Relationships FOR FINAL EXAM, CHEMISTRY 163B

definitions for U, H, A, and G :

total differentials for: dU, dH, dA, and dG :

For reversible adiabatic path, ideal gas:

- $T_1^{\frac{\overline{C}_V}{R}} V_1 = T_2^{\frac{\overline{C}_V}{R}} V_2$ (adiabatic reversible path)
- $P_1 V_1^{\frac{\overline{C}_P}{\overline{C}_V}} = P_2 V_2^{\frac{\overline{C}_P}{\overline{C}_V}}$ (adiabatic reversible path, PV $^{\gamma}$ = constant)
- $\dfrac{T_1^{\frac{\overline{C}_P}{R}}}{P_1} = \dfrac{T_2^{\frac{\overline{C}_P}{R}}}{P_2}$ (adiabatic reversible path)

Energy and enthalpy:

- $(\Delta H_{reaction})_T = \Delta U_{reaction} + \Delta n_{gas} RT$
- $\left(\dfrac{\partial H}{\partial T}\right)_P = C_p = n\overline{C}_p; \qquad \Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_P dT$

For ideal gas:

- $\Delta U = C_V \Delta T = n\overline{C}_V \Delta T$
- $\Delta H = C_P \Delta T = n\overline{C}_P \Delta T$
- $\left(\overline{C}_P - \overline{C}_V\right) = R \quad and \quad \left(C_P - C_V\right) = nR$
- $\overline{C}_V = \dfrac{3}{2} R \quad and \quad C_V = \dfrac{3}{2} nR \quad (monatomic\ ideal\ gas)$

For ideal, reversible, Carnot Engine:

- $\varepsilon = \dfrac{-w_{total}}{q_H} = 1 - \dfrac{T_L}{T_H}$

Some entropy relationships:

- $\left(\dfrac{\partial S}{\partial T}\right)_p = \dfrac{C_P}{T} = \dfrac{n\overline{C}_P}{T} \quad ; \quad \left(\dfrac{\partial S}{\partial T}\right)_V = \dfrac{C_V}{T} = \dfrac{n\overline{C}_V}{T}$
- $\Delta S_{mixing,\, ideal\ gasses} = -n_{total} R \sum_i X_i \ln X_i \quad (where\ X_i\ is\ mole\ fraction\ component\ i)$

Free energy relationships (*others you should be able to quickly derive using "thermodynamics" math*):

$$(\Delta G)_{reaction} = \Delta G^o + RT\ln Q$$

- $$(\Delta \mu_i)_{reaction} = \Delta \mu_i^o + RT\ln Q$$

$$Q = \prod_i \left(\frac{\gamma_i P_i}{1\,bar}\right)^{\nu_i} \quad [or\ Q = \prod_i \left(\frac{\gamma_i c_i}{1M\ or\ 1m}\right)^{\nu_i}]$$

- relationship of ΔG to K_{eq}: you should know from above
- derivatives of G, ΔG wrt T and P_i (you should be able to derive and integrate to get, for example, $\Delta G(P_2) = \ldots$)

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

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

$$\left(\frac{\partial (\Delta G_{reac}/T)}{\partial \left(\frac{1}{T}\right)}\right)_P = \Delta H_{reac}$$

- $$\left(\frac{\partial \ln K_{eq}}{\partial T}\right)_P = \frac{\Delta H^o_{reac}}{RT^2} \qquad \ln\left(\frac{K_{T_2}}{K_{T_1}}\right) = -\left(\frac{\Delta H^o_{reac}}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad if\ \ \Delta H^o_{reac}\ indepent\ of\ T$$

- calculation of fugacity (for non-ideal gas)

$$\ln \gamma_i = \ln\left(\frac{f_i}{P_i}\right) = \frac{1}{RT}\int_0^P \left(\bar{V}_i - \frac{RT}{P_i}\right) dP_i$$

Partial molar properties:

- $$\bar{\boldsymbol{V}}_{\boldsymbol{i}} = \left(\frac{\partial \boldsymbol{V}}{\partial \boldsymbol{n_i}}\right)_{T,P,n_j \neq n_i}$$
- $$\bar{\boldsymbol{G}}_{\boldsymbol{i}} = \boldsymbol{\mu_i} = \left(\frac{\partial \boldsymbol{G}}{\partial \boldsymbol{n_i}}\right)_{T,P,n_j \neq n_i}$$
- $$\boldsymbol{V} = \sum_i^N \boldsymbol{n_i} \bar{\boldsymbol{V}}_{\boldsymbol{i}}$$

$$\boldsymbol{X_A}\left(\frac{\partial \bar{\boldsymbol{V}}_{\boldsymbol{A}}}{\partial \boldsymbol{n_A}}\right)_{T,P,n_B} = -\boldsymbol{X_B}\left(\frac{\partial \bar{\boldsymbol{V}}_{\boldsymbol{B}}}{\partial \boldsymbol{n_A}}\right)_{T,P,n_B}$$ **Gibbs-Duhem for volume of two-component system**

Phase equilibria:

- f=c–p+2
- $$\left(\frac{dP}{dT}\right)_{phase\ equilib} = \frac{\Delta\bar{S}_\phi}{\Delta\bar{V}_\phi} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi}$$
- (s ⇆ g and ℓ ⇆ g), sublimation and vaporization.

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

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta\bar{H}_{vap}}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \quad if\ \Delta\bar{H}_{vaporization}\ independent\ of\ T$$

$$\left[\frac{T_{bp}}{T^\circ_{bp}}\right] = \frac{1}{\left[1-\frac{RT^\circ_{bp}}{\Delta\bar{H}_{vap}}ln\left(\frac{P_{atm}}{1\,atm}\right)\right]} \qquad T^\circ_{bp}\text{is boiling point at 1 atm}$$

- Solid ⇆ liquid equilibrium (fusion/melting)

$$P_2 - P_1 = \frac{\Delta\bar{H}_{fusion}}{(\bar{V}_\ell - \bar{V}_s)}\ln\left[\frac{T_2}{T_1}\right]$$

Ideal Solutions:

- Know Raoult's Law for ideal solutions
- $\mu_i^{soln}(T,X_i) = \mu_i^{\ell\bullet}(T) + RT\ln X_i$
- $\Delta G_{mix} = \sum_k n_k RT\ln X_k$
- $\Delta S_{mix} = -\sum_k n_k R\ln X_k$

Colligative properties:

- freezing point lowering:

$$\gamma_B X_B = \exp\left[-\frac{\Delta\bar{H}_{melting}}{R}\left[\frac{1}{T_f}-\frac{1}{T_f^\bullet}\right]\right] \qquad T_f = \frac{T_f^\bullet\Delta\bar{H}_{B\ melting}}{\Delta\bar{H}_{B\ melting} - RT_f^\bullet\ln\left(\gamma_B X_B\right)}$$

- boiling point elevation:

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

- osmotic pressure:

$$\pi = \frac{-RT\ln\left(\gamma_B X_B\right)}{\bar{V}_B} \qquad \pi \approx \frac{n_A RT}{V_B} = \frac{n_{solute}RT}{V_{solvent}} \quad for\ dilute\ solution$$

Electrochemistry:

- $\Delta\mu_{reaction} = -n\mathcal{F}\Phi_{cell}$
- $$\Phi = \Phi^\circ - \frac{RT}{n\mathcal{F}}\ln Q$$
$$\Phi = \Phi^\circ - \frac{0.02569}{n}\ln Q \quad at\ T = 298.15K$$