5.12 - Using the Fact that S is a State Function to Determine the Dependence of S on V & T

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dS = \frac{1}{T}\left[C_v\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{P}{T}dV = \frac{C_v}{T}dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \quad \& \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V\right] - \frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$ internal pressure

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}$$

$$\Rightarrow dS = \frac{C_v}{T}dT + \frac{\beta}{\kappa}dV$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_v}{T}dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa}dV$$

5.13 The Dependence of S on T & P

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

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

$$dS = \frac{C_P}{T} dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \& \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\left(\frac{\partial H}{\partial P}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\beta$$

$$dS = \frac{C_P}{T} dT - V\beta \, dP$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta \, dP$$

6.1 The Gibbs Energy and the Helmholtz Energy

+ Spontaneous Process:

$$dS \geq \frac{dq}{T}$$

$$-dU + dw_{total} + TdS \geq 0$$

$$-dU + dw_{exp} + dw_{nonexp} + TdS \geq 0$$

$$-dU - P_{ext}\,dV + dw_{nonexp} + TdS \geq 0$$

since $w = 0$, $dU = 0$ (isolated system) $\Rightarrow dS \geq 0$

$$TdS = d(TS) \quad \text{(isolated system)}$$

$$\Rightarrow -dU + TdS \geq -dw_{exp} - dw_{nonexp}$$

$$d(U - TS) \leq dw_{exp} + dw_{nonexp}$$

+ Helmholtz Free Energy

$dT = 0 \qquad dA \leq dw_{exp} + dw_{nonexp} - SdT$

$$dA \leq dw_{exp} + dw_{nonexp}$$

T is constant, Helmholtz energy is a measure of the maximum amount of work that can be produced by the system. Only equal for reversible work

$$dw_{nonexp} = dw_{exp} = 0$$

$$dA \leq 0$$

Since $H = U + PV$

$$d(U + PV - TS) = d(H - TS) \leq dw_{nonexp}$$

$$dG - dw_{nonexp} \leq 0$$

$$dG \leq 0$$

$$dS - \frac{dq}{T} \geq 0$$

$$dS + dS_{surr} \geq 0$$

depends on concentrations of reactants & products

$$\Delta G_R = \Delta H_R - T\Delta S_R$$

Spontaneous: $\Delta H_R < 0$ & $\Delta S_R > 0$

Never spontaneous: $\Delta H_R > 0$ & $\Delta S_R < 0$

At constant V & T ; $\Delta A_R < 0$

$$\Delta A_R = \Delta U_R - T\Delta S_R$$

6.2 The Differential Forms of U, H, A, & G

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = U + PV - TS$$

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \& \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \& \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \& \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \& \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U(S,V)}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U(S,V)}{\partial V}\right)_S\right)_V$$

Maxwell relations: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = V\beta$$

6.3 The Dependence of the Gibbs & Helmholtz Energies on P, V, and T

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \& \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \& \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\int_{P^\circ}^{P} dG = G(T,P) - G^\circ(T,P^\circ) = \int_{P^\circ}^{P} V\,dP'$$

$$G(T,P) = G^\circ(T,P^\circ) + \int_{P^\circ}^{P} V\,dP' \approx G^\circ(T,P^\circ) + V(P-P^\circ)$$

$$G(T,P) = G^\circ(T) + \int_{P^\circ}^{P} V\,dP' = G^\circ(T) + \int_{P^\circ}^{P} \frac{nRT}{P'}\,dP' = G^\circ(T) + nRT\ln\frac{P}{P^\circ}$$

Gibbs - Helmholtz equation

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\,\frac{d\left(\frac{1}{T}\right)}{dT}$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2} = \frac{-H}{T^2}$$

$$\frac{d\left(\frac{1}{T}\right)}{dT} = -\frac{1}{T^2}$$

$$\Rightarrow \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_p = \left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_p \left(\frac{dT}{d\left(\frac{1}{T}\right)}\right) = -\frac{H}{T^2}\,(-T^2) = H$$

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \int_{T_1}^{T_2} \Delta H \, d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$