	19
8.9	<i>Regular Solutions</i>	20
8.10	<i>Chemical Potentials in Gas Mixtures</i>	22

## 8.1 Mixtures and Solutions defined; measures of composition

Up to this stage, we have dealt almost exclusively with systems containing only one component. These simple substances can exist (at equilibrium) in up to three phases, the limit imposed by the phase rule. The one-component system is fixed in composition. A two-component system possesses a single composition variable, which is considered by the phase rule as a degree of freedom. At this point, the reader is advised to review Sect. 1.11, where the meanings of components and phases are explained in more detail.

The objective of the present chapter is to understand the thermodynamics of single-phase, two-component (binary) systems. The sole exception to this restriction is the treatment in Sect. 8.3 of the gas-vapor mixture, from which vapor can condense into a liquid. Two component systems that do not change composition during a process, such as air flowing through a valve or water which does not dissociate into its component elements, are effectively pseudo-one component systems and can be handled by the methods used for true one-component systems. For the most part, we will explore the thermodynamic characteristics of mixtures of ideal gases and the simplest models of nonideal binary solid or liquid solutions. This chapter is a necessary preliminary to the analyses of multicomponent, multiphase equilibria and chemical reactions that are presented in succeeding chapters.

Before starting, clarification of the terms “mixture” and “solution” is in order. These terms are nearly, but not quite, synonymous. A *solution* unequivocally refers to a homogeneous system of two or more components. This term is applied to liquids and solids, but not to gases. Salt dissolved in water is an aqueous solution of NaCl; a gold-silver alloy is a solid solution of these two elements. However, air is a *mixture* of oxygen and nitrogen (plus minor species), not a solution of O<sub>2</sub> in N<sub>2</sub>. A multiphase system of a single component is referred to as a mixture of phases, but it is not a mixture of components. Reference to a mixture of steam and liquid water is acceptable terminology, but a salt solution would never be called a mixture. These semantic distinctions between mixtures and solutions are usually clear from the context in which the words are used.

Several measures of composition (or concentrations) are available. The most commonly used is the *mole fraction*, which for component *i* is defined by:

$$x_i = \frac{n_i}{n} \quad \text{where} \quad n = \sum n_i \quad (8.1)$$

*n* is the total moles in the system and *n<sub>i</sub>* is the number of moles of component *i*. By definition, the sum of the mole fractions is unity. In analogous fashion, the mass fraction of species *i* is equal to the mass of *i* divided by the total mass. The mole (or mass) fraction unit is used for gas mixtures, non-aqueous liquid solutions, and solid solutions. In aqueous solutions, these units are generally avoided in favor of volumetric units such as moles or mass of *i* per unit volume of solution.

In this chapter, the temperature and total pressure are specified. The only variables or degrees of freedom are the concentrations, of which there are N-1 independent values for an N-component system.

## 8.2 Ideal mixtures and ideal solutions

Ideality in a multicomponent system means that the components interact with each other (on a molecular level) with the same intensity as the component molecules interact amongst themselves. In an ideal gas mixture, there are no intermolecular interactions in either the pure components or in the mixture. Pure solids and liquids must exhibit strong intermolecular attractions simply to exist as condensed phases. A binary solution of A and B is ideal if the average of the A-A and B-B intermolecular forces is just equal to the strength of the A-B interaction.

The mixing process starts from prescribed quantities of the pure components at specified temperature and pressure. The mixture is at the same T and p. If the mixture or solution is ideal, this process does not release or absorb heat from the surroundings and the combined volume is the sum of the individual volumes of the pure constituents:

$$V = \sum n_i v_i \quad \text{or} \quad v = V / n = \sum x_i v_i \quad (8.2a)$$

Absent pV work and heat exchange with the surroundings, the First law requires that the internal energy of the mixture be equal to the sum of the values of the pure components, or:

$$U = \sum n_i u_i \quad \text{or} \quad u = U / n = \sum x_i u_i \quad (8.2b)$$

where  $u_i$  is the molar internal energy of component i and  $u$  is the internal energy per mole of mixture or solution. Because mixing occurs at constant pressure and there is no change in system volume, a similar equation applies to the enthalpy:

$$H = \sum n_i h_i \quad \text{or} \quad h = H / n = \sum x_i h_i \quad (8.2c)$$

Since the specific heats  $C_V$  and  $C_P$  are temperature derivatives of  $u$  and  $h$ , respectively, the same mixing rules apply:

$$C_V = \sum x_i C_{Vi} \quad \text{and} \quad C_P = \sum x_i C_{Pi} \quad (8.2d)$$

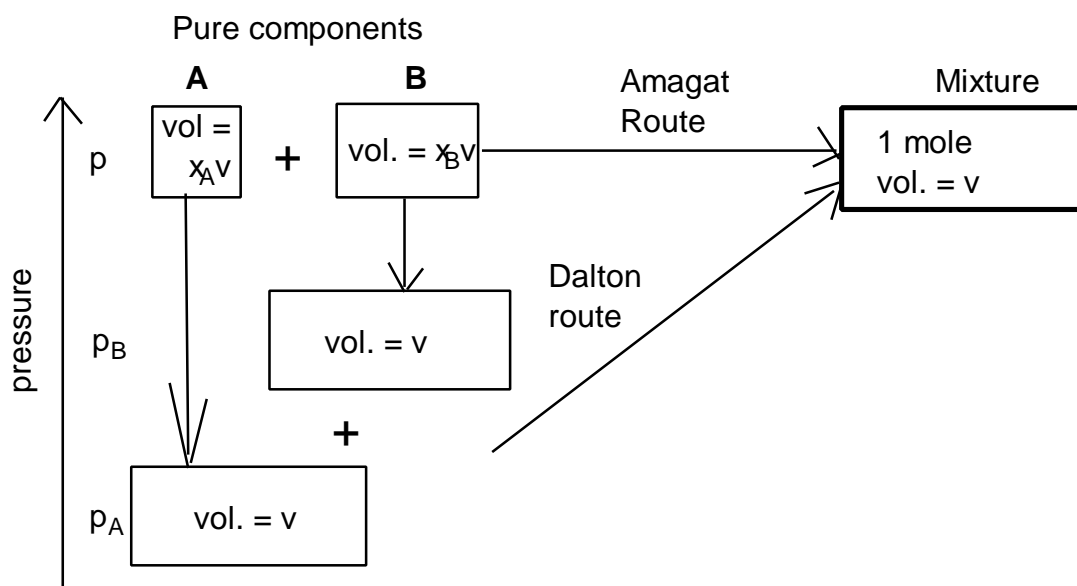
where  $C_{Vi}$  and  $C_{Pi}$  are the molar specific heats of pure component i.

The entropy of an ideal mixture or solution is not as transparent as are  $U$  and  $H$ . This issue is best deferred until the fundamentals of ideal gas mixtures are investigated in more detail.

## Ideal gas

The mixture properties given by Eqs (8.2a) – (8.2d) apply to ideal gas mixtures as well as to ideal condensed-phase solutions. In the latter, the concentrations in solution are distinct from and unrelated to the total pressure on the system. In gas mixtures, however, the total pressure is the sum of the *partial pressures* of the individual components; total pressure and composition are intimately related.

