

## Review Topics Weeks 4-6+

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.

- 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 2<sup>nd</sup> 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
  - $$\sum \frac{q}{T} = \frac{q_H}{T_H} + \frac{q_L}{T_L} = 0$$

- $\epsilon$  of any Carnot engine ('any working substance') has the same dependence on  $T_H$  and  $T_L$
- Any reversible cyclic process can be described 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)
  - $\Delta S_{total=universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$
  - 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)
    - $TdS = \bar{d}q$      $TdS = \bar{d}q_{\text{rev}}$     ( $P_{\text{ext}})_{\text{rev}}=P_{\text{int}}\equiv P$
    - $dU = TdS - PdV$      $U(S,V)$     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 2<sup>nd</sup> 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
  - $\Delta S_{\text{sys}}$     disorders system
  - $\Delta S_{\text{surr}} + \Delta S_{\text{sys}} \geq 0$
  
- Calculation of  $\Delta G$  for physical processes (expansion of gasses, phase changes, etc.)
- Calculation of  $\Delta G_{\text{reaction}}$  from  $\Delta G_f$  or  $\Delta H_f$  and  $\Delta S$  or reactants and products

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

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

○

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

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

○

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

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

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

$$= 8.3144 \text{ J K}^{-1}$$

$$= 0.082057 \text{ L atm K}^{-1}$$

$$= 0.083144 \text{ L bar K}^{-1}$$

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

- Equilibrium and  $\Delta G$  and  $\Delta \mu$

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

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

○

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

○

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

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

- Pressure dependence

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

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

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

- Temperature dependence

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

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

- more rigorously (later)

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

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

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

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

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

$$\text{From } \frac{(\Delta \mu_i^{\circ})_{\text{reaction}}}{T} = -R \ln K_{\text{eq}}$$

$$\left( \frac{\partial \ln K_{\text{eq}}}{\partial T} \right)_P = \frac{\Delta H_{\text{reac}}}{RT^2}$$

- Le Chatlier's Principle