Samantha Jacques HW 6

I. 5.12 Using the Fact that S is a State function to determine the dependence of S on V and T

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

1. dS is written in terms of the partial derivative with respect to V and T

B. 1/T and P/T

1. Are greater than zero, the entropy of a system increases with the internal energy at conitant volume
2. Increases with the volume at constant internal energy

C. $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$

1. Equating the coefficients of dT and dV from 2 equations

II. 5.13 The Dependence of S on T and P

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

1. The total differential dS
2. Shows how S varies with Temperature and Pressure

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

1. The pressure dependence of the entropy at constant temperature
2. Total dS can be written
   a. $dS = \frac{C_P}{T} dT - V\beta dP$
3. Integration of both sides along a reversible path yields
   a. $\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} V\beta dP$

III. 6.1 The Gibbs Energy and the Helmholtz energy

A. $TdS \geq đq$

1. The fundamental expression governing spontaneity is the Clausius inequality
2. The equality is only satisfied for a reversible process
   a. $đq = dU - đw$
   b. $-dU - P_{external} dV + đw_{nonexpansion} + TdS \geq 0$

B. Isothermal Process

1. $-dU + TdS \geq -đw_{expansion} - đw_{nonexpansion}$
2. $d(U+TS) \leq đw_{expansion} - đw_{nonexpansion}$

C. Helmholtz energy

1. $dA \leq 0$
2. $dV = 0$
   a. $dw_{expansion} = 0$
3. $d(U+PV-TS) = d(H-TS) \leq dw_{non\,expansion}$

II. 6.2 The differential Forms of U, H, A, and G

A. Natural Variables

1. $dU = TdS - PdV$
   a. $dH = TdS - PdV + PdV + VdP = TdS + VdP$
   b. $dA = TdS - PdV - TdS - SdT = -SdT - PdV$
   c. $dG = TdS + VdP - TdS - SdT = -SdT + VdP$
2. Form expresses the internal energy as $U(S,V)$
   a. enthalpy $H(S,P)$
   b. Helmholtz $A(T,V)$
   c. Gibbs energy $G(T,P)$
3. $dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

B. Maxwell Relations

1. Have been derived using only U, H, A and G
2. 4 relations are extremely useful
   a. $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
   b. $\left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial S}{\partial V}\right)_P$
   c. $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K}$
   d. $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = V\beta$

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

A. $\left(\frac{\partial G}{\partial T}\right)_P = -S$ and $\left(\frac{\partial G}{\partial P}\right)_T = V$
   1. Gibbs energy decreases with increasing temperature it increases with increasing temperature
   2. Integrated at constant T
      a. $\int_{P^\circ}^{P} dG = G(T,P) - G^\circ(T,P^\circ) = \int_{P^\circ}^{P} V\,dP$

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