Two routes for forming 1 mole of an ideal gas mixture from  $x_A$  and  $x_B$  moles of pure components A and B are shown in Fig. 8.1. Both mixing processes are conducted isothermally at temperature  $T$ .  $x_A$  and  $x_B$  are the mole fractions of A and B in the mixture, so  $x_A + x_B = 1$ . In the diagram, the molar volume  $v = RT/p$ , where  $p$  is the pressure of the initial pure components and of the final mixture.



**Fig. 8.1** Two methods of mixing  $x_A$  moles of pure A with  $x_B$  moles of pure B to form 1 mole of an ideal gas mixture. The temperature is constant and  $v = RT/p$ .

The upper path in Fig. 8.1, called the Amagat route, simply mixes the two pure components at constant pressure  $p$ . The lower path, called the Dalton route, is more circuitous but produces the same end result. In this route, the pure components are first isothermally expanded from their initial volumes to the final volume  $v$  of the mixture. The initial states of A and B at pressure  $p$  obey the ideal gas law:

$$p(x_A v) = x_A RT$$

$$p(x_B v) = x_B RT$$

The volumes of the pure components at pressure  $p$  are placed in parentheses.

When expanded to volume  $v$ , the pressures of the pure components are reduced according to the ideal gas law:

$$p_A v = x_A RT \qquad p_B v = x_B RT$$

Comparing the left hand sides of the above pairs of equations shows that the reduced pressures are:

$$p_A = x_A p \qquad p_B = x_B p \qquad (8.3)$$

When the two expanded volumes of A and B are mixed as shown in Fig. 8.1, the pressures  $p_A$  and  $p_B$  are retained in the mixture. This is the origin of the term “partial” pressures. Adding the two equations in (8.3) yields:

$$p_A + p_B = p \qquad (8.4)$$

The partial pressures play dual roles as measures of mixture composition and as contributions to the total gas pressure. Equations (8.3) and (8.4) are collectively known as Dalton’s rule.

The components of an ideal gas mixture individually obey the ideal gas law. Each constituent species independently occupies the same volume at the same temperature as the others. The equation of state for species  $i$  in a general multicomponent gas mixture is:

$$p_i V = n_i RT \qquad (8.5)$$

The mixture obeys the ideal gas law at the specified total pressure:

$$pV = nRT \qquad (8.6)$$

### Entropy of mixing

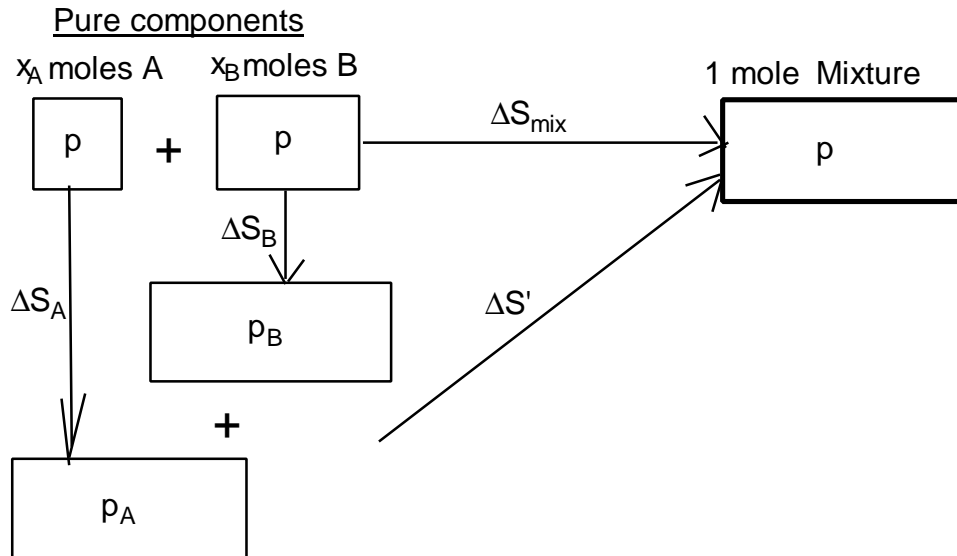
In isothermal, isobaric mixing of ideal substances, all thermodynamic properties remain unchanged:

$$\Delta V_{\text{mix}} = 0 \qquad \Delta U_{\text{mix}} = 0 \qquad \Delta H_{\text{mix}} = 0 \qquad (8.7)$$

except for the entropy. Despite the absence of intermolecular interactions in ideal gases, mixing of pure components increases the entropy because the mixture is more random state than the separated pure components; mixing is an irreversible process that requires work to undo\*. The irreversible nature of mixing resides in the Amagat route in Fig. 8.1, which entails an entropy increase  $\Delta S_{\text{mix}}$ . The utility of the Dalton route in this figure is that it provides a way of calculating  $\Delta S_{\text{mix}}$ . Figure 8.2 shows the entropy changes for the various steps in the two routes. Because the change in a thermodynamic property is path-independent, these entropy changes are related by:

---

\* examples are all chemical separation processes. An extreme case is the separation of the isotopes of uranium



**Fig. 8.2 Entropy changes associated with the Amagat and Dalton Routes for mixing pure components A and B.**

$$\Delta S_{\text{mix}} = \Delta S_A + \Delta S_B + \Delta S' \quad (8.8)$$

The first two terms on the right represent isothermal pressure changes for which the entropy changes are given by Eq (3.10):

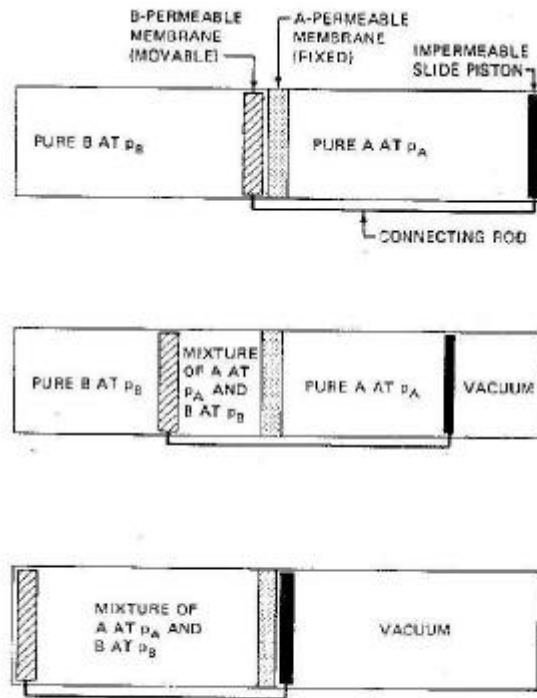
$$\Delta S_A = -R x_A \ln(p_A/p) \quad \Delta S_B = -R x_B \ln(p_B/p) \quad (8.9)$$

The entropy change on mixing by the Dalton path,  $\Delta S'$ , is zero.

Proof of this assertion is based on the cylinder-piston apparatus shown in Fig. 8.3. The pure components at their reduced pressures are initially contained in compartments separated by a fixed membrane that is permeable to component A but that will not pass component B. These two compartments are equivalent to the two lower boxes in Fig. 8.2, and the two pistons and the central membrane represent the lower plus sign in Fig. 8.2.

