

Colligative Properties

In the following derivations freezing point depression, boiling point elevation, and osmotic pressures of solutions we approach the problem in four steps:

- I. The pure solvent is originally in equilibrium in the two phases.
- II. Addition of solute lowers the chemical potential of the solvent in the solution phase
- III. Temperature (freezing point depression, boiling point elevation) or pressure (osmotic pressure) must be altered to reestablish equilibrium between the solution and the pure solvent phase.
- IV. Obtain relationships between X_B and change in T or P.

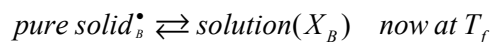
NOTE: *A* refers to solute component, *B* refers to solvent component.

A. Freezing point depression

$$\begin{array}{l}
 \left. \begin{array}{l}
 \text{pure solid}_B^* \rightleftharpoons \text{pure liquid}_B^* \quad \text{at } T_f^* \quad \text{normal melting } T_{\text{fusion}} \\
 \mu_B^{s*}(T_f^*) = \mu_B^{l*}(T_f^*) \\
 \Delta\mu_B(T_f^*) = \mu_B^{l*}(T_f^*) - \mu_B^{s*}(T_f^*) = 0 \\
 \Delta\bar{H}_B(T_f^*) = \Delta\bar{H}_{B \text{ melting}} > 0
 \end{array} \right\} \text{I.}
 \end{array}$$

$$\begin{array}{l}
 \left. \begin{array}{l}
 \text{still at } T_f^*, \text{ add } X_A \text{ solute resulting in } X_B \text{ for solvent} \\
 \mu_B^{s*}(T_f^*) \equiv \mu_B^{\text{solid}}(T_f^*) \\
 \mu_B^{\ell}(T_f^*) \equiv \mu_B^{\text{solvent}} \equiv \mu_B^{\ell(\text{in soln})}(T_f^*) = \mu_B^{l*}(T_f^*) + RT_f^* \ln(\gamma_B X_B) \\
 \Delta\mu_B(T_f^*) = \mu_B^{\ell}(T_f^*) - \mu_B^{s*}(T_f^*) = \Delta\mu_B^*(T_f^*) + RT_f^* \ln(\gamma_B X_B) \\
 \text{where } \Delta\mu_B^*(T_f^*) = \mu_B^{l*}(T_f^*) - \mu_B^{s*}(T_f^*) \\
 \text{and } \Delta\mu_B^*(T_f^*) = 0 \text{ since pure liquid and solid are in equilibrium at } T_f^* \\
 \Delta\mu_B(T_f^*) = RT_f^* \ln(\gamma_B X_B) < 0
 \end{array} \right\} \text{II.} \\
 \text{thus the forward reaction (melting of the solid) would occur spontaneously at } T_f^*
 \end{array}$$

Changing T to reestablish equilibrium with solid at new temperature T_f :



we will utilize the change in $\frac{\Delta\mu}{T}$ since its temperature dependence is less complicated than that of $\Delta\mu$:

$$\left(\frac{\partial \frac{\Delta\mu}{T}}{\partial T} \right)_P = -\frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} \quad \text{and} \quad \frac{\Delta\mu_B(T_f^*)}{T_f^*} = R \ln(\gamma_B X_B)$$

$$\begin{aligned}
 \text{III.} \quad & \int_{T_f^*}^{T_f} d\left(\frac{\Delta\mu_B}{T}\right)_P = -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT \\
 & \left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P - \left(\frac{\Delta\mu_B(T_f^*)}{T_f^*}\right)_P = -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT \\
 & \text{with} \\
 & \left(\frac{\Delta\mu_B(T_f)}{T_f}\right)_P = 0 \text{ since } \Delta\mu(T_f) = 0 \text{ since return to equilibrium at new } T_f \\
 & \text{and } \left(\frac{\Delta\mu_B(T_f^*)}{T_f^*}\right)_P = R \ln(\gamma_B X_B) \text{ from II.}
 \end{aligned}$$

$$\begin{aligned}
 -R \ln(\gamma_B X_B) &= -\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT \quad (\sim \text{eqn 9.31 E\&R}) \\
 R \ln(\gamma_B X_B) &+ \left[-\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT \right] = 0
 \end{aligned}$$

this last line is written to indicate that the drop in $\frac{\mu_B}{T}$ due to dissolving solute must be balanced the change $\frac{\Delta\mu_B}{T}$ due to the temperature variation

$$\begin{aligned}
 \text{IV.} \quad & R \ln(\gamma_B X_B) = \int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{B \text{ melting}}}{T^2} dT \\
 & \Delta\bar{H}_{B \text{ melting}} \sim \text{independent of } T \\
 & R \ln(\gamma_B X_B) = -\Delta\bar{H}_{B \text{ melting}} \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right] \\
 & \text{since } lhs < 0 \Rightarrow T_f < T_f^* \text{ (freezing point depression)}
 \end{aligned}$$

