

Review Topics **the Entire Quarter !!!**

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.

- Mathematical techniques (to be employed throughout course as needed)
 - Exact and inexact differentials
 - State functions

- Equations of state
 - Thermodynamic variables (P, V, T, variables for w_{other}) and ideal gas thermometer to operationally measure T
 - $P = F/A$
 - System and surroundings
 - Ideal Gas
 - $PV = nRT$
 - $E = (3/2) nRT$ (monatomic; no "internal" structure, translational kinetic energy in 3 dimensions)
 - Approximation for real gasses
 - Van der Waals $\left(P - \frac{a}{\bar{V}^2} \right) (\bar{V} - nb) = RT$; physical meaning of a and b
 - Other approximate equations of state exist (e.g. Virial power series expansion)

- Work
 - $w = \text{force} \cdot \text{displacement}$
 - $\bar{d}w$ inexact differential, depends on path
 - $\bar{d}w = -P_{\text{ext}} dV$ (P-V work)
 - $w = \int \bar{d}w$
 - $w = -P_{\text{ext}} \Delta V$ ($P_{\text{ext}} = \text{constant}$, $w_{\text{other}} = 0$)
 - $w = -n R T \ln (V_f / V_i)$ (isothermal, reversible, ideal gas, $w_{\text{other}} = 0$)

- Heat
 - $\bar{d}q$ inexact differential depends on path
 - $\bar{d}q = C dT$
 - $q = \int C dT$

- First Law of Thermodynamics
 - U = internal energy
 - $dU = \bar{d}q + \bar{d}w$ (definition, for closed system)
 - Equivalent statements of First Law of Thermodynamics
 - U is a state function
 - dU is an exact differential
 - $\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$

- $H \equiv U + (PV)_{internal}$
- H is a state function
- $\Delta H = \Delta U + \Delta (PV) = \Delta U + P_f V_f - P_i V_i$
- Differential relationships for state functions
(n_i = number moles of substance i; $ov_1 \dots ov_M$ are "other variables" that might define the energy of the system and be involved in w_{other} . For example charge, position with respect gravitational attraction, etc)
- $dU(T, V, n_1, \dots, n_K, ov_1, \dots, ov_M) = \left(\frac{\partial U}{\partial T}\right)_{V, n, ov} dT + \left(\frac{\partial U}{\partial V}\right)_{T, n, ov} dV + \sum_i^K \left(\frac{\partial U}{\partial n_i}\right)_{T, V, n_{j \neq i}, ov} dn_i + \sum_i^M \left(\frac{\partial U}{\partial ov_i}\right)_{T, V, n, ov_{j \neq i}} dov_i$
- $dH(T, P, n_1, \dots, n_K, ov_1, \dots, ov_M) = \left(\frac{\partial H}{\partial T}\right)_{P, n, ov} dT + \left(\frac{\partial H}{\partial P}\right)_{T, n, ov} dP + \sum_i^K \left(\frac{\partial H}{\partial n_i}\right)_{T, P, n_{j \neq i}, ov} dn_i + \sum_i^M \left(\frac{\partial H}{\partial ov_i}\right)_{T, P, n, ov_{j \neq i}} dov_i$

more commonly (for closed system, $dn_i = 0$; and no work other, $\vec{d}w_{other} = 0$)

- $dU(T, V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$
 - $dH(T, P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$
- Definitions relationships (closed system)
 - $dU = \vec{d}q - P_{ext} dV + \vec{d}w_{other}$
 - $\Delta U_V = q_V + \vec{d}w_{other}$ (const V) "heat is ΔU at constant V"
 - $n\bar{C}_V \equiv \left(\frac{dq}{dT}\right)_V \Rightarrow dU_V = n\bar{C}_V dT + \vec{d}w_{other}$ (const V)
 - $dH = \vec{d}q + V dP + \vec{d}w_{other}$ ($P_{ext} = P_{internal}$; thus usually for a reversible process; but OK for any infinitesimal process)
 - $\Delta H_P = q_P + w_{other}$ (const P_{ext} ; $P_{initial} = P_{final} = P_{ext}$) "heat is ΔH at constant P"
 - $n\bar{C}_P \equiv \left(\frac{dq}{dT}\right)_P \Rightarrow dH_P = n\bar{C}_P dT + \vec{d}w_{other}$ (const P)

- Derived consequences (closed system, $\bar{d}w_{other} = 0$)

$$dU = n\bar{C}_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- with $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{dq}{dV}\right)_T - P$

- $dU_V = n\bar{C}_V dT$ (const V, any system)

but with $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas

- $dU = n\bar{C}_V dT$ (ideal gas, any path)

$$dH = n\bar{C}_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

- with $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{dq}{dP}\right)_T + V$

- $dH_P = n\bar{C}_P dT$ (const P, any system)

since for ideal gas $dH = dU + d(PV) = dU + d(nRT) = dU + nR dT$
and $dU = n\bar{C}_V dT$