The apparatus in Fig. 8.3 also contains moveable pistons connected by a rigid rod. The pistons are frictionless and can move from right to left with requiring work to be done on them; the net force on the connected pistons is zero because  $p_B$  acts equally on both faces of the B-permeable membrane and  $p_A$  acting on the right hand face of the B-permeable membrane is balanced by the same pressure acting on the left hand face of the slide membrane.

As the moveable pair of connected pistons moves to the left, component B flows without resistance into the mixture region and component A does likewise through the fixed central membrane.



**Fig. 8.3** Apparatus for mixing ideal gases without an entropy change

There is no internal energy change during mixing because  $U$  for ideal gases is independent of pressure or volume. Since  $W = 0$  and  $\Delta U = 0$ , the First law requires that  $Q = 0$ . Since the process is reversible, the Second law yields  $\Delta S' = Q/T = 0$ .

Using this result along with Eq (8.9) in Eq (8.8) and expressing the pressure ratios by Dalton's rule, Eq (8.3), yields:

$$\Delta S_{\text{mix}} = -R(x_A \ln x_A + x_B \ln x_B) \quad (8.10)$$

Eq (8.10) applies to one mole of a binary solution. For other quantities of solution and more than two components, the more general form of the entropy of mixing formula is:

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x_i \quad (8.11)$$

Although derived for ideal gases, Eq (8.11) applies to ideal solutions of solids and liquids as well. For solid solutions, the derivation relies on statistical thermodynamic methods and is beyond the scope of these notes.

For nonideal solutions or mixing processes that are neither isothermal nor isobaric, or for initial states that are mixtures rather than pure components, Eq (8.11) is but one component of the entropy change. These effects are illustrated in the following examples.

Example: Calculate the changes in enthalpy and entropy when two moles of helium (species 1) at  $T_1 = 100^\circ\text{C}$  and  $p_1 = 1 \text{ atm}$  are mixed with one mole of nitrogen (species 2) at  $T_2 = 200^\circ\text{C}$  and  $p_2 = 0.5 \text{ atm}$ . Mixing takes place adiabatically and the mixture volume is the same as the sum of the volumes of the initial pure species. This process represents opening of a valve between two insulated tanks of the gases and allowing their contents sufficient time to mix to a uniform state.

We first calculate the temperature, pressure, volume, and composition of the mixture, whose properties are designated without a subscript. The composition is characterized by the helium mole fraction  $x = n_1/n = 0.667$ . The nitrogen mole fraction is  $1-x = 0.333$ . The mixture volume is the sum of the volumes of the two tanks:

$$V = V_1 + V_2 = n_1RT_1/p_1 + n_2RT_2/p_2 = 0.141 \text{ m}^3$$

To calculate the mixture temperature, the First law is applied. Since the tanks are insulated ( $Q = 0$ ) and do no work because they do not change volume ( $W = 0$ ), the First law requires the internal energy of the mixture to equal the sum of the internal energies of the pure gases. For ideal gases the internal energy is dependent on temperature only and can be expressed in terms of the heat capacities as follows:

$$nC_V(T - T_{\text{ref}}) = n_1C_{V1}(T_1 - T_{\text{ref}}) + n_2C_{V2}(T_2 - T_{\text{ref}})$$

$T_{\text{ref}}$  is an arbitrary reference temperature and  $C_{V1} = (3/2)R$  and  $C_{V2} = (5/2)R$  are the specific heats at constant volume of helium and nitrogen, respectively. Using Eq (8.4), the specific heat of the mixture is the mole-fraction average of the two pure species:  $C_V = (11/6)R$ . Solving the above equation for  $T$  yields:

$$T = x \frac{C_{V1}}{C_V} T_1 + (1-x) \frac{C_{V2}}{C_V} T_2 = 145.5^\circ \text{C}$$

The final pressure is obtained from applying the ideal gas law to the mixture:

$$p = \frac{nRT}{V} = \frac{3 \times 8.314 \times (145.5 + 273)}{0.141} \times 10^{-5} \frac{\text{atm}}{\text{Pa}} = 0.74 \text{ atm}$$

To obtain the enthalpy change upon mixing the pure gases, the specific heats at constant pressure are needed. These are equal to the specific heats at constant volume plus the gas constant:  $C_{P1} = C_{V1} + R = (5/2)R$  and  $C_{P2} = C_{V2} + R = (7/2)R$ . The mixture  $C_P$  is:

$$C_P = xC_{P1} + (1-x)C_{P2} = (17/6)R$$

The enthalpy change for the mixing process is:

$$\Delta H = n [C_P(T - T_{\text{ref}}) - xC_{P1}(T_1 - T_{\text{ref}}) - (1-x)C_{P2}(T_2 - T_{\text{ref}})] = 305 \text{ J}$$

(the terms involving  $T_{\text{ref}}$  cancel).

To calculate the entropy change, the pure components must first be brought to the final  $p$  and  $T$  of the mixture. Using Eq (3.10), this step incurs the following changes in entropy:

$$\Delta S_1 = n_1 \left[ C_{p1} \ln \left( \frac{T}{T_1} \right) - R \ln \left( \frac{p}{p_1} \right) \right] = 1.18R$$

$$\Delta S_2 = n_2 \left[ C_{p2} \ln \left( \frac{T}{T_2} \right) - R \ln \left( \frac{p}{p_2} \right) \right] = -0.82R$$

The entropy of mixing at constant temperature and pressure is given by Eq (8.11):

$$\Delta S_{\text{mix}} = -R[n_1 \ln x + n_2 \ln(1-x)] = 1.91R$$

The entropy change for the process is:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_{\text{mix}} = 2.27R = 18.9 \text{ J/mole}$$

**Example:** Two moles of an ideal equimolar A-B solution (designated No. 1) are mixed with three moles of a similar solution containing 20 mole percent of A (No. 2). Both are at the same temperature. What is the entropy change when these two solutions are mixed to form solution 3?

The method is to start from the pure components (1.6 moles of A and 3.4 moles of B) and prepare solutions 1, 2, and 3 from them. The difference in the mixing entropies is the desired result. The entropy gains in preparing the two initial solutions from the pure components are:

$$\Delta S_{\text{mix1}} = -R[(1)\ln(0.5) + (1)\ln(0.5)] = 1.39R$$

$$\Delta S_{\text{mix2}} = -R[(0.6)\ln(0.2) + (2.4)\ln(0.8)] = 1.50R$$

The mole fraction of A in mixture number 3 is 0.32 and its mixing entropy is:

$$\Delta S_{\text{mix3}} = -R[(1.6)\ln(0.32) + (3.4)\ln(0.68)] = 3.13R$$

The entropy change due to combining solutions 1 and 2 to form solution 3 is:

$$\Delta S = \Delta S_{\text{mix3}} - \Delta S_{\text{mix1}} - \Delta S_{\text{mix2}} = 0.24R = 2.0 \text{ J/K}$$

Inclusion of the entropy of mixing in situations with components at different initial conditions (pressure and/or temperature) is the topic of Problem 8.1. Modification of the entropy-change calculation is also required if the phase of one species is initially different from that of the mixture (i.e., dissolving a solid into a liquid, see problem 8.7).

