

Review Topics Weeks 8-10

The material for these last three weeks 'touches' on topics in E&R chapters 6 -10. Your major responsibility will be for material covered **IN LECTURE** (see handouts), and as outlined below and in problem sets rather than all of the details in E&R.

- Corrections for nonideality (first look)

$$\mu_i(T) = \mu_i^\circ(T) + RT \ln a_i$$

$a_i = \text{activity}$

- $a_i = \left(\frac{\gamma_i P_i}{1 \text{ bar}} \right)$ or $a_i = \left(\frac{\gamma_i c_i}{1 M} \right)$, etc.

where $\gamma_i = \text{activity coefficient}$

[for gases activity is same as 'fugacity']

- activity of pure liquids and solids = 1
- Example of calculation of fugacity from experimental measures or from equation of state

$$\lim_{P_i \rightarrow 0} f_i \rightarrow P_i$$

$$\ln \left(\frac{f_i}{P_i} \right) = \ln(\gamma_i) = \frac{1}{RT} \int_0^{P_i} \left(\bar{V}_i - \frac{RT}{P_i} \right) dP_i = \frac{1}{RT} \int_0^{P_i} \left(\bar{V}_i^{\text{actual}} - \bar{V}_i^{\text{ideal}} \right) dP_i = \int_{P_i \rightarrow 0}^{P_i} \frac{(z-1)}{P'} dP', \quad \text{where } z = \frac{\bar{V}_i^{\text{actual}}}{\bar{V}_i^{\text{ideal}}}$$

get $\bar{V}(P_i)$ or z from equation of state or measurement

- Writing Q and K_{eq} with activities and activity coefficients

- One component phase equilibria

- $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots$ chemical potential of each component same in each phase
- $\left(\frac{\partial \mu_i^\alpha}{\partial T} \right)_P = -\bar{S}_i^\alpha$ if $\mu_i^\alpha \neq \mu_i^\beta$, how the relative entropies and changes in T will lead to

phase equilibrium

- Phase rule: $f=2+c-p$ ($f=3-p$ for one component)
- P vs T for one-component phase equilibrium:

$$\left(\frac{dP}{dT} \right)_{\text{phase equilib}} = \frac{\Delta \bar{S}_\phi}{\Delta \bar{V}_\phi} = \frac{\Delta \bar{H}_\phi}{T \Delta \bar{V}_\phi}$$

- One component (P vs T) phase diagrams

- Phases present

- Slope of $\left(\frac{dP}{dT} \right)_{\text{phase equilib}} = \frac{\Delta \bar{S}_\phi}{\Delta \bar{V}_\phi} = \frac{\Delta \bar{H}_\phi}{T \Delta \bar{V}_\phi}$ for $s \leftrightarrow \ell$, $s \leftrightarrow g$, and $\ell \leftrightarrow g$ lines on phase

diagram

- Triple point
- Critical point

- Vapor pressure over pure liquids and solids
 - (s ⇌ g and ℓ ⇌ g), sublimation and vaporization.

$$\left(\frac{d \ln P}{dT}\right)_{\text{phase equilib}} = \frac{\Delta \bar{H}_{\text{vaporization}}}{RT^2} \quad (\text{Clausius - Clapeyron})$$

$$\begin{aligned} \ln \left[\frac{P_2}{P_1} \right] &= \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{vaporization}}}{T^2} dT \\ &= -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \text{if } \Delta \bar{H}_{\text{vaporization}} \text{ independent of } T \end{aligned}$$

- Solid ⇌ liquid equilibrium (fusion/melting)

$$\left(\frac{dP}{dT}\right)_{\text{phase equilib}} = \frac{\Delta \bar{H}_{\text{fusion}}}{T(\bar{V}_\ell - \bar{V}_s)}$$

$$P_2 - P_1 = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\text{fusion}}}{T(\bar{V}_\ell - \bar{V}_s)} dT$$

$$P_2 - P_1 = \frac{\Delta \bar{H}_{\text{fusion}}}{(\bar{V}_\ell - \bar{V}_s)} \ln \left[\frac{T_2}{T_1} \right] \quad \text{if } \Delta \bar{H}_{\text{fusion}} \text{ and } \Delta V_{\text{fusion}} \text{ independent of } T$$