$$\begin{aligned}
 \gamma_B X_B &= \exp \left[-\frac{\Delta\bar{H}_{B \text{ melting}}}{R} \left[\frac{1}{T_f} - \frac{1}{T_f^*} \right] \right] \\
 -\frac{R}{\Delta\bar{H}_{B \text{ melting}}} \ln(\gamma_B X_B) + \frac{1}{T_f^*} &= \frac{1}{T_f} \quad (\text{eqn 9.32 E\&R}_{4th}) \\
 T_f &= \frac{T_f^* \Delta\bar{H}_{B \text{ melting}}}{\Delta\bar{H}_{B \text{ melting}} - RT_f^* \ln(\gamma_B X_B)}
 \end{aligned}$$

this is all of the thermodynamics.

In the dilute solute approximation, the expression can be further reduced to the usual introductory chemistry expression $\Delta T = -K_f m$ where m is the concentration of the solute in molality (n_A per 1 kg of solvent) and K_f is a constant related to the molecular weight of the solvent, ΔH_f , and T_f^* . (see eqns 9.33 E&R_{4th})

B. Boiling Point Elevation

(very similar treatment to freezing point depression)

I. $\left. \begin{array}{l} \text{pure liquid}_B^* \rightleftharpoons \text{pure vapor}_B^* \text{ at } T_{b.p.}^* \text{ normal boiling } T_{\text{boiling point}}^*, P_B^* = 1 \text{ atm} \\ \mu_B^{\ell}(T_{bp}^*) = \mu_B^v(T_{bp}^*) \\ \Delta\mu_B^*(T_{bp}^*) = \mu_B^v(T_{bp}^*) - \mu_B^{\ell}(T_{bp}^*) = 0 \\ \Delta\bar{H}_B(T_{bp}^*) = \Delta\bar{H}_{B \text{ vaporization}} > 0 \end{array} \right\}$

still at T_{bp}^* , add X_A solute resulting in X_B for solvent

$$\mu_B^{\ell}(T) \equiv \mu_B^{\text{solvent}} \equiv \mu_B^{\ell(\text{in soln})}(T^*) = \mu_B^{\ell}(T_{bp}^*) + RT_{bp}^* \ln(\gamma_B X_B)$$

before vapor pressure drops

$$\Delta\mu_B(T_{bp}^*) = \mu_B^v(T_{bp}^*) - \mu_B^{\ell}(T_{bp}^*) = \Delta\mu_B^*(T_{bp}^*) - RT_{bp}^* \ln(\gamma_B X_B)$$

$$\text{where } \Delta\mu_B^*(T_{bp}^*) = \mu_B^v(T_{bp}^*) - \mu_B^{\ell}(T_{bp}^*) = 0$$

II. since pure liquid and vapor are in equilibrium at T_{bp}^*

$$\Delta\mu_B(T_{bp}^*) = -RT_{bp}^* \ln(\gamma_B X_B) > 0$$

(note this has opposite sign from freezing point depression;

in the two cases the solution phase has shifted from product side

to reactant side, keeping $\Delta H > 0$)

thus the reverse reaction ($\ell \leftarrow v$; lowering of P_B^v) would occur spontaneously at T_{bp}^*

Changing T to reestablish equilibrium with vapor at new T_{bp} and $P_B^v = 1 \text{ atm}$:

solution (X_B) \rightleftharpoons pure vapor $_B^*$ at new T_{bp} , $P_B^* = 1 \text{ atm}$

we will utilize $\frac{\Delta\mu}{T}$ since its temperature dependence is less complicated than that of $\Delta\mu$:

$$\left(\frac{\partial \frac{\Delta\mu}{T}}{\partial T} \right)_P = -\frac{\Delta\bar{H}_{B \text{ vaporization}}}{T^2} \text{ and } \frac{\Delta\mu_B(T)}{T} \text{ from above}$$

$$\begin{aligned}
 \text{III.} \quad & \int_{T_{bp}^*}^{T_{bp}} d\left(\frac{\Delta\mu_B}{T}\right)_P = - \int_{T_{bp}^*}^{T_{bp}} \frac{\Delta\bar{H}_{B \text{ vaporization}}}{T^2} dT \\
 & \left(\frac{\Delta\mu_B(T_{bp})}{T_{bp}}\right)_P - \left(\frac{\Delta\mu_B(T_{bp}^*)}{T_{bp}^*}\right)_P = - \int_{T_{bp}^*}^{T_{bp}} \frac{\Delta\bar{H}_{B \text{ vaporization}}}{T^2} dT \\
 & \text{with} \\
 & \left(\frac{\Delta\mu_B(T_{bp})}{T_{bp}}\right)_P = 0 \text{ since at 'new' equilibrium } \Delta\mu(T_{bp}) = 0 \\
 & \text{and } \left(\frac{\Delta\mu_B(T_{bp}^*)}{T_{bp}^*}\right)_P = -R \ln(\gamma_B X_B) \text{ from relation in II}
 \end{aligned}$$