Although the mixing entropy formula was derived for ideal solutions, it is also present in mixtures of species that behave nonideally (see problem 8.8). Other exercises in mixing entropy are problems 8.16 and 8.19

### 8.3 Gas-Vapor Mixtures

One of the gas mixtures of greatest practical importance is the gas - vapor combination, with air being the gas and water the vapor. The thermodynamic behavior of

this mixture affects the weather and engineered devices such as air conditioners. In these applications, air can be treated as an inert ideal gas. Potter and Somerton (p. 252) also give a short discussion of gas-vapor mixtures.

Water in the gas phase can also be considered to behave ideally because its concentration in air is low. This two-component gas mixture (air is treated as a single species) obeys Dalton's rule discussed in the preceding section. However, the water component of the gas mixture is condensable; that is, the partial pressure of water vapor cannot exceed the vapor pressure of liquid water. In addition to the water vapor - air mixture, the system may also contain liquid water. In this limit, the gas phase is *saturated* with water.

If liquid water is absent, the partial pressure of water may be less than the vapor pressure. The *relative humidity*  $\phi$  quantitatively characterizes the water content of air as the ratio of the partial pressure of water to the vapor pressure of water:

$$\phi = p_v/p_{\text{sat}} \quad (8.13)$$

where  $p_v$  is the partial pressure of water vapor and  $p_{\text{sat}}$  is the vapor pressure, also called the saturation pressure. This property could be read from the steam tables (Chap 2). However, because the temperature in practical applications is generally between 0 and 100°C, the representation of  $p_{\text{sat}}$  by the Clausius-Clapyron equation (Sect. 6.4) is simpler and sufficiently accurate. In the temperature range of interest, the vapor pressure of water is\*:

$$p_{\text{sat}} = 1.67 \times 10^6 \exp(-5300/T), \text{ atm} \quad (8.14)$$

Like all thermodynamic properties of pure substances, the vapor pressure is in principle a function of two thermodynamic variables. Eq (8.14) shows only the temperature dependence. There is also dependence of  $p_{\text{sat}}$  on total pressure, but this effect is very small (see problem 8.6

The partial pressure of the air component is  $p_a$  and the total pressure (usually 1 atm) is denoted by  $p$ . Dalton's rule gives:

$$p = p_a + p_v \quad (8.15)$$

Equation (8.14) gives the partial pressure of water vapor in saturated air at a specified temperature. The inverse view of saturation gives the temperature at which saturation occurs in air with a specified water vapor partial pressure. This temperature is called the *dew point* because the phenomenon describes the first appearance of dew on grass as the night air cools. The dew point is obtained from Eq (8.14) by replacing  $p_{\text{sat}}$  by  $p_v$  and  $T$  by  $T_{\text{DP}}$ , the dew point:

$$T_{\text{DP}} = \frac{5300}{\ln(1.67 \times 10^6 / p_v)} \quad (8.16)$$

---

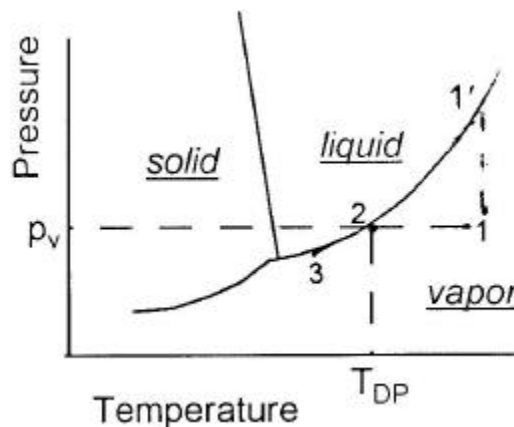
\* The vapor pressure depends very slightly on total pressure as well as on temperature (see problem 8.6)

where  $p_v$  is expressed in atm and  $T_{DP}$  in Kelvins.

The onset of liquid water condensation is shown in the p-T diagram of Fig. 8.4. The unsaturated air in state 1 has a relative humidity given by  $p_v/p_{sat}(T_1)$ , where  $p_v$  is specified. When this gas is cooled at constant total pressure, both  $p_v$  and  $p_a$  remain constant until the saturation curve at state 2 is reached. The temperature at state 2 is the dew point given by Eq (8.16). Upon further cooling from state 2 to state 3, water condenses from the gas,  $p_v$  (now equal to  $p_{sat}$ ) decreases as determined by Eq (8.14), and  $p_a$  increases to keep the total pressure constant.

**Example:** Unsaturated air is cooled in a closed container from state 1 where  $T_1 = 35.2^\circ\text{C}$ ,  $\phi = 0.7$ , to state 3 on the saturation curve at  $5^\circ\text{C}$ . Cooling occurs at a constant pressure of 1 atm. Calculate:

- the dew point of the gas in state 1
- the fraction of water condensed at state 3
- the heat removed from the container per mole of air during cooling from state 1 to state 2 and from state 2 to state 3.



**Fig. 8.4 The p - T diagram of water showing one unsaturated state (No. 1) and two saturated states ( Nos. 2 and 3)**

The saturation pressure associated with the air temperature of state 1 is on the liquid-vapor curve in Fig. 8.4 (point 1') directly above point 1. As calculated from Eq (8.14) for  $T_1 = 35.2^\circ\text{C}$  (308.2 K),  $p_{sat1} = 0.0568$  atm. The relative humidity is 70%, so Eq (8.13) gives  $p_{v1} = 0.0398$  atm. The dew point of air with this partial pressure of water lies on the saturation curve at state 2 in Fig. 8.4. From Eq (8.16),  $T_2 = T_{DP} = 301.9$  K ( $28.9^\circ\text{C}$ ). Because the air is just saturated in state 2,  $p_{sat2} = p_{v2} = p_{v1} = 0.0398$  atm (the water partial pressure does not change on cooling from 1 to 2).

The fraction of the water vapor in the gas phase in state 1 (or in state 2) that condenses when state 3 is attained is obtained by combining Dalton's rule and the vapor pressure curve. The number of moles of water ( $n_v$ ) per mole of air ( $n_a$ ) in the gas in states 2 is determined from Eq (8.3):

$$\frac{p_v}{p_a} = \frac{x_{v2}}{x_a} = \frac{n_{v2}/n_{tot}}{n_a/n_{tot}} \quad \text{or} \quad \frac{n_{v2}}{n_a} = \frac{p_{sat2}}{p - p_{sat2}} = \frac{0.0398}{0.96} = 0.041$$

where  $p = 1$  atm is the total pressure. In state 3,  $T_3 = 5^\circ\text{C}$  (278 K) and Eq (8.14) gives  $p_{sat3} = 0.0088$  atm. The vapor-to-air mole ratio is

$$\frac{n_{v3}}{n_a} = \frac{p_{sat3}}{p - p_{sat3}} = \frac{0.0088}{0.99} = 0.0089$$

Since all of the air remains in the gas phase,  $n_a$  is constant. The fraction of the initial water condensed in state 3 is:

$$f = \frac{n_{v2} - n_{v3}}{n_{v2}} = \frac{0.041 - 0.0089}{0.041} = 0.79$$

Because the cooling process is isobaric, the heat removed is equal to the enthalpy decrease (Sect. 3.4). From state 1 to state 2, only sensible heat is extracted from the gas mixture. The specific heats at constant pressure of water and air are 33 and 29 J/mole-K, respectively, so the mixture heat capacity is:

$$n_{tot}C_P = n_{v2}C_{Pw} + n_aC_{Pa} = 0.041 \times 33 + 1 \times 29 = 30.3 \text{ J/K - mole air}$$

The heat removed per mole of air is:

$$Q_{12} = H_2 - H_1 = n_{tot}C_P(T_1 - T_{DP}) = 30.3 \times (35.2 - 28.9) = 191 \text{ J/mole air}$$

Even though liquid water continuously condenses during cooling from state 2 to state 3, heat removal is broken into two distinct but hypothetical steps as shown in Fig. 8.5.