- Ideal solutions

- Similar within and between component forces
- $P_A = X_A P_A^*$ and $P_B = X_B P_B^*$ **Raoult's Law**
- $\mu_i^{\text{soln}}(T, X_i) = \mu_i^{\ell*}(T) + RT \ln X_i$ (ideal solution ⇒ $\gamma_i = 1$)
- Thermodynamics of ideal solutions
 - $\Delta V_{\text{mix}} = \Delta H_{\text{mix}} = \Delta U_{\text{mix}} = 0$
 - $\Delta G_{\text{mix}} = \sum_k n_k RT \ln X_k$
 - $\Delta S_{\text{mix}} = -\sum_k n_k R \ln X_k$

- Multicomponent phase equilibria
 - Phase rule $f=2+c-p$
 - T vs X_A phase diagrams (P constant)
 - Understand the Cd-Bi diagram (handout #48, slide 4, et al; and E&R Fig 9.26)
 - Understand the benzene-toluene T vs X_{benzene} phase diagram (handout #48, slide 23, et al; and E&R Fig. 9.6) and fractional distillation
- Colligative properties (X_B is mole fraction of *solvent* in solution)
 - Change of solvent chemical potential upon solution formation at T and P:

$$\mu_B^{\text{soln}}(T, P) = \mu_B^{\circ}(T, P) + RT \ln[\gamma_B X_B]$$
 - Correction of X_B for formation of ions in dilute solutions of electrolytes.
 - Freezing point lowering:
 - Start: $\text{pure solid}_B^{\circ} \rightleftharpoons \text{pure liquid}_B^{\circ}$ at T_f° normal melting T_{fusion}
 - Add X_A and change T: $\text{pure solid}_B^{\circ} \rightleftharpoons \text{solution}(X_B)$ at T_f
 - Change in $\Delta\mu_B$ due to solution formation: $RT \ln[\gamma_B X_B] - 0$
 - Change in $\Delta\mu_B$ due to $T_f^{\circ} \rightarrow T_f$: $-\int_{T_f^{\circ}}^{T_f} \frac{\Delta\bar{H}_{\text{fusion}}}{T^2} dT$
 - Net change in $\Delta\mu_B = 0$

$$RT \ln[\gamma_B X_B] = -\Delta\bar{H}_{\text{fusion}} \left[\frac{1}{T_f} - \frac{1}{T_f^{\circ}} \right]$$
 - $\gamma_B X_B = \exp \left[-\frac{\Delta\bar{H}_{\text{fusion}}}{R} \left[\frac{1}{T_f} - \frac{1}{T_f^{\circ}} \right] \right]$

$$T_f = \frac{T_f^{\circ} \Delta\bar{H}_{\text{fusion}}}{\Delta\bar{H}_{\text{fusion}} - RT_f^{\circ} \ln(\gamma_B X_B)}$$
 - Boiling point elevation:
 - Start: $\text{pure liquid}_B^{\circ} \rightleftharpoons \text{pure vapor}_B^{\circ}$ at $T_{\text{b.p.}}^{\circ}$ normal boiling $T_{\text{b.p.}}, P_B^{\circ} = 1 \text{ atm}$
 - Add X_A and change T: $\text{solution}(X_B) \rightleftharpoons \text{pure vapor}_B^{\circ}$ at $T_{\text{bp}}, P_B^{\circ} = 1 \text{ atm}$
 - Change in $\Delta\mu_B$ due to solution formation: $0 - RT \ln[\gamma_B X_B]$
 - Change in $\Delta\mu_B$ due to $T_{\text{b.p.}}^{\circ} \rightarrow T_{\text{b.p.}}$: $-\int_{T_{\text{b.p.}}^{\circ}}^{T_{\text{bp}}} \frac{\Delta\bar{H}_{\text{vaporization}}}{T^2} dT$
 - Net change in $\Delta\mu_B = 0$

