Review Topics Weeks 4-5

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 <u>isolated system</u> 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.
  - $\varepsilon = \dfrac{-w_t}{q_H} = 1 - \dfrac{T_L}{T_H}$
  - Reverse process corresponds to refrigerators and heat pumps
  - $\sum \dfrac{q}{T} = \dfrac{q_H}{T_H} + \dfrac{q_L}{T_L} = 0$

- ○ 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

  - ○ $dS = \dfrac{đ q_{rev}}{T}$; $\Delta S = \int \dfrac{đ q_{rev}}{T}$; $\oint \dfrac{đ q_{rev}}{T} = 0$

  - ○ $\Delta S \geq \int \dfrac{đ q}{T}$; $0 \geq \oint \dfrac{đ q}{T}$; $(= \text{for reversible process}; > \text{for spontaneous ['real'] process})$

  - ○ $\Delta S_{total \equiv universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$

  - ○ S is a state function; dS is an exact differential

  - ○ Dependence of S on
    - ▪ T: $\left(\dfrac{\partial \bar{S}}{\partial T}\right)_V = \dfrac{\bar{C}_V}{T}$; $\left(\dfrac{\partial \bar{S}}{\partial T}\right)_P = \dfrac{\bar{C}_P}{T}$
    - ▪ P: $\left(\dfrac{\partial \bar{S}}{\partial P}\right)_T = -\left(\dfrac{\partial \bar{V}}{\partial T}\right)_P$
    - ▪ V: $\left(\dfrac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_{\bar{V}}$
    - ▪ Phase: $\Delta S = \dfrac{\Delta H_{equilibrium\ phase\ change}}{T_{equilibrium\ phase\ change}}$

  - ○ Calculation of entropy changes for changes in P, V, T, phase

  - ○ Third Law and calculations using Third Law Entropies: $\bar{S}^o(T)$

  - ○ $\Delta S^0_{reaction}(T) = \sum_i v_i \bar{S}^0_i(T)$

  - ○ Entropy of mixing: $\Delta S = -n_{total} R \sum_i X_i \ln X_i$ $\quad where\ X_i = \dfrac{n_i}{n_{total}}$

  - ○ 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≡U+PV
    - A≡U-TS
    - G≡H-TS

  - and their total differentials (no work other, closed systems)
    - TdS = $đ$q
    - 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