First, the mixture is cooled from  $T_2$  to  $T_3$  without condensation. The heat effect of this step is removal of sensible heat. Second, the required quantity of water is condensed at temperature  $T_3$ , during which the heat of condensation (vaporization) is released. The heat of vaporization  $\Delta h_{vap}$  is obtained from Eq (8.14); the Clausius-Clapyron equation [Eq(6.11)] implies that the argument of the exponential term is equal to  $\Delta h_{vap}/RT$ . Therefore,  $\Delta h_{vap} = 5300 \times 8.314 = 44,000$  J/mole and:

$$Q_{23} = H_2 - H_3 = n_{tot}C_P(T_2 - T_3) + f(n_{v2}/n_a)\Delta h_{vap} = 725 + 1425 = 2150 \text{ J/mole air}$$

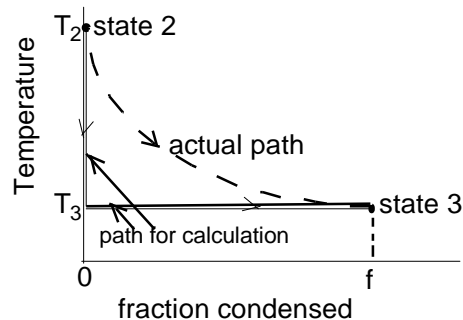


Fig 8.5 Diagram for heat removal calculation from state 2 to state 3

Problems 8.2, 8.12, 8.13, 8.15, and 8.21 explore other aspects of the above condensation process.

#### 8.4 Nonideal Liquid and Solid Solutions: Partial Molar Properties

Although gas mixtures can for most purposes be treated as ideal, liquid and solid solutions are generally significantly nonideal. The strong intermolecular interactions that are responsible for the existence of pure condensed phases are also the source of their deviations from ideality when mixed in solutions. Nonideal behavior affects all extensive properties of solid and liquid solutions, namely V, U, H, S, F, and G. Nonideality is manifest as a departure from linear variation of these properties with changes in the number of moles of one of the components. Linearity in ideal solutions is shown by the formulas for U and H given by Eqs (8.2b) and (8.2c).

The mathematical description of nonideal solution behavior is identical for all six extensive properties cited above. For simplicity, the theory is presented only for the enthalpy. The total and specific enthalpy of a nonideal solution is written in the same form as those for ideal solutions in Eq (8.2c). The sole change is replacement of the molar enthalpies of the pure components ( $h_i$ ) by a quantity called the *partial molar enthalpy*, denoted by  $\bar{h}_i$ :

$$H = \sum n_i \bar{h}_i \quad (8.17)$$

The partial molar property for species i depends on temperature and on the composition of the solution. For both properties, the effect of total pressure is negligible. The composition dependence renders  $\bar{h}_i$  considerably more difficult to determine than the corresponding molar property of the pure species,  $h_i$ .

The physical meaning of  $\bar{h}_i$  is best shown by explicitly including the mole numbers of each species in solution in writing its total enthalpy. Taking the differential of  $H(T, p, n_1, n_2, \dots)$  at constant T and p yields:

$$dH = \sum_i \left( \frac{\partial H}{\partial n_i} \right)_{T, p, n_j} dn_i \quad \text{or} \quad dH = \sum_i \bar{h}_i dn_i \quad (8.18)$$

where the partial derivative with respect to  $n_i$  is taken with the number of moles of all other components held constant. This partial derivative is the partial molar enthalpy of species i in the solution:

$$\bar{h}_i = \left( \frac{\partial H}{\partial n_i} \right)_{T, p, n_j} \quad (8.19)$$

Eq (8.19) has a definite physical meaning:  $\bar{h}_i$  represents the change in the enthalpy of a solution when a small quantity of species i is added while the amounts of all other

components are held constant. Equation (8.18) can be “integrated” in a physical sense by simultaneously adding the pure components to a vessel at rates proportional to their concentrations in the solution. This procedure maintains all concentrations constant during the process, and demonstrates that Eq (8.18) is consistent with Eq (8.17).

A very important relation can be deduced from these two equations. The total differential of Eq (8.17) is  $dH = \sum n_i d\bar{h}_i + \sum \bar{h}_i dn_i$ , which, when combined with Eq (8.18) yields:

$$\sum_i n_i d\bar{h}_i = 0 \quad (8.20)$$

The most useful form of the above equations are those in terms of mole fractions rather than mole numbers and specialized for an A-B binary solution. Dividing Eq (8.17) by the total moles of A and B gives the molar enthalpy of the solution:

$$h = x_A \bar{h}_A + x_B \bar{h}_B \quad (8.21)$$

where  $x_A + x_B = 1$ . Similar treatment of Eq (8.20) yields:

$$x_A d\bar{h}_A + x_B d\bar{h}_B = 0 \quad (8.22)$$

Taking the total differential of Eq (8.21) and taking Eq (8.22) into account produces the analog of Eq (8.18):

$$dh = \bar{h}_A dx_A + \bar{h}_B dx_B \quad (8.23)$$

For a detailed proof of this equation, see problem 8.14.

The importance of Eq (8.22) is that it permits  $\bar{h}_B$  to be determined if the variation of  $\bar{h}_A$  with composition is known. This relation is obtained by integrating Eq (8.22) from  $x_A = 0$  (where  $\bar{h}_B = h_B$  because the solution is pure B) to an arbitrary mole fraction of A:

$$\bar{h}_B - h_B = - \int_0^{x_A} \frac{x'_A}{1-x'_A} \frac{d\bar{h}_A}{dx'_A} dx'_A \quad (8.24)$$

If the dependence of  $\bar{h}_A$  with  $x_A$  is determined experimentally, Eq (8.24) permits  $\bar{h}_B$  to be calculated. Independent measurement of  $\bar{h}_B$  is not needed.

On occasion, it is necessary to invert Eq (8.21) to express the partial molar properties in terms of the molar property. For this purpose, Eq (8.23) is divided by  $dx_A$ , and since  $dx_B = -dx_A$ , the result is  $dh/dx_A = \bar{h}_A - \bar{h}_B$ . Multiplying this equation by  $x_B$  and adding the result to Eq (8.21) gives:

$$\bar{h}_A = h + x_B dh/dx_A \quad (8.25a)$$

and a similar approach yields:

$$\bar{h}_B = h + x_A dh/dx_B \quad (8.25b)$$

### 8.5 Nonideal Solutions: Excess Properties

An alternative to the rather abstract partial molar property approach to solution nonideality is the “excess” property method, which describes solutions in terms of their deviations from ideal behavior. Using an A-B binary solution with enthalpy as the thermodynamic property, the excess property formulation for the solution enthalpy is:

$$h = x_A h_A + x_B h_B + h^{ex} \quad (8.26)$$

where the first two terms on the right represent the combined enthalpies of the pure components (or of the solution if it were ideal) and  $h^{ex}$  is the excess enthalpy. This term is due solely to nonideality of the solution due to interactions of A and B at the molecular level.

