

## 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  $K_{\text{eq}}$  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
  - ( $s \rightleftharpoons g$  and  $\ell \rightleftharpoons g$ ), 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  $\rightleftharpoons$  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  $\Rightarrow \gamma_i = 1$ )
- 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  $X_{\text{benzene}}$  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:
 
$$\mu_B^{\text{soln}}(T, P) = \mu_B^{\text{pure}}(T, P) + RT \ln[\gamma_B X_B]$$
  - Correction of  $X_B$  for formation of ions in dilute solutions of electrolytes.
  - Freezing point lowering:
    - Start:  $\text{pure solid}_B^* \rightleftharpoons \text{pure liquid}_B^*$  at  $T_f^*$  normal melting  $T_{\text{fusion}}$
    - Add  $X_A$  and change T:  $\text{pure solid}_B^* \rightleftharpoons \text{solution}(X_B)$  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  $T_f^* \rightarrow T_f$ :  $-\int_{T_f^*}^{T_f} \frac{\Delta\bar{H}_{\text{fusion}}}{T^2} dT$
    - Net change in  $\Delta\mu_B = 0$ 

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

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

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

- 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  $\mu_{\text{left}}$  due to solution formation:  $RT \ln[\gamma_B X_B]$
  - Change in  $\mu_{\text{left}}$  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:
    - $\Delta\mu_{\text{reaction}} = -n\mathcal{F}\Phi^\ddagger$
    - $\Delta\mu_{\text{reaction}} = -n\mathcal{F}\Phi$  for reversible cell ( $\Phi_{\text{rev}} > \Phi^\ddagger$ )
    - ( $\Phi \equiv \Phi_{\text{cell}}$  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  $\Phi_{\text{cell}}$ :

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

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

- 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  $\gamma_{\pm}$  for electrolytes (note  $\gamma_{\pm} \leq 1$ )