9.4: Liquid and Solid Mixtures of Nonelectrolytes

Homogeneous liquid and solid mixtures are condensed phases of variable composition. Most of the discussion of condensed-phase mixtures in this section focuses on liquids. The same principles, however, apply to homogeneous solid mixtures, often called solid solutions. These solid mixtures include most metal alloys, many gemstones, and doped semiconductors.

The relations derived in this section apply to mixtures of nonelectrolytes—substances that do not dissociate into charged species. Solutions of electrolytes behave quite differently in many ways, and will be discussed in the next chapter.

9.4.1 Raoult's law

In 1888, the French physical chemist François Raoult published his finding that when a dilute liquid solution of a volatile solvent and a nonelectrolyte solute is equilibrated with a gas phase, the partial pressure p_A of the solvent in the gas phase is proportional to the mole fraction x_A of the solvent in the solution:

$$p_A = x_A p_A^*$$ (9.4.1)

Here p_A^* is the saturation vapor pressure of the pure solvent (the pressure at which the pure liquid and pure gas phases are in equilibrium).

Consider the *solvent*, A, of a solution that is dilute enough to be in the ideal-dilute range. In this range, the solvent fugacity obeys Raoult's law, and the partial molar quantities of the solvent are the same as those in an ideal mixture. Formulas for these quantities were given in Eqs. 9.4.8–9.4.13 and are collected in the first column of Table 9.2. The formulas show that the chemical potential and partial molar entropy of the solvent, at constant T and p, vary with the solution composition and, in the limit of infinite dilution ($x_A \to 1$), approach the values for the pure solvent. The partial molar enthalpy, volume, internal energy, and heat capacity, on the other hand, are independent of composition in the ideal-dilute region and are equal to the corresponding molar quantities for the pure solvent.

Next consider a *solute*, B, of a binary ideal-dilute solution. The solute obeys Henry's law, and its chemical potential is given by $\mu_B = \mu_{x,B}^{\mathrm{ref}} + RT \ln x_B$ (Eq. 9.4.24) where $\mu_{x,B}^{\mathrm{ref}}$ is a function of T and p, but not of composition. μ_B varies with the composition and goes to $-\infty$ as the solution becomes infinitely dilute ($x_A \to 1$ and $x_B \to 0$).

For the partial molar entropy of the solute, we use $S_B = -(\partial \mu_B / \partial T)_{p,\{n_i\}}$ (Eq. 9.2.48) and obtain

$$S_B = -\left(\frac{\partial \mu_{x,B}^{\mathrm{ref}}}{\partial T}\right)_p - R \ln x_B$$ (9.4.36)

The term $-(\partial \mu_{x,B}^{\mathrm{ref}} / \partial T)_p$ represents the partial molar entropy $S_{x,B}^{\mathrm{ref}}$ of B in the fictitious reference state of unit solute mole fraction. Thus, we can write Eq. 9.4.36 in the form

$$S_B = S_{x,B}^{\mathrm{ref}} - R \ln x_B$$ (9.4.37)
(ideal-dilute solution
of a nonelectrolyte)

This equation shows that the partial molar entropy varies with composition and goes to $+\infty$ in the limit of infinite dilution. From the expressions of Eqs. 9.4.27 and 9.4.28, we can derive similar expressions for S_B in terms of the solute reference states on a concentration or molality basis.

The relation $H_B = \mu_B + T S_B$ (from Eq. 9.2.46), combined with Eqs. 9.4.24 and 9.4.37, yields

$$H_B = \mu_{x,B}^{\mathrm{ref}} + T S_{x,B}^{\mathrm{ref}} = H_{x,B}^{\mathrm{ref}}$$ (9.4.38)

showing that at constant T and p, the partial molar enthalpy of the solute is constant throughout the ideal-dilute solution range. Therefore, we can write

$$H_B = H_B^{\infty}$$ (9.4.39)
(ideal-dilute solution
of a nonelectrolyte)

where H_B^{∞} is the partial molar enthalpy at infinite dilution. By similar reasoning, using Eqs. 9.2.49–9.2.52, we find that the partial molar volume, internal energy, and heat capacity of the solute are constant in the ideal-dilute range and equal to the values at

infinite dilution. The expressions are listed in the second column of Table 9.2.

When the pressure is equal to the standard pressure p°, the quantities H_B^∞, V_B^∞, U_B^∞, and $C_{p,B}^\infty$ are the same as the standard values H_B°, V_B°, U_B°, and $C_{p,B}^\circ$.

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