Since the partial molar properties and the excess properties describe the same physical phenomenon, they must be related. The connection between  $h^{ex}$  and the partial molar enthalpies is obtained by equating the right hand sides of Eqs (8.21) and (8.26):

$$h^{ex} = x_A (\bar{h}_A - h_A) + x_B (\bar{h}_B - h_B) \quad (8.27)$$

A direct connection between  $\bar{h}_A$  and  $h^{ex}$  can be obtained by substituting Eq (8.24) into Eq (8.27), dividing the resulting equation by  $x_B$ , and taking the derivative with respect to  $x_A$ . This procedure yields:

$$\bar{h}_A - h_A = (1 - x_A)^2 \frac{d}{dx_A} \left( \frac{h^{ex}}{1 - x_A} \right) \quad (8.28)$$

Knowledge of  $h^{ex}$  as a function of  $x_A$  gives  $\bar{h}_A - h_A$  and Eq (8.27) then yields  $\bar{h}_B - h_B$ . The utility of this approach is that (at least for the enthalpy), the excess property is amenable to experimental determination.

Example:  $x_A$  moles of pure liquid A and  $x_B = 1 - x_A$  moles of pure B, both at temperature T, are mixed in a vessel maintained in a large water bath also held at temperature T. As a result of forming the solution, the temperature of the water bath is observed to increase by a small amount  $\Delta T$ . How is this temperature rise related to the excess enthalpy of solution?

Upon combining the two pure components, the enthalpy of the solution is less than that of the pure components by  $h^{ex}$ . Because formation of the solution occurs at constant pressure, the First law (Sect. 3.4) requires that the enthalpy change appear as heat transferred from the solution

to the water bath. This exchange of heat causes the water bath to increase in temperature. With  $C_p$  denoting the specific heat of water, the excess enthalpy of the solution is:

$$h^{\text{ex}} = -C_p \Delta T$$

A variant of this example is analyzed in problem 8.3.

Like the partial molar property method, the excess functions apply to other solution properties: volume, internal energy, entropy, Helmholtz free energy, and Gibbs free energy.

## 8.6 The Chemical Potential

The thermodynamic term “work” can be viewed as the product of a capacity factor (or quantity of something) and a difference in a potential. Table 8.1 lists several examples of this breakdown of work expressions for mechanical, electrical, thermal, and chemical processes.

**Table 8.1 Work as Capacity times Potential Difference**

Process	Capacity	Potential	Work
Lower a weight	mass	gravitational	$mg\Delta h$
pumping a fluid <sup>a</sup>	fluid volume	pressure	$V\Delta p$
electrical	charge	electrostatic	$q\Delta\Phi$
thermal <sup>b</sup>	heat	temperature	$(Q_H/T_H) \Delta T$
chemical <sup>c</sup>	moles of $i$	chemical	$n_i \Delta g_i$

<sup>a</sup> See Eq (4.12); adiabatic process

<sup>b</sup> See Sect. 4.3

<sup>c</sup> Isothermal, isobaric process; pure substance; see Eq (5.16)

Although rate processes are not part of thermodynamics, they involve the same potentials as those responsible for producing work. The basic rate laws are of the form:

$$\text{flux} = \text{coefficient} \times \text{potential gradient}$$

Table 8.2 shows the four common rate laws of this type.

**Table 8.2 Flux as a kinetic coefficient times a potential gradient**

Rate Process	Rate coefficient	potential	flux	name of law
heat conduction	thermal conductivity	temperature	$-k\nabla T$	Fourier's
momentum transfer(fluid)	viscosity	pressure	$-\mu\nabla p$	Newton's
Electricity flow	electrical conductivity	electrostatic	$-\kappa\nabla\Phi$	Ohm's
Diffusion	diffusion coefficient	chemical	$-(D_{c_i}/kT) \nabla\mu_i$	Fick's

Chemical reactions and interphase mass transfer are also driven by imbalances of the chemical potentials of species in the system.

The *chemical potential* is as important a thermodynamic driving force as temperature and pressure. This potential drives individual chemical species from one phase to another, from one molecular form to another, or from regions of high concentration to regions of low concentration.

The chemical potential is directly related to the Gibbs free energy of a system. For a one-component system, the chemical potential is identical to the molar Gibbs free energy of the pure substance. In solutions or mixtures, the chemical potential is simply another name for the partial molar Gibbs free energy. The discussion in Sects. 8.4 and 8.5, in which the enthalpy was used to illustrate partial molar and excess properties, applies to the Gibbs free energy; one need only replace  $h$  everywhere by  $g$ .

The reason that the *partial molar Gibbs free energy* is accorded the special name “chemical potential” is not only to shorten a cumbersome five-word designation. More important is the role of the chemical potential in phase equilibria and chemical equilibria when the restraints are constant temperature and pressure. The connection between the Gibbs free energy of a system at fixed  $T$  and  $p$  and the equilibrium state is given by Eq (5.11). We will utilize this equilibrium condition in the following chapters. For the remainder of the present chapter, the relation between the Gibbs free energy of a multicomponent system and the chemical potentials of its constituents is developed.

The chemical potential is embedded in the equation for the differential of the Gibbs free energy of a solution at fixed  $T$  and  $p$  analogous to Eq (8.18) for the enthalpy:

$$dG = \sum_i \left( \frac{\mathcal{G}}{\mathcal{h}_i} \right)_{T,p,n_j} dn_i \quad (8.29)$$

The partial derivatives that serve as coefficients of  $dn_i$  are the partial molar Gibbs free energies, or the chemical potentials, of each component of the solution:

$$\mathbf{m} = \bar{g}_i = \left( \frac{\mathcal{G}}{\mathcal{h}_i} \right)_{T,p,n_j} \quad (8.30a)$$

For a one-component system,  $G = ng$ , where  $g$  is the molar free energy. Consequently, for the pure substance, Eq (8.30a) reduces to:

$$\mu = g \quad (8.30b)$$

No subscript appears on the properties in Eq (8.30b) because only one component is involved in what is presumed to be a single phase. However, in a system with more than one phase, subscripting is needed to denote the phase in which a component is located.

Following the lines of the treatment of  $h$  and  $\bar{h}_i$  in Sect. 8.4, the following fundamental relations between  $g$  and  $\mu_i$  are obtained:

$$G = \sum_i n_i \bar{m}_i \quad \text{or} \quad g = \sum_i x_i \bar{m}_i \quad (8.31)$$

$$dG = \sum_i \bar{m}_i dn_i \quad \text{or} \quad dg = \sum_i \bar{m}_i dx_i \quad (8.32)$$

$$\sum_i n_i d\bar{m}_i = 0 \quad \text{or} \quad \sum_i x_i d\bar{m}_i = 0 \quad (8.33)$$

The last of this trio of relations is called the Gibbs-Duhem equation. It's extreme importance to solution thermodynamics is the connection it provides between the nonideal behavior of one component with the deviations from ideality of the other components. This property is especially useful for binary systems, and Eq (8.33) will be applied to A-B solutions later in this chapter.

