1 review

Boltzmann probability:

$$S = -k \sum p_i \ln p_i$$

Entropy of mixing:

$$S = R \sum x_i \ln x_i$$

Standard Entropy:

$$S^\circ = \int_0^{298} \frac{Cp}{T} dT$$

2 Section 4A - Gibbs and Auxillary functions

Gibbs:

$$dG = dH - Tds$$

2.1 Gibbs derivation

All systems tend toward a lower "Energy state". This process acquires entropy (maximizes configuration). Consider the three laws applied to a reversible process:

- 1st law:
  $dU = \delta q - \delta w$
  $dU = \delta q_{rev} - PdV$ (I)

- 2nd law:
  $dS \geq \frac{\delta q}{T}$
  $dS = \frac{\delta q_{rev}}{T}$
  $\delta q_{rev} = Tds$ (II)

- 3rd law:
  $S = 0$ at 0K

- Enthalpy:
  $H \equiv U + PV$
  $dH = dU + PdV + vdP$ (III)

2.2 cont.

(II) ∘ (I): $dU = Tds - PdV$ (IV)
(IV) ∘ (III): $dH = (Tds - PdV) + PdV + VdP$
$dH = TdS + VdP$ (IV)

2.3 For a process at constant T and P

$(IV)\Big|_{P,T}$: $dH = Tds$

- This equation is a criteria for sponteneity

- It displays an equilibrium which can be used to predict the direction of a reaction

- This equation balances both:

    - enthalpy (naturally lower energy state is preferred)
    - entropy (naturally tends towards a statistically favored state)

2.4 Gibbs Free Energy

$$G \equiv H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

$$dG = dU + V\,dP + P\,dV - S\,dT - T\,dS$$

$$dG = \delta q - \delta w + V\,dP + P\,dV - S\,dT - T\,dS$$

$$dG = T\,dS - P\,dV + V\,dP + P\,dV - S\,dT - T\,dS$$

$$dG = V\,dP - S\,dT$$

The final line indicates that the equilibrium criteria varies with temperature and pressure

$\frac{\delta G}{\delta T}\big|_P = -S$	$\frac{\delta G}{\delta P}\big|_T = V$	$\frac{\delta H}{\delta P}\big|_S = V$	$\frac{\delta H}{\delta S}\big|_P = T$

2.5 Gibbs: Standard State

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T$$

3 First order Homogenous functions

$$F(x_1, ..., x_i) = \frac{dF}{dx_1}x_1 + \frac{dF}{dx_2}x_2 + ... + \frac{dF}{dx_i}x_i$$

Applying this theorem to Thermodynamic equations:

$$G(P, T, n) = \frac{dG}{dP}P + \frac{dG}{dT}T + \frac{dG}{dn}n$$

4 Legendre Transform