

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 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 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
 - $dS = \frac{\vec{d}q_{rev}}{T}$; $\Delta S = \int \frac{\vec{d}q_{rev}}{T}$; $\oint \frac{\vec{d}q_{rev}}{T} = 0$
 - $\Delta S \geq \int \frac{\vec{d}q}{T}$; $0 \geq \oint \frac{\vec{d}q}{T}$; (= 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)
 - $TdS = \bar{d}q$ $TdS = \bar{d}q_{\text{rev}}$ $(P_{\text{ext}})_{\text{rev}}=P_{\text{int}}\equiv P$
 - $dU = TdS - PdV$ $U(S,V)$ 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