Equations similar to Eqs (8.31) - (8.33) apply to other solution thermodynamic properties:  $v$  and  $\bar{v}_i$ ,  $u$  and  $\bar{u}_i$ , and  $s$  and  $\bar{s}_i$ .

## 8.7 Activity and Activity Coefficient

Although the thermodynamic behavior of species in solution is ultimately tied to their chemical potentials, a connection between this property and the concentration of the component is needed. This connection is made via a quantity called the *activity* of a solution species and the related property designated as the *activity coefficient*. The activity is a measure of the thermodynamic "strength" of a component in a solution compared to that of the pure substance; the purer, the stronger. As an example, when alcohol is mixed with water its effectiveness is reduced. Fanciers of single-malt scotches recognize this fact by imbibing only the straight liquor undiluted by either water or ice.

The link between chemical potential and concentration consists of two parts. In the first part, the chemical potential and the activity of a solution component are related by the equation:

$$\mu_i = g_i + RT \ln a_i \quad (8.34)$$

This equation defines the activity  $a_i$ . The definition has been chosen so that the activity tends to unity for pure  $i$ ; that is,  $\mu_i = g_i$ , the molar free energy of pure  $i$ . Activity varies monotonically with concentration. Therefore, when component  $i$  becomes infinitely dilute in the solution,  $a_i \rightarrow 0$  and its logarithm approaches  $-\infty$ . This is also the limit of the

chemical potential of  $i$  at infinite dilution. This inconvenient behavior of the chemical potential at zero concentration is avoided by using the activity in practical thermodynamic calculations involving species in solution. Another reason for the choice of the mathematical form of the relation between  $\mu_i$  and  $a_i$  embodied in Eq (8.34) is that the activity is directly measurable as the ratio of the equilibrium pressure exerted by a component in solution to the vapor pressure of the pure substance. This important connection is discussed in Chap. 9.

The second part of the relation between chemical potential and concentration is the definition of the activity coefficient as the ratio of the activity to the mole fraction:

$$\gamma_i = a_i/x_i \quad (8.35)$$

The mole fraction is the preferred concentration unit when dealing with nonaqueous or solid solutions. In aqueous solutions, the concentration unit most commonly used is molarity, or moles of a component per unit volume of solution.

The activity coefficient has the following properties:

- it is unity for a pure substance (i.e., when  $x_i = 1$ )
- it approaches a constant value as  $x_i \rightarrow 0$
- it can be either greater than or less than unity
- it is unity for all concentrations if the solution is ideal
- it is a function of solution composition, temperature.

The reason that  $\gamma_A \rightarrow 1$  in an A-B binary solution dilute in component B is because A molecules are surrounded mainly by other A molecules; the interactions are predominantly of the A-A type, so component A behaves as if it were pure. This limiting behavior is called Raoult's law. At the other extreme, the activity coefficient of A in a solution dilute in A approaches a constant value characteristic of the A-B intermolecular interactions. This behavior is termed Henry's law. A more detailed description of Raoult's and Henry's laws is presented in Chap. 9.

A useful connection between the activity coefficients of species in a solution is obtained by eliminating  $a_i$  between Eqs (8.34) and (8.35) and substituting the resulting equation into the Gibbs-Duhem equation, Eq (8.33). This procedure yields\*:

$$\sum_i x_i d \ln g = 0$$

This equation is particularly useful for two component (A-B) solutions, where it becomes:

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0. \quad (8.36a)$$

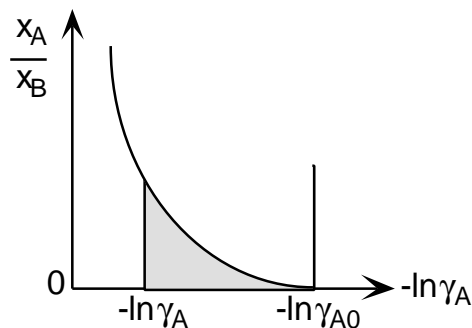
\* This result makes use of:  $\sum x_i d \ln x_i = \sum x_i (1/x_i) dx_i = \sum dx_i = d \sum x_i = 0$

For example, problem 8.5 shows how this equation can be used to assess the validity of formulas for  $h^{\text{ex}}$ . In another equally important application, the above equation can be integrated to give the Gibbs free energy analog of Eq (8.24) for the enthalpy:

$$\ln g_B = - \int_{\ln g_{A0}}^{\ln g_A} \frac{x_A}{x_B} d \ln g_A \quad (8.36b)$$

where  $\gamma_{A0}$  is the limiting value of the activity coefficient of A as  $x_A$  approaches zero.

In this limit  $\gamma_B$  approaches unity, which accounts for the zero lower limit of the integral of  $d \ln \gamma_B$ . This extraordinary relation permits the activity coefficient of B to be computed from the measurement of the activity coefficient of A over a composition range starting from pure B. Figure 8.6 shows the graphical implementation of Eq (8.36b). The curve intersects the horizontal axis at a value  $-\ln \gamma_{A0}$ . The curve asymptotically approaches an ordinate value of infinity as  $\ln \gamma_A \rightarrow 0$  (i.e., as  $x_A \rightarrow 1$ ). The shaded area in this plot is  $\ln \gamma_B$  at the solution composition  $x_A$ .



**Fig. 8.6** Graphical determination of  $g_B$  from the dependence of  $g_A$  on  $x_A$ .

Problem 8.11 is an example of the specific use of Eq (8.36b). Other exercises dealing with either Eqs (8.36a) or (8.36b) are problems 8.9, 8.10, 8.17, 8.18 and 8.20.

### 8.8 Excess Gibbs Free Energy

The molar Gibbs free energy of a solution ( $g$ ) can be written in terms of pure-component contributions ( $g_A$  and  $g_B$ ) and an excess value ( $g^{\text{ex}}$ ) as in Eq (8.26) for the enthalpy. However, an important contribution needs to be added. For a binary solution, the terms contributing to  $g$  are:

$$g = x_A g_A + x_B g_B + g^{\text{ex}} + g_{\text{mix}} \quad (8.37)$$

$g^{\text{ex}}$  contains the effects of solution nonideality. The last term on the right hand side arises from the entropy of mixing, and is present in ideal as well as nonideal solutions. According

to the definition given by Eq (5.6), any of the Gibbs free energies in Eq (8.37) can be expressed in terms enthalpy and entropy. In particular,  $g_{\text{mix}} = h_{\text{mix}} - Ts_{\text{mix}} = -Ts_{\text{mix}}$  because  $h_{\text{mix}} = 0$  (by the definition of an ideal solution). With  $s_{\text{mix}}$  given by Eq (8.11) for a binary solution and divided by the total solution moles, Eq (8.37) becomes:

$$g = x_A g_A + x_B g_B + g^{\text{ex}} + RT(x_A \ln x_A + x_B \ln x_B) \quad (8.38)$$

## 8.9 Regular Solutions

Nonideal behavior of a solution is contained in the  $g^{\text{ex}}$  term in Eq (8.38). The excess Gibbs free energy includes contributions from the excess enthalpy and the excess entropy:

$$g^{\text{ex}} = h^{\text{ex}} - Ts^{\text{ex}} \quad (8.39)$$

For ideal solutions, both  $h^{\text{ex}}$  and  $s^{\text{ex}}$  are zero. The behavior of a fair number of nonideal binary solutions can adequately represented by the *regular solution* model. In this theory, the molecules mix randomly as they do in ideal solutions, so that:

$$s^{\text{ex}} = 0 \quad (8.40)$$

That is, there is no tendency for either like or unlike molecules to cluster.

