Review Topics Weeks 1-3

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 $\left(P - \dfrac{a}{V^2} \right) \left(\overline{V} - nb \right) = RT$; physical meaning of a and b
    - Other approximate equations of state exist (e.g. Virial power series expansion)
- Work
    - w= force • displacement
    - $đw$ inexact differential, depends on path
    - $đw = -P_{ext}\, dV$ (P-V work)
    - $w = \int đw$
    - $w = -P_{ext}\, \Delta V$ (P_{ext} = constant, w_{other} = 0)
    - $w = -n\,R\,T \ln (V_f / V_i)$ (isothermal, reversible, ideal gas, w_{other} = 0)

- Heat
    - $đq$ inexact differential depends on path
    - $đq = C\, dT$
    - $q = \int C\, dT$

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

- $H \equiv U + (PV)_{internal}$
- 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; $ov_1 .. ov_M$ 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)

- $$dU(T,V,n_1,...,n_K,ov_1,...,ov_M) = \left(\frac{\partial U}{\partial T}\right)_{V,n,ov} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n,ov} dV + \sum_i^K \left(\frac{\partial U}{\partial n_i}\right)_{T,V,n_{j\neq i},ov} dn_i + \sum_i^M \left(\frac{\partial U}{\partial ov_i}\right)_{T,V,n,ov_{j\neq i}} dov_i$$

- $$dH(T,P,n_1,...,n_K,ov_1,...,ov_M) = \left(\frac{\partial H}{\partial T}\right)_{P,n,ov} dT + \left(\frac{\partial H}{\partial P}\right)_{T,n,ov} dP + \sum_i^K \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_{j\neq i},ov} dn_i + \sum_i^M \left(\frac{\partial H}{\partial ov_i}\right)_{T,P,n,ov_{j\neq i}} dov_i$$

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

- $$dU(T, V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- $$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

- Definitions relationships (closed system)

  - $dU = \bar{d}q - P_{ext} dV + \bar{d}w_{other}$

  - $\Delta U_V = q_v + \bar{d}w_{other}$ (const V) "heat is ΔU at constant V"

  - $n\overline{C}_V \equiv \left(\frac{dq}{dT}\right)_V \quad \Rightarrow \quad dU_V = n\overline{C}_V \, dT + \bar{d}w_{other}$ (const V)

  - $dH = \bar{d}q + V \, dP + \bar{d}w_{other}$ ($P_{ext} = P_{internal}$; thus usually for a reversible process; but OK for any infinitesimal process)

  - $\Delta H_P = q_P + w_{other}$ (const P_{ext} ; $P_{intial} = P_{final} = P_{ext}$) *"heat is ΔH at constant P"*

  - $n\overline{C}_P \equiv \left(\frac{dq}{dT}\right)_P \quad \Rightarrow \quad dH_P = n\overline{C}_P \, dT + \bar{d}w_{other}$ (const P)

- Derived consequences (closed system, $đw_{other} = 0$)

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

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

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

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

  ■ $dU = n\,\overline{C}_v\,dT$ (ideal gas, any path)

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

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

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

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

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

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

  Constant volume
  ■ $w = 0$
  ■ $q_V = \Delta U_V = n\,\overline{C}_V\,\Delta T$
  ■ $\Delta H_V = \Delta U_V + V\,\Delta P = \Delta U_V + V\,(P_f - P_i)$

  Constant pressure
  ■ $q_p = \Delta H_P = n\,\overline{C}_P\,\Delta T$
  ■ $w = -\,P\Delta V$
  ■ $\Delta U_P = q + w$

Ideal gasses

- $\overline{C}_P = \overline{C}_V + R$

- $\overline{C}_V = \frac{3}{2} R$ for monatomic ideal gas

- $\Delta U = n \overline{C}_v \Delta T$ (any path)

- $\Delta H = n \overline{C}_P \Delta T$ (any path)

Isothermal path

- $q = -w$
- $\Delta U = 0$
- $\Delta H = 0$

- $w = -n R T \ln \dfrac{V_f}{V_i} \tilde{=} n R T \ln \dfrac{P_i}{P_f}$ (reversible path , note $-$ sign)

- $w = -P_{ext}\Delta V$ (constant P_{ext} expansion/compression)

Adiabatic path

- $q = 0$
- $\Delta U = w = n \overline{C}_V \Delta T$

- $\Delta H = \Delta U + \Delta (PV) = \Delta U + P_f V_f - P_i V_i = n \overline{C}_P \Delta T$

- $T_1^{\frac{\overline{C}_V}{R}} V_1 = T_2^{\frac{\overline{C}_V}{R}} V_2$ (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^{γ} = constant)

- $\dfrac{T_1^{\frac{\overline{C}_P}{R}}}{P_1} = \dfrac{T_2^{\frac{\overline{C}_P}{R}}}{P_2}$ (adiabatic reversible path)

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