Review Topics Weeks 7-10

The material for these last four 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.

- Introduction to multicomponent systems
  - Partial molar volume as illustration of more general partial molar quantities
    - $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j \neq n_i}$
    - Conceptual interpretation of partial molar volume versus molar volume
  - Total differentials for multicomponent systems $(đw_{other} = 0)$

$$U(S,V,n_1,....,n_N) \qquad dU = TdS - PdV + \sum_{i=1}^{N}\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j \neq n_i} dn_i$$

$$H(S,P,n_1,....,n_N) \qquad dH = TdS + VdP + \sum_{i=1}^{N}\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j \neq n_i} dn_i$$

$$A(T,V,n_1,....,n_N) \qquad dA = -SdT - PdV + \sum_{i=1}^{N}\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j \neq n_i} dn_i$$

$$G(T,P,n_1,....,n_N) \qquad dG = -SdT + VdP + \sum_{i=1}^{N}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} dn_i$$

  - Chemical potential is partial molar Gibbs free energy

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq n_i} \equiv \mu_i$$

  - Total extensive property is sum of partial molar properties, e. g.

$$V_{total} = \sum_i^N n_i \bar{V}_i \qquad G = \sum_i^N n_i \bar{G}_i \qquad H = \sum_i^N n_i \bar{H}_i$$

  - Many thermodynamic relationships among variables for pure systems hold for partial molar quantities for each component, e.g.

$$G \equiv H - TS \quad \Rightarrow \quad \bar{G}_i = \bar{H}_i - T\bar{S}_i$$

or

$$H \equiv U + PV \quad \Rightarrow \quad \bar{H}_i = \bar{U}_i + P\bar{V}_i$$

  - Gibbs-Duhem relationship

$$\sum_{i=1}^{N} X_i \left(\frac{\partial \bar{V}_i}{\partial n_A}\right)_{T,P,n_j \neq n_A} = 0$$

- Corrections for nonideality (first look)

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

  $a_i = activity$

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

    $where\ \gamma_i = activity\ coefficient$

    $[for\ gases\ activity\ is\ same\ as\ 'fugacity']$
  - activity of pure liquids and solids = 1
  - Example of calculation of fugacity from experimental measures or from equation of state

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

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

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

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

- One component phase equilibria
  - $\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \ldots$ chemical potential of each component same in each phase
  - $\left(\dfrac{\partial \mu_i^\alpha}{\partial T}\right)_P = -\overline{S}_i^\alpha$ 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:

    $$\left(\frac{dP}{dT}\right)_{phase\ equilib} = \frac{\Delta\overline{S}_\phi}{\Delta\overline{V}_\phi} = \frac{\Delta\overline{H}_\phi}{T\Delta\overline{V}_\phi}$$
  - One component (P vs T) phase diagrams
    - Phases present
    - Slope of $\left(\dfrac{dP}{dT}\right)_{phase\ equilib} = \dfrac{\Delta\overline{S}_\phi}{\Delta\overline{V}_\phi} = \dfrac{\Delta\overline{H}_\phi}{T\Delta\overline{V}_\phi}$ for s↔ℓ, s↔g, and ℓ↔g lines on phase diagram
    - Triple point
    - Critical point

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

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

$$\ln\left[\frac{P_2}{P_1}\right] = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta \bar{H}_{vaporization}}{T^2} dT$$

$$= -\frac{\Delta \bar{H}_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad if\ \Delta \bar{H}_{vaporization}\ independent\ of\ T$$

  - Solid ⇆ liquid equilibrium (fusion/melting)