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

- Osmotic pressure
 - Start: $\text{pure liquid}_B^*(P_0, \text{left}) \rightleftharpoons \text{pure liquid}_B^*(P_0, \text{right})$ at T
 - Add X_A and change P : $\text{solution}(X_B, P_0 + \pi, \text{left}) \rightleftharpoons \text{pure solvent}(P_0, \text{right})$
 - Change in μ_{left} due to solution formation: $RT \ln[\gamma_B X_B]$
 - Change in μ_{left} due to $P_0 \rightarrow P_0 + \pi$: $\pi \bar{V}_B$
 - Net change in $\mu_{\text{left}} = 0$
 - $\pi = \frac{-RT \ln[\gamma_B X_B]}{\bar{V}_B}$ dilute solutions $\pi \approx \frac{n_{\text{solute}} RT}{V_{\text{solvent}}}$
- Obtaining activity coefficients from measurement of colligative properties
- Electrochemistry
 - Const T and P : $\Delta\mu_{\text{reaction}} \leq W_{\text{other}}$
 - For electrochemical cell:
 - $\Delta\mu_{\text{reaction}} = -n\mathcal{F}\Phi^\dagger$
 - $\Delta\mu_{\text{reaction}} = -n\mathcal{F}\Phi$ for reversible cell ($\Phi_{\text{rev}} > \Phi^\dagger$)
 - ($\Phi \equiv \Phi_{\text{cell}}$ is electromotive force; EMF is denoted as \mathcal{E} in many texts)
 - $\Phi = \Phi^\circ - \frac{RT}{n\mathcal{F}} \ln Q$ **Nernst Equation**
 - $\Phi = \Phi^\circ - \frac{0.02569}{n} \ln Q$ at $T = 298.15\text{K}$
 - $\Phi^\circ = \frac{RT}{n\mathcal{F}} \ln K_{\text{eq}}$
 - $\Phi^\circ = \frac{0.02569}{n} \ln K_{\text{eq}}$ at $T = 298.15\text{K}$
 - Responsible for three particular redox reactions (Handout #54, slides 5 et al, 7 et al, 20 et al.
 - Obtaining activity coefficients from measurement of cell EMF's
 - All thermodynamic relationships for $\Delta\mu_{\text{reaction}}$ can be applied to Φ_{cell} :

$$\left(\frac{\partial \Delta\mu}{\partial T}\right)_P = -\Delta\bar{S} \quad \Rightarrow \quad \left(\frac{\partial \Phi}{\partial T}\right)_P = \frac{\Delta\bar{S}}{n\mathcal{F}}$$

$$\left(\frac{\partial}{\partial T} \frac{\Delta\mu}{T}\right)_P = \frac{-\Delta\bar{H}}{T^2} \quad \Rightarrow \quad \left(\frac{\partial}{\partial T} \frac{\Phi}{T}\right)_P = \frac{\Delta\bar{H}}{n\mathcal{F}T^2}, \text{ etc}$$

- Concluding factoids
 - Thermodynamics is useful
 - Electrical potential across membranes (e.g. neurons) can be calculated using Nernst equation
 - Non-idealities in solutions
 - Azeotropes and eutectics: constant boiling and melting solutions
 - Negative deviation from Raoult's Law (stronger forces; high boiling azeotrope)
 - Positive deviation from Raoult's Law (weaker forces; low boiling azeotrope)
 - Gibbs-Duhem:
 - partial molar properties for differing components are interdependent
 - Debye-Huckel
 - Theoretical method for calculating γ_{\pm} for electrolytes (note $\gamma_{\pm} \leq 1$)