- $dH_P = n(\bar{C}_V + R) dT = n\bar{C}_P dT$ (ideal gas, any path)
with $\bar{C}_P = \bar{C}_V + R$ for ideal gas

- Evaluating q , w , ΔU , ΔH for various processes (closed system, no w_{other})

Constant volume

- $w = 0$
- $q_V = \Delta U_V = n\bar{C}_V \Delta T$
- $\Delta H_V = \Delta U_V + V \Delta P = \Delta U_V + V (P_f - P_i)$

Constant pressure

- $q_P = \Delta H_P = n\bar{C}_P \Delta T$
- $w = -P\Delta V$
- $\Delta U_P = q + w$

Ideal gasses

- $\bar{C}_p = \bar{C}_v + R$
- $\bar{C}_v = \frac{3}{2} R$ for monatomic ideal gas
- $\Delta U = n \bar{C}_v \Delta T$ (any path)
- $\Delta H = n \bar{C}_p \Delta T$ (any path)

Isothermal path

- $q = -w$
- $\Delta U = 0$
- $\Delta H = 0$
- $w = -n R T \ln \frac{V_f}{V_i} = n R T \ln \frac{P_i}{P_f}$ (reversible path, note – sign)
- $w = -P_{\text{ext}} \Delta V$ (constant P_{ext} expansion/compression)

Adiabatic path

- $q = 0$
- $\Delta U = w = n \bar{C}_v \Delta T$
- $\Delta H = \Delta U + \Delta(PV) = \Delta U + P_f V_f - P_i V_i = n \bar{C}_p \Delta T$
- $T_1^{\bar{C}_v} V_1 = T_2^{\bar{C}_v} V_2$ (adiabatic reversible path)
- $P_1 V_1^{\frac{\bar{C}_p}{\bar{C}_v}} = P_2 V_2^{\frac{\bar{C}_p}{\bar{C}_v}}$ (adiabatic reversible path, $PV^\gamma = \text{constant}$)
- $\frac{T_1^{\bar{C}_p}}{P_1} = \frac{T_2^{\bar{C}_p}}{P_2}$ (adiabatic reversible path)

- **Thermochemistry**

- $\Delta H_{\text{reaction}} = (H_{\text{products}} - H_{\text{reactants}})$ (vs ΔH for physical change)
- $\Delta H_P = q_P$
- standard states
- definition of $\bar{H}_f^\circ \equiv \Delta \bar{H}_f^\circ$
- $\Delta H_{\text{reaction}}^\circ = \sum_i \nu_i \bar{H}_f^\circ$ where ν_i are stoichiometric coefficients
- Hess's Law
- $\Delta H_{\text{reaction}} = \Delta U_{\text{reaction}} + \Delta n_{\text{gas}} RT$
- $\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$
- ΔH from bond enthalpies
- Heats of reactions in ionic solution

- Statements of the Second Law of Thermodynamics
 - Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [Andrews. p37]
 - It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin's Statement* [Raff p 157]; *Carnot Cycle*
 - It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius's Statement, refrigerator*
 - In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
~ *Caratheodory's statement* [Andrews p. 58]
 - Important statements regarding entropy and statistical disorder
 - Greater number of microstates, greater disorder
 - Each allowed microstate is equally probable
 - the overwhelming number of microstates correspond to macrostates with almost identical macroscopic properties
 - W, the number of microstates corresponding to the macrostate, is a measure of the DISORDER of the system in that macrostate
 - A system "meanders" through all available microstates; but you are only likely to observe it in one of the overwhelming number that correspond to the equilibrium macrostate
 - W, the number of microstates corresponding to the macrostate, depends on the populations of various energy levels
 - Adiabatic, reversible, work changes the energy of system but not the populations of the energy levels (the disorder, W)
 - Reversible heat transfers change the populations of the energy levels (and thus W)
- Carnot engines (reversible, $q_H > 0$ at T_H ; $q_L < 0$ at T_L ; $w_t < 0$)
 - Demonstration of machine consistent with 2nd Law (i.e. in a cyclic process, heat can be converted to work if and only if heat is returned to surroundings at a lower temperature.
 - $$\varepsilon = \frac{-w_t}{q_H} = 1 - \frac{T_L}{T_H}$$
 - Reverse process corresponds to refrigerators and heat pumps
 - $$\sum \frac{q}{T} = \frac{q_H}{T_H} + \frac{q_L}{T_L} = 0$$
 - ε of any Carnot engine ("any working substance") has the same dependence on T_H and T_L
 - Any reversible cyclic process can be describes as a sum of (infinitesimal) Carnot cycles, thus the properties of any cyclic process are combinations of those of Carnot cycles
- Thermal properties of entropy and entropy calculations