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

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

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

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

- 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 $\left(X_B \text{ is mole fraction of solvent in solution}\right)$
  - Change of solvent chemical potential upon solution formation at T and P: $\mu_B^{soln}(T,P) = \mu_B^{\ell\bullet}(T,P) + RT\ln\left[\gamma_B X_B\right]$
  - Correction of X_B for formation of ions in dilute solutions of electrolytes.
  - Freezing point lowering:
    - Start: $pure\ solid_B^{\bullet} \rightleftarrows pure\ \ell iquid_B^{\bullet} \quad at\ T_f^{\bullet} \quad normal\ melting\ T_{fusion}$
    - Add X_A and change T: $pure\ solid_B^{\bullet} \rightleftarrows solution(X_B) \quad at\ T_f$
    - Change in $\Delta\mu_B$ due to solution formation: $RT\ln\left[\gamma_B X_B\right] - 0$
    - Change in $\Delta\mu_B$ due to $T^{\bullet}_f \rightarrow T_f$: $-\int_{T_f^{\bullet}}^{T_f} \frac{\Delta\bar{H}_{fusion}}{T^2} dT$
    - Net change in $\Delta\mu_B$ =0
      $$R\ln\left[\gamma_B X_B\right] = -\Delta\bar{H}_{fusion}\left[\frac{1}{T_f} - \frac{1}{T_f^{\bullet}}\right]$$
    - $$\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{fusion}}{R}\left[\frac{1}{T_f} - \frac{1}{T_f^{\bullet}}\right]\right]$$
      $$T_f = \frac{T_f^{\bullet}\Delta\bar{H}_{fusion}}{\Delta\bar{H}_{fusion} - RT_f^{\bullet}\ln\left(\gamma_B X_B\right)}$$
  - Boiling point elevation:
    - Start: $pure\ liquid_B^{\bullet} \rightleftarrows pure\ vapor_B^{\bullet} \quad at\ T_{b.p.}^{\bullet} \quad normal\ boiling\ T_{b.p.}, P_B^{\bullet} = 1\ atm$
    - Add X_A and change T: $solution\ (X_B) \rightleftarrows pure\ vapor_B^{\bullet} \quad at\ T_{bp}\ , P_B^{\bullet} = 1\ atm$
    - Change in $\Delta\mu_B$ due to solution formation: $0 - RT\ln\left[\gamma_B X_B\right]$
    - Change in $\Delta\mu_B$ due to $T^{\bullet}_{b.p.} \rightarrow T_{b.p.}$: $-\int_{T_f^{\bullet}}^{T_f} \frac{\Delta\bar{H}_{vaporization}}{T^2} dT$
    - Net change in $\Delta\mu_B$ =0
    - $$\gamma_B X_B = \exp\left[\frac{\Delta\bar{H}_{vaporization}}{R}\left[\frac{1}{T_{bp}} - \frac{1}{T_{bp}^{\bullet}}\right]\right]$$
      $$T_{bp} = \frac{T_{bp}^{\bullet}\Delta\bar{H}_{vaporization}}{\Delta\bar{H}_{vaporization} + RT_{bp}^{\bullet}\ln\left(\gamma_B X_B\right)}$$

- Osmotic pressure
  - Start:: $pure\ \ell iquid_B^\bullet(P_0,left) \rightleftarrows pure\ \ell iquid_B^\bullet(P_0,right) \quad at\ T$
  - Add X_A and change P: $solution\,(X_B,P_0+\pi,left) \rightleftarrows pure\ solvent(P_0,right)$
  - 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 μ_{left} =0
  - $\pi = \dfrac{-RT\ln[\gamma_B X_B]}{\bar{V}_B}$ dilute solutions $\pi \approx \dfrac{n_{solute}RT}{V_{solvent}}$
- Obtaining activity coefficients from measurement of colligative properties

- Electrochemistry
  - Const T and P: $\Delta\mu_{reaction} \le w_{other}$
  - For electrochemical cell:

    $\Delta\mu_{reaction} = -n\mathcal{F}\Phi^{\dagger}$

    $\Delta\mu_{reaction} = -n\mathcal{F}\Phi$ for reversible cell ($\Phi_{rev} > \Phi^{\dagger}$)

    ($\Phi \equiv \Phi_{cell}$ is electromotive force; EMF is denoted as $\mathcal{E}$ in many texts)
  - $$\Phi = \Phi^\circ - \frac{RT}{n\mathcal{F}}\ln Q \qquad \textit{Nernst Equation}$$
    $$\Phi = \Phi^\circ - \frac{0.02569}{n}\ln Q \quad at\ T = 298.15K$$
  - $$\Phi^\circ = \frac{RT}{n\mathcal{F}}\ln K_{eq}$$
    $$\Phi^\circ = \frac{0.02569}{n}\ln K_{eq} \quad at\ T = 298.15K$$
  - Responsible for three particular redox reactions (Handout #56, slides 4et al, 12(6)et al, 19 et al.

  - Obtaining activity coefficients from measurement of cell EMF's

  - All thermodynamic relationships for $\Delta\mu_{reaction}$ can be applied to Φ_{cell}:

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

$$\left(\frac{\partial\frac{\Delta\mu}{T}}{\partial T}\right)_P = \frac{-\Delta\bar{H}}{T^2} \qquad \Rightarrow \left(\frac{\partial\frac{\Phi}{T}}{\partial T}\right)_P = \frac{\Delta\bar{H}}{n\mathcal{F}T^2}$$, 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 $\gamma_{\pm}$ for electrolytes (note $\gamma_{\pm} \leq 1$)