$$\begin{aligned}
 R \ln(\gamma_B X_B) &= - \int_{T_{bp}^*}^{T_{bp}} \frac{\Delta\bar{H}_{B \text{ vaporization}}}{T^2} dT \\
 -R \ln(\gamma_B X_B) &+ \left[- \int_{T_{bp}^*}^{T_{bp}} \frac{\Delta\bar{H}_{B \text{ vaporization}}}{T^2} dT \right] = 0
 \end{aligned}$$

Here the increase in $\left(\frac{\Delta\mu_B}{T}\right)$ due to dissolving solute (*first term*) must be balanced by the change in $\left(\frac{\Delta\mu_B}{T}\right)$ due to the temperature variation (*second term*). [Since 'solution' is reactant, decrease in $\frac{\mu_B^c}{T}$ due to dissolving solute increases $\left(\frac{\Delta\mu_B}{T}\right)$]

$$R \ln(\gamma_B X_B) = - \int_{T_{bp}^*}^{T_{bp}} \frac{\Delta \bar{H}_{B \text{ vaporization}}}{T^2} dT$$

$\Delta \bar{H}_{B \text{ vaporization}} \sim$ independent of T

$$R \ln(\gamma_B X_B) = + \Delta \bar{H}_{B \text{ vaporization}} \left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*} \right]$$

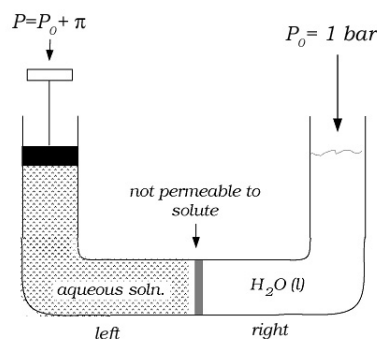
IV. since $l h s < 0 \Rightarrow T_{bp} > T_{bp}^*$ (boiling point elevation)

$$\ln(\gamma_B X_B) = + \frac{\Delta \bar{H}_{B \text{ vaporization}}}{R} \left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*} \right]$$

$$\gamma_B X_B = \exp \left[\frac{\Delta \bar{H}_{B \text{ vaporization}}}{R} \left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^*} \right] \right]$$

$$T_{bp} = \frac{T_{bp}^* \Delta \bar{H}_{B \text{ vaporization}}}{\Delta \bar{H}_{B \text{ vaporization}} + R T_{bp}^* \ln(\gamma_B X_B)}$$

C. Osmosis



- I. $\text{pure liquid}_B^*(P_0, \text{left}) \rightleftharpoons \text{pure liquid}_B^*(P_0, \text{right}) \quad \text{at } T$
 'left' and 'right' refer to compartments separated by solute impermeable membrane
 $\mu_B^*(P_0, \text{left}) = \mu_B^*(P_0, \text{right})$
- II. $\text{add } X_A \text{ solute to liquid in 'left' compartment resulting in } X_B \text{ for solvent}$
 $\mu_B^l(P_0, \text{left}) = \mu_B^*(P_0, \text{left}) + RT \ln(\gamma_B X_B)$
 $\mu_B^l(P_0, \text{left}) < \mu_B^*(P_0, \text{right})$
 so the solvent B moves spontaneously left \leftarrow right (i.e. diluting solution)
- III. $\text{changing } P(\text{left}) \text{ to reestablish equilibrium with pure solvent at } P_0 \text{ in right:}$
 $\text{solution } (X_B, P_0 + \pi, \text{left}) \rightleftharpoons \text{pure solvent}(P_0, \text{right})$
 $\left(\frac{\partial \mu_B^{\text{left}}}{\partial P} \right)_T = \bar{V}_B$
 assuming solvent is incompressible (\bar{V}_B doesn't change with pressure at constant T)
 th change in μ_B^{left} due to excess pressure π is $\bar{V}_B (P_0 + \pi - P_0) = \pi \bar{V}_B$
- IV. $\text{total } \Delta \mu_B^{\text{left}} = \mu_B(P_0 + \pi, X_B, \text{left}) - \mu_B^*(P_0, \text{left}) = 0 \text{ to reestablish equilibrium with } \mu_B^*(P_0, \text{right})$
 $\pi \bar{V}_B + RT \ln(\gamma_B X_B) = 0 \quad (\text{eqn 9.39 E\&R})$
 i.e., change in μ_B due to excess pressure the negative of change in μ_B from solution formation

$$\pi = \frac{-RT \ln(\gamma_B X_B)}{\bar{V}_B}$$