When  $s^{\text{ex}} = 0$ , the excess Gibbs free energy reduces to the excess enthalpy. The analytical formulation of  $h^{\text{ex}}$  in terms of composition is restricted by the limiting behavior of the solution enthalpy ( $h$ ) as the solution approaches pure A and pure B. In these limits,  $h \rightarrow h_A$  and  $h \rightarrow h_B$ , respectively. Examination of Eq (8.26) shows that to satisfy these limits,  $h^{\text{ex}}$  must be zero at  $x_A = 0$  and at  $x_B = 0$ . The simplest function that obeys these restraints is the symmetric expression:

$$h^{\text{ex}} = \Omega x_A x_B \quad (8.41)$$

where  $\Omega$  is a temperature-independent property of the A-B binary pair called the *interaction energy*. The form of Eq (8.41) is supported by molecular modeling, which suggests that  $\Omega$  is equal to the difference between the energy of attraction (bond energy) of the A-B pair and the mean of the bond energies of the A-A and B-B interactions.

Despite its simplicity, Eq (8.41) applies to a remarkably wide variety of solutions, including binary metal alloys such as thallium-tin, binary oxides such as  $\text{UO}_2\text{-Nd}_2\text{O}_3$ , and solutions of organic compounds such as benzene-cyclohexane. For the regular solution model to apply, the intermolecular attractions must be of a general nature, not specific such as hydrogen bonding when water is one component. In addition, the two molecules must be approximately the same size to preserve randomness of mixing and thus insure the validity of Eq (8.40).

Problem 8.3 deals with an extreme case of solution nonideality, illustrated by mixing of sulfuric acid and water.

Equations (8.40) and (8.41) define a regular solution. A-B combinations that satisfy Eq (8.40) but exhibit more complex formulas for  $h^{\text{ex}}$  that are asymmetric in composition are termed sub-regular solutions. However, the functional dependence of  $h^{\text{ex}}$  on composition is restricted. The activity coefficients  $\gamma_A$  and  $\gamma_B$  can be deduced from  $h^{\text{ex}}$  by applying the Gibbs-free-energy analogs of Eqs (8.25a) and (8.25b) (recall that in the discussion of Sect. 8.4, the enthalpy was used as a stand-in for any thermodynamic property except temperature and pressure). Replacing  $h$  by  $g$  and  $\bar{h}_i$  by  $\bar{g}_i = \mu_i$  in Eqs (8.25a) and (8.25b) yields:

$$\mathbf{m}_A = g + x_B \frac{dg}{dx_A} \quad \text{and} \quad \mathbf{m}_B = g + x_A \frac{dg}{dx_B} \quad (8.42)$$

Substituting Eq (8.38) into the above equation and comparing the resulting formulas for  $\mu_A$  and  $\mu_B$  with those obtained by eliminating the activity between Eqs (8.34) and (8.35) yields:

$$RT \ln \mathbf{g}_A = g^{\text{ex}} + x_B \frac{dg^{\text{ex}}}{dx_A} \quad \text{and} \quad RT \ln \mathbf{g}_B = g^{\text{ex}} + x_A \frac{dg^{\text{ex}}}{dx_B} \quad (8.43)$$

Equations (8.43) apply to any nonideal binary solution, with  $g^{\text{ex}}$  expressed in terms of  $h^{\text{ex}}$  and  $s^{\text{ex}}$  by Eq (8.39). For a regular solution,  $s^{\text{ex}}$  is zero and  $h^{\text{ex}}$  is given by Eq (8.41), and Eq (8.43) reduces to:

$$RT \ln \mathbf{g}_A = \Omega x_B^2 \quad \text{and} \quad RT \ln \mathbf{g}_B = \Omega x_A^2 \quad (8.44)$$

The activity coefficients must satisfy the Gibbs-Duhem equation, which for an A-B binary solution is  $x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$ . Not all  $h^{\text{ex}}$  functions of composition fit this restraint (see problem 8.5). However, problem 8.4 demonstrates that the activity coefficients of Eq (8.44), which are based on the  $h^{\text{ex}}$  of Eq (8.41), satisfy the Gibbs-Duhem equation, Eq (8.36a).

Since the interaction parameter  $\Omega$  is not a function of temperature, the logarithm of the activity coefficient varies inversely with temperature. Equations (8.43) form the basis for the analysis of binary phase diagrams in Chap. 9.

Proofs of Eqs (8.42) – (8.44) are left as an exercise (problem 8.4). As shown in problem 8.10, the activity coefficients given by Eq (8.44) obey the Gibbs-Duhem requirement of Eq (8.36a). Activity coefficient formulas that do not satisfy this restriction are incorrect.

### 8.10 Chemical Potentials in Gas Mixtures

The analysis in Sect. 8.2 of the entropy change associated with mixing of ideal gases at fixed  $T$  and  $p$  was based on the *absence* of an entropy change *if the pure gases are at the partial pressures that they will have in the mixture* (see Eq (8.9)). Since the gases are ideal, neither is there an enthalpy change in the mixing process. With both the enthalpy and entropy of each species unaltered, the Gibbs free energy must also remain constant during this mode of mixing. Since the Gibbs free energy of a species in a solution or a gas mixture is the same as its chemical potential, the above argument can be summarized by the equation:

$$\mu_i \text{ (in mixture at } p_i) = g_i \text{ (pure, at } p_i) \quad (8.45)$$

Contrary to condensed phases, the Gibbs free energy of a pure gas is pressure-dependent. In order to provide a common pressure reference for all pure gases (arbitrarily chosen at 1 atm),  $g_i$  in the above equation is expressed in terms of  $g_i^\circ$ , which is the molar Gibbs free energy of species  $i$  at temperature  $T$  and 1 atm pressure. The effect of the difference in pressure between  $p_i$  and 1 atm is obtained by combining Eq (7.15) with the ideal gas law:

$$\frac{dg_i}{dp} = \frac{RT}{p} \quad (8.46)$$

Integrating this equation from  $p_i$  to 1 atm and using Eq (8.45) yields:

$$\mu_i = g_i^\circ + RT \ln p_i. \quad (8.47)$$

The reference condition denoted by the superscript zero is called a *standard state* of the pure gas. In the above analysis, it has been set at 1 atm, which is convenient when dealing with permanent gases such as air. With this standard state,  $p_i$  must be expressed numerically in units of atmospheres.

However, other choices for the standard state are possible. If the gas is condensable (e.g., water), the standard state might be chosen as the vapor pressure of the liquid at the specified temperature  $T$ . This reference state will be used in the discussion of vapor-liquid equilibrium in the following chapter.