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Reading Assignment 6

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<u>5.12 - Using the Fact that S is a State Function to Determine the</u>
<u>Dependence of S on V and T</u>

I. Entropy of a system increases with the internal energy at constant V

A. Entropy also increases with volume at constant U

   1. Internal Energy not a variable under experimental control

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

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

      c.
$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \cdot T \left(\frac{\partial P}{\partial T}\right)_V$$

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

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

      f. For reversible paths,
$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{K} dV$$

Over →

5.13 – The Dependence of S on T and P

I. Experiments are normally carried out at constant pressure

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

1. S is an increasing function of the temperature

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

3. $\dfrac{1}{\cancel{T}} \cdot (-\cancel{T})\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial V}{\partial T}\right)_P = -V\beta$

4. $dS = \dfrac{C_P}{T} dT - V\beta \, dP$

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

   for <u>reversible</u> paths only

6.1 – The Gibbs Energy and the Helmholtz Energy

I. Clausius inequality

A. $T dS \geq đq$

1. for only reversible processes

B. $-dU + đw + T dS \geq 0$, since $đq = dU - đw$

1. Can rewrite to identify type of work

a. $-dU - \underbrace{P_{ext} dV}_{\substack{\text{expansion} \\ \text{work}}} + đw_{nonexpansion} + T dS \geq 0$

C. For isolated system, $dS \geq 0$

D. For isothermal system, $T dS = d(TS)$

1. $-dU + T dS \geq -đw_{exp} - đw_{nonexp}$ ⎫
2. $d(U - TS) \leq đw_{exp} + đw_{nonexp}$ ⎬ equivalent

<u>6.1 Cont'd...</u>

II. Helmholtz energy

   A. State Function $(U-TS)$

   B. denoted as "A"

   C. $dA - đw_{exp} - đw_{nonexp} \leq 0$

      1. can calculate max work system can do on surroundings for ~~iso~~

        isothermal process (reversible)

      2. $đw_{wtotal} = đw_{exp} + đw_{nonexp} \geq dA$

III. Reactions under constant pressure more than constant volume

   A. Constant P and T

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

   B. Gibbs energy

      1. State Function $(H-TS)$

      2. denoted as "G"

      3. $dG - đw_{nonexp} \leq 0$

        a. can calculate maximum nonexpansion work in reaction

IV. Value of G to determine spontaneous change + direction of reaction

   A. $\Delta G_R = \Delta H_R - T\Delta S_R$, for macroscopic change at <u>constant P and T</u>

   B. $\Delta A_R = \Delta U_R - T\Delta S_R$, for macroscopic change at <u>constant V and T</u>

<u>6.2 - The Differential Forms of U, H, A, and G</u>

I. Differentials for U, H, A, and G (natural variables)

   A. $dU = \boxed{TdS - PdV}$

   B. $dH = TdS - PdV + PdV + VdP = \boxed{TdS + VdP}$

                                calculate change in energy for processes

   C. $dA = TdS - PdV - TdS - SdT = \boxed{-SdT - PdV}$

   D. $dG = TdS + VdP - TdS - SdT = \boxed{-SdT + VdP}$

                                  calculate direction of processes + max work produced

II. Maxwell Relations

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

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

> involve constant S for one partial derivative
> ↳ reversible, adiabatic process

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

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

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

I. Helmholtz energy of a pure substance decreases as either Temperature or Volume increases.

II. Gibbs energy decreases with increasing temperature, and Gibbs energy increases with increasing pressure

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

for reversible path and ideal gas behavior

IV. Gibbs – Helmholtz equation

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

1. Can be rewritten as

a. $\left(\dfrac{\partial[G/T]}{\partial[1/T]}\right)_P = -\dfrac{H}{T^2}(-T^2) = H$

b. $\int_{T_1}^{T_2} d\left(\dfrac{\Delta G}{T}\right) = \dfrac{\Delta G(T_1)}{T_1} + \Delta H(T_1)\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$