George Paxos Reading HW 6

5.12 Using the fact that S is a state function to determine dependence of S on V and T

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

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

S = entropy V = Volume

T = Temp. C_V = heat capacity constant V

Temperature dependence $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$

Volume dependence $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \frac{\partial U}{\partial V}\right]_T$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(dV/dT)_P}{(dV/dP)_T} = \frac{\beta}{K}$$

$$dS = \frac{C_V}{T} dT + \frac{\beta}{K} dV$$

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

also no phase changes

We can now measure entropy using only changes in Temperature and Volume.

5.13 The Dependence of S on T and P.

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

S = entropy, T = temp., P = pressure, C_P = heat capacity, ΔP, H = enthalpy, V = Volume

$$\left(\frac{\partial S}{\partial T}\right) = \frac{C_P}{T} \text{ and } \left(\frac{\partial S}{\partial P}\right) = \frac{1}{T}\left[\left(\frac{dH}{dP}\right) - V\right]$$

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

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

We can now calculate entropy from change in Temperature and Pressure,

6.1 The Gibbs Energy and Helmholtz Energy

For $\Delta T = 0$

$$-dU + T\,dS \geq -đw_{expansion} - đw_{nonexpansion} \quad \text{or}$$
$$d(U - TS) \leq -đw_{expand} + đw_{nonexpand}$$

Helmholtz energy $= A$

$$dA - đw_{expansion} - đw_{nonexpansion} \leq 0$$

$$dA \leq 0$$

For $\Delta P = 0$,

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

Gibbs free energy $= G$

$\Delta T, P = 0$ $\quad dG - đw_{nonexpansion} \leq 0$

if no $w_{nonexpand}$ then

$$dG \leq 0$$

Now we can consider spontaneity without measuring changes in the surroundings. We can also calculate maximum nonexpansion work

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

- ΔG_R: Gibbs free energy
- ΔH_R: Enthalpy
- T: Temp.
- ΔS_R: entropy

at eq $\Delta G_R = 0$

$\Delta H_R < 0$, $\Delta S_R > 0$ spontaneous

$\Delta H_R > 0$, $\Delta S_R < 0$ non-spontaneous

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

when no non expansion work is possible

6.2 Differential forms of U, H, A, G

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

$$dU = TdS - PdV$$
$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$

natural variables = S, T, P, and V

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

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

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

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

Maxwell Relations for differential form of U, H, A, G

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

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

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

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

6.3 The dependence of the Gibbs and Helmholtz energies on P, V, and T

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

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

$$\Delta T = 0 \quad \int_{P^0}^{P} dG = G(T,P) - G^0(T,P^0) = \int_{P^0}^{P} V\,dP$$

For reversible and ideal gas

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

dependence of G on T $\left(\frac{\partial[G/T]}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G\frac{d[1/T]}{dT}$

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

Gibbs-Helmholtz equation

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

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

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

ΔH should be independent of T, if not the integral must be evaluated using ΔH_f° and temp.-dependent expression of $C_{p,m}$ for reactants and products