

CHEMISTRY 312

Colligative Properties

These notes deal with two of the commonly treated “colligative properties”: boiling point elevation and freezing point depression. Vapor pressure lowering and osmotic pressure will not be covered. These properties hang together (“colligate”) through the idea of a “dilute ideal” solution, i.e. a solution in which the chemical potential for the solvent (component 1) is accurately represented by

$$\mu_1(\text{so ln}, T, x_1) = \mu_1^*(\text{liq}, T) + R T \ln x_1 \quad (1)$$

Here, $\mu_1^*(\text{liq}, T)$ is the chemical potential of the pure solvent at temperature T . [For liquids and solids, we ignore the slight dependence of this μ on the total pressure. For gases, of course, the pressure dependence cannot be ignored].

Boiling point elevation

The boiling point of a solution (or solvent) is defined as the temperature at which the equilibrium vapor pressure is 1 atm. We will develop an expression for determining how much that temperature will change if a small amount of non-volatile solute (component 2) is added.

For this treatment we assume that the vapor phase behaves as an ideal gas

$$\mu_1(\text{g}, T, P) = \mu_1^0(\text{g}, T) + R T \ln (P) \quad (2)$$

The P in this equation is both the total pressure and the partial pressure P_1 since component 2 is assumed to have no partial pressure.

The condition for boiling is that the chemical potential of 1 in the solution equals the chemical potential of the gas at a pressure of 1 atm

$$\mu_1(\text{so ln}, T_b, x_1) = \mu_1^0(\text{g}, T_b) + R T_b \ln (P_{\text{atm}}) \quad (3)$$

P_{atm} is the value of 1 atm pressure in whatever pressure units being used. If the pressure unit is bars, P_{atm} has the value 1.01325.

Equations (3) and (1) can be combined to give

$$\mu_1^*(\text{liq}, T_b) + R T_b \ln x_1 = \mu_1^0(\text{g}, T_b) + R T_b \ln (P_{\text{atm}}) \quad (4)$$

which can be rearranged as

$$\begin{aligned} R \ln (x_1) &= \frac{[\mu_1^0(\text{g}, T_b) + R T_b \ln (P_{\text{atm}})] - \mu_1^*(\text{liq}, T_b)}{T_b} \\ &= \frac{{}_{\text{vap}}G(T_b, 1 \text{ atm})}{T_b} \end{aligned} \quad (5)$$

The second line recognizes the numerator in the rhs of the first line as the change in Gibbs free energy for evaporation of one mole of solvent at a pressure of 1 atm.

Now differentiate both sides with respect to $\ln (x_1)$ and use the Gibbs-Helmholtz equation for the temperature derivative of G/T :

$$R = \frac{dT_b}{d \ln x_1} \frac{\left(\frac{{}_{\text{vap}}G}{T} \right)}{T} = - \frac{dT_b}{d \ln x_1} \frac{{}_{\text{vap}}H}{T_b^2} \quad (6)$$

This rearranges to

$$\frac{d(1/T_b)}{d \ln x_1} = \frac{{}_{\text{vap}}H}{R} \quad (7)$$

where H_{vap} is the enthalpy of vaporization of one mole of solvent. Now integrate this expression from $x_1=1$ to the value of x_1 in the solution:

$$\frac{1}{T_b} - \frac{1}{T_b^*} = -\frac{{}_{\text{vap}}H}{R} [\ln x_1 - \ln (1)] \quad (8)$$

T_b^* is the boiling point of pure solvent. Note that $\ln x_1 = \ln (1-x_2) = -x_2$ and rearrange to obtain

$$T = T_b - T_b^* = \frac{R T_b T_b^*}{\text{vap}H} - \frac{R (T_b^*)^2}{\text{vap}H} \quad (9)$$

In terms of the molality $m = 1000 x_2/M_1$

$$T_b = K_b m \quad \text{where} \quad K_b = \frac{R (T_b^*)^2 M_1}{\text{vap}H} . \quad (10)$$

Freezing point depression

The derivation is quite similar to that of the boiling point elevation.

Here, the assumption is that, when the solution freezes, the solid phase is pure solvent. The criterion for equilibrium in this case is:

$$\mu_1(\text{soln}, T_f, x_1) = \mu_1^*(\text{liq}, T_f) + R T_f \ln x_1 = \mu_1^*(\text{solid}, T_f) \quad (11)$$

This is easily rearranged to give

$$R \ln x_1 = \frac{\mu_1^*(\text{solid}, T_f) - \mu_1^*(\text{liq}, T_f)}{T_f} = \frac{-\text{fus}G}{T_f} \quad (12)$$

where $\text{fus}G$ is the change in the Gibbs free energy for fusion (solidification) of one mole of pure solvent at temperature T_f . The same procedure as above (differentiate both sides with respect to $\ln x_1$, rearrange, then integrate) yields the result

$$T_f = \frac{-RT_f^2}{\text{fus}H} x_2 = -K_f m \quad \text{where} \quad K_f = \frac{R T_f^2 M_1}{\text{fus}H} .$$