- $dS = \frac{\bar{d}q_{rev}}{T}$; $\Delta S = \int \frac{\bar{d}q_{rev}}{T}$; $\oint \frac{\bar{d}q_{rev}}{T} = 0$
- $\Delta S \geq \int \frac{\bar{d}q}{T}$; $0 \geq \oint \frac{\bar{d}q}{T}$; (= for reversible process; > for spontaneous ['real'] process)
- $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
- S is a state function; dS is an exact differential
- Dependence of S on
 - T: $\left(\frac{\partial \bar{S}}{\partial T}\right)_V = \frac{\bar{C}_V}{T}$; $\left(\frac{\partial \bar{S}}{\partial T}\right)_P = \frac{\bar{C}_P}{T}$
 - P: $\left(\frac{\partial \bar{S}}{\partial P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P$
 - V: $\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$
 - Phase: $\Delta S = \frac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$
- Calculation of entropy changes for changes in P, V, T, phase
- Third Law and calculations using Third Law Entropies: $\bar{S}^o(T)$
- $\Delta S_{reaction}^o(T) = \sum_i \nu_i \bar{S}_i^o(T)$
- Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ where $X_i = \frac{n_i}{n_{total}}$
- Qualitative assessment of factors affecting $\bar{S}(T, P, V)$ and $\Delta S_{reaction}$
- Derivation of various thermodynamic relationships
 - mathematical tools
 - properties of exact differentials
 - “dividing through” by ‘d?’
 - Euler-Maxwell relationships
 - state functions
 - $U = q + w$
 - $H \equiv U + PV$
 - $A \equiv U - TS$
 - $G \equiv H - TS$
 - and their total differentials (no work other, closed systems)

- $TdS = \bar{d}q$ $TdS = \bar{d}q_{\text{rev}}$ ($P_{\text{ext}})_{\text{rev}} = P_{\text{int}} = P$
- $dU = TdS - PdV$ $U(S,V)$ internal energy
- $dH = TdS + VdP$ $H(S,P)$ enthalpy
- $dA = -SdT - PdV$ $A(T,V)$ Helmholtz free energy
- $dG = -SdT + VdP$ $G(T,P)$ Gibbs free energy

- 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
 - $-\frac{\Delta G_{T,P}}{T} = -\frac{\Delta H}{T} + \Delta S \geq 0$
 - $\Delta S_{\text{surr}} \geq -\frac{(\Delta H_p)_{\text{sys}}}{T}$ disorders surroundings
 - ΔS_{sys} disorders system
 - $\Delta S_{\text{surr}} + \Delta S_{\text{sys}} \geq 0$
- Calculation of ΔG for physical processes (expansion of gasses, phase changes, etc.)
- Calculation of $\Delta G_{\text{reaction}}$ from ΔG_f or ΔH_f and ΔS or reactants and products

- $\Delta G_{T,P}$ at arbitrary partial pressures (concentrations) for ideal gasses

$$\bar{G}_r(P) = \bar{G}_r^\circ(P=1 \text{ bar}) + RT \ln\left(\frac{P}{1 \text{ bar}}\right)$$

◦

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

where $\underline{R} = R \times (\text{mol})$ and $\bar{v}_i = v_i \times (\text{mol}^{-1})$

$= 8.3144 \text{ J K}^{-1}$
 $= 0.082057 \text{ L atm K}^{-1}$
 $= 0.083144 \text{ L bar K}^{-1}$

$\bar{v}_i = \frac{v_i}{\text{mol}} = [\text{unitless}]$

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

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

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

- Equilibrium and ΔG and $\Delta \mu$

- $\Delta G=0$; $\Delta \mu=0$

- $(\Delta G^\circ)_{\text{reaction}} = -RT \ln K_{\text{eq}}$

- $(\Delta \mu_i^\circ)_{\text{reaction}} = -RT \ln K_{\text{eq}}$

- interpretation of $\Delta \mu^\circ$ vs $-RT \ln K_{\text{eq}}$

- How G , $\Delta G_{\text{reaction}}$, and K_{eq} vary with T and with P

- Pressure dependence

- $\left(\frac{\partial G}{\partial P} \right)_T = V \quad \left(\frac{\partial \Delta_{\text{reac}} G}{\partial P} \right)_T = \Delta_{\text{reac}} V$

- $G_T(P_2) = G_T(P_1) + \int_{P_1}^{P_2} V dP \stackrel{\text{ideal gas}}{=} G_T(P_1) + nRT \ln \frac{P_2}{P_1}$

- $\Delta_{\text{reac}} G_T(P_2) = \Delta_{\text{reac}} G_T(P_1) + \int_{P_1}^{P_2} \Delta_{\text{reac}} V dP$

- Temperature dependence

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

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

- *more rigorously (later)*

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

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

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

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

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

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

- Corrections for nonideality (first look)

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

$a_i = \text{activity}$

- $a_i = \left(\frac{\gamma_i P_i}{1 \text{ bar}} \right)$ 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

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

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

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

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

- 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 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 #56, slides 4 et al, 12(6) et al, 19 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} :

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

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

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