Review Topics Weeks 6-7

In reviewing material one should not memorize the entries as 'plug-in' formulas. But should understand i) how they arise from the basic laws of thermodynamics; ii) what are the limits on their generality and under what special conditions they apply; and iii) how they qualitatively reflect the 'logic' of the natural world and, in some cases, the underlying properties of molecules and matter.

- Free energy defined
    - $A \equiv U - TS$
    - $G \equiv H - TS$
    - $dA = -SdT - PdV$
    - $dG = -SdT + VdP$

- Free energy: equilibrium (=) and spontaneity (<)
    - $\Delta A_{T,V} \leq 0$
    - $\Delta G_{T,P} \leq 0$

- Relationship of $\Delta G_{T,P} \leq 0$ to 2nd Law
    - $$-\frac{\Delta G_{T,P}}{T} = -\frac{\Delta H}{T} + \Delta S \geq 0$$

    $$\Delta S_{surr} \geq -\frac{\left(\Delta H_P\right)_{sys}}{T} \quad \text{disorders surroundings}$$

    - ΔS_{sys} disorders system

    $$\Delta S_{surr} + \Delta S_{sys} \geq 0$$

- Calculation of ΔG for physical processes (expansion of gasses, phase changes, etc.)

- Calculation of $\Delta G_{reaction}$ from ΔG_f or ΔH_f and ΔS or reactants and products

- $\Delta G_{T,P}$ at arbitrary partial pressures (concentrations) for ideal gasses
    - $$\bar{G}_T(P) = \bar{G}_T^o(P = 1\,bar) + RT \ln\left(\frac{P}{1\,bar}\right)$$

    $$\mu_i(P,T) = \mu_i^o(T) + RT \ln\left(\frac{P_i}{1\,bar}\right)$$

    $$\left(\Delta G\right)_{reaction} = \Delta G^o + \underline{R}T \ln Q$$
    - $$\left(\Delta \mu_i\right)_{reaction} = \Delta \mu_i^o + \underline{R}T \ln Q$$

    $$Q = \prod_i \left(\frac{P_i}{1\,bar}\right)^{\bar{v}_i} \quad [or \; Q = \prod_i \left(\frac{c}{1\,M}\right)^{\bar{v}_i}]$$

$$\boxed{\begin{array}{l} where \; \underline{R} = R \times (mol) \quad and \quad \bar{v}_i = v_i \times \left(mol^{-1}\right) \\ \qquad = 8.3144 \; J\,K^{-1} \\ \qquad = 0.082057 \; L\,atm\,K^{-1} \\ \qquad = 0.083144 \; L\,bar\,K^{-1} \\ \bar{v}_i = \dfrac{v_i}{mol} = [unitless] \end{array}}$$

- Equilibrium and ΔG and Δμ
  - ΔG=0 ; Δμ=0
  - $(\Delta G^o)_{reaction} = -\underline{R}T \ln K_{eq}$

    $(\Delta \mu_i^o)_{reaction} = -\underline{R}T \ln K_{eq}$
  - interpretation of Δμ° vs −$\underline{R}$T ln K_{eq}

- How G, ΔG$_{reaction}$, and K$_{eq}$ vary with T and with P
  - Pressure dependence
    - $\left(\dfrac{\partial G}{\partial P}\right)_T = V$ $\left(\dfrac{\partial \Delta_{reac} G}{\partial P}\right)_T = \Delta reac V$

    - $G_T(P_2) = G_T(P_1) + \displaystyle\int_{P_1}^{P_2} VdP \overset{ideal\ gas}{=} G_T(P_1) + nRT \ln \dfrac{P_2}{P_1}$

    - $\Delta_{reac} G_T(P_2) = \Delta_{reac} G_T(P_1) + \displaystyle\int_{P_1}^{P_2} \Delta_{reac} VdP$

  - Temperature dependence

    $\left(\dfrac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$ $\bar{S}$ is molar entropy of pure substance

    $\left(\dfrac{\partial \Delta G_{reaction}}{\partial T}\right)_P = -\Delta S_{reaction}$ $\Delta S_{reaction} \approx \displaystyle\sum_i \nu_i (\bar{S}_i)_{pure}$

    - *more rigorously   (later)*

    $\left(\dfrac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i$ $[\bar{S}_i = \left(\dfrac{\partial S}{\partial n_i}\right)_{T,P,n_j}$ = *partial molar entropy*]

    $\left(\dfrac{\partial \Delta \mu}{\partial T}\right)_P = -\Delta S$ $\Delta S = \displaystyle\sum_i \nu_i \bar{S}_i = \sum_i \nu_i \left(\dfrac{\partial S}{\partial n_i}\right)_{T,P,n_j}$

    $\dfrac{G}{T} = \dfrac{H}{T} - S$

    - $\left(\dfrac{\partial (G/T)}{\partial T}\right)_P = -\dfrac{H}{T^2}$

    $\left(\dfrac{\partial (\Delta G_{reac}/T)}{\partial T}\right)_P = -\dfrac{\Delta H_{reac}}{T^2}$

    - From $\dfrac{(\Delta \mu_i^o)_{reaction}}{T} = -\underline{R} \ln K_{eq}$

    $\left(\dfrac{\partial \ln K_{eq}}{\partial T}\right)_P = \dfrac{\Delta H_{reac}}{\underline{R}T^2}$

  - Le Chatlier's Principle

- 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

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