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Macro. P. chem.

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Reading HW #6

5.12.) Using "S is a State Function" to Determine the Dependence of S on V and T

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

dS ↙ $\left(\frac{\partial S}{\partial T}\right)_V$ $\left(\frac{\partial S}{\partial V}\right)_T \rightarrow \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$

5.13.) The Dependence of S on T and P

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

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

6.1.) The Gibbs Energy and the Helmholtz Energy

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

$$dG - đw_{expansion} \leq 0$$

Constant P & T
Spontaneity $\Delta G_R < 0$

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

no nonexpansion work is possible
Constant V & T
Spontaneity $\Delta A_R < 0$

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

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

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

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

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

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

$\Delta H \rightarrow$ independent of T over temp

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

Volume is independent of pressure

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