Reading HW

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \underbrace{\frac{1}{T}\left[C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{P}{T} dV}_{\frac{1}{T}dU + \frac{P}{T}dV} = \frac{C_V}{T} dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

equating coefficients

$$\rightarrow \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] = \left(\frac{\partial P}{\partial T}\right) = \frac{\beta}{\kappa}$$

$$\downarrow$$

$$T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\rightarrow dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \quad / \int$$

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

5.13 The Dependence of S on T & P

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

$$U = H - PV$$

$$dU = TdS - \cancel{PdV} = dH - \cancel{PdV} - VdP$$

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

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

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

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

$$\downarrow$$

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

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

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

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

6.1 The Gibbs Energy & the Helmholtz Energy

$TdS \geq đq$ Clausius inequality

$-dU - P_{ex} dV = đw_{nonexpansion} + T dS \geq 0$

isothermal $-dU + TdS \geq -đw_{exp} - đw_{nonexp} \Leftrightarrow d(\underbrace{U-TS}) \leq đw_{exp} + đw_{nonexp}$

$A = U - TS$ = Helmholtz energy

$\rightarrow dA - đw_{exp} - đw_{nonexp} \leq 0$

const. V $\Rightarrow đw_{exp} = 0$ as $dV = 0$

if nonexpansion work is not possible $\rightarrow dA \leq 0$

$\hookrightarrow$ const. P + const. T $\rightarrow PdV = d(PV)$ $\quad TdS = d(TS)$

$H = U + PV$

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

Gibbs Energy : G $\rightarrow$ state function

Condition for spontaneity & equilibrium: $dG - đw_{nonexp} \leq 0$

Const. V & T

for const. P & T $\quad dG \leq 0$

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

chemical reaction

$\rightarrow$ chem. rxn never spontaneous when $\Delta H_R > 0$ & $\Delta S_R < 0$

$\rightarrow$ rxn always spontaneous when $\Delta H_R < 0$ & $\Delta S_R > 0$

$\Delta G_R = 0$ – rxn mixture at EQUILIBRIUM

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

$\hookrightarrow$ const. V & T

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

$$\left.\begin{aligned} H &= U + PV \\ A &= U - TS \\ G &= H - TS = U + PV - TS \end{aligned}\right\} \longrightarrow \begin{aligned} dU &= TdS - PdV \\ dH &= TdS + VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned} \qquad \left.\begin{aligned} &U(S,V) \\ &H(S,P) \\ &A(T,V) \\ &G(T,P) \end{aligned}\right\} \text{natural variables}$$

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

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

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

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

Maxwell relations

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

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

$\left(\frac{\partial A}{\partial T}\right)_V = -S$ & $\left(\frac{\partial A}{\partial V}\right)_T = -P$ → A of a pure substance decreases as either T or V increase

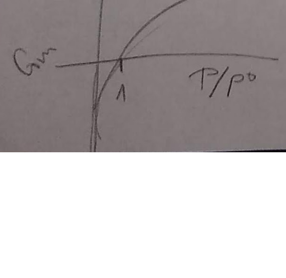
$\left(\frac{\partial G}{\partial T}\right)_P = -S$ & $\left(\frac{\partial G}{\partial P}\right)_T = V$ → G decreases w/ increasing T
→ G increases w/ increasing P

$$\int_{P^\circ}^{P} dG = G(T,P) - G^\circ(T,P^\circ) = \int_{P^\circ}^{P} V dP' \qquad P^\circ = 1 \text{ bar}$$

→ for solids & liquids $\approx G^\circ(T,P^\circ) + V(P - P^\circ)$

for gases

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



$$\left(\frac{\partial[G/T]}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\left(\frac{d[1/T]}{dT}\right) = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2} = \boxed{-\frac{H}{T^2}}$$

$$\rightarrow \left(\frac{\partial[G/T]}{\partial[1/T]}\right)_p = \left(\frac{\partial[G/T]}{\partial T}\right)_p \left(\frac{dT}{d(1/T)}\right) = -\frac{H}{T^2}(-T^2) = H$$

$G = H - TS$

$$\left(\frac{\partial\left[\frac{G}{T}\right]}{\partial T}\right)_p = -\frac{H}{T^2} \iff \left(\frac{\partial\left[\frac{G}{T}\right]}{\partial\left[\frac{1}{T}\right]}\right)_p = H$$

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

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