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Reading Assignment 5

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

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

Since $1/T$ and $P/T > 0$, the entropy increases with internal energy at constant volume, and increases with volume at constant internal energy.

First write the total differential dS in terms of partial deriv. with respect to V and T :

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

To evaluate $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$ for dS :

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

The expression for $(\partial S/\partial V)_T$ is not a form that allows for a direct comparison with experiment to be made.

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

Taking the mixed second derivative:

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T} \left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T\right)_V \right] - \frac{1}{T^2} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

Simplify:

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

Then a practical equation is obtained for the dependence of entropy on volume under const. temp:

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

The result of these considerations is that dS can be expressed in terms of dT and dV

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

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

5.13: The dependence of S on T and P

The total differential dS is written:

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

Starting from the relation $U = H - PV$, du :

$$du = T ds - P dV = dH - P dV - V dP$$

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

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

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

We equate the mixed second partial derivatives of $\left(\frac{\partial S}{\partial T} \right)_P$ and $\left(\frac{\partial S}{\partial P} \right)_T$:

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

These mixed partial derivatives evaluated:

$$\left(\frac{\partial}{\partial P} \left(\frac{\partial S}{\partial T} \right)_P \right)_T = \frac{1}{T} \left(\frac{\partial C_P}{\partial P} \right)_T = \frac{1}{T} \left(\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T} \right)_P \right)_T$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial P} \right)_T \right)_P = \frac{1}{T} \left[\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P} \right)_T \right]_P - \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{T^2} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right]$$

$$\frac{1}{T} \left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P} \right) \right)_P = \frac{1}{T} \left[\left(\frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P} \right) \right)_P - \left(\frac{\partial V}{\partial T} \right)_P \right] - \frac{1}{T^2} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right]$$

Simplify:

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

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

The total differential (dS) can be written as:

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

Integrating both sides:

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

6.1 The Gibbs Energy and the Helmholtz Energy

The fundamental expression governing spontaneity is the Clausius inequality, written as:

$$TdS \geq dq$$

The equality is satisfied only for a reversible process since

$$dq = du - \sigma w, \quad TdS \geq du - \sigma w \quad \text{or} \quad -du + \sigma w + TdS \geq 0$$

It is useful to distinguish between expansion work, in which work arises from a volume change in system and nonexpansion work:

$$-du - P_{\text{external}} dV + \sigma w_{\text{nonexp.}} + TdS \geq 0$$

For isothermal processes, $TdS = d(TS)$

$$-du + TdS \geq -\sigma w_{\text{expansion}} - \sigma w_{\text{nonexpansion}} \quad \text{or}$$

$$d(U - TS) \leq \sigma w_{\text{expansion}} + \sigma w_{\text{nonexpansion}}$$

The combination of state functions $U - TS$, which has the units of energy, defines a new state function that we call the Helmholtz energy, abbreviated A .

$$dA - \sigma w_{\text{expansion}} - \sigma w_{\text{nonexpansion}} \leq 0$$

$$\sigma w_{\text{total}} = \sigma w_{\text{expansion}} + \sigma w_{\text{nonexpansion}} \geq dA$$

If nonexpansion work also not possible in the transformation
 $\delta w_{\text{expansion}} = \delta w_{\text{nonexpansion}} = 0$, the condition that defines spontaneity and equilibrium becomes:

$$dA \leq 0$$

Using the relation $H = U + PV$:

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

The combination of state functions $H - TS$, has units of energy defines new state function called the Gibbs Energy, G .

$$dG - \delta w_{\text{nonexpansion}} \leq 0$$

$$dG \leq 0$$

Clausius inequality

$$dS - \frac{\delta q}{T} \geq 0$$

$$dS + dS_{\text{surroundings}} \geq 0$$

Maximum nonexpansion work: can be produced by a chemical transformation

For macroscopic changes at constant P and T in which no nonexpansion work is possible, the condition for spontaneity is $\Delta G_r < 0$ where:

$$\Delta G_r = \Delta H_r - T \Delta S_r$$

The entropic contribution to ΔG_r is greater for higher \uparrow temp.

A chemical transformation is always Spontaneous if $\Delta H_r < 0$ and $\Delta S_r > 0$

A chemical transform. is always Nonspontaneous if $\Delta H_r > 0$ and $\Delta S_r < 0$

- The relative magnitudes of ΔU_r and $T\Delta S_r$ determine if chemical transformation is spontaneous.
- If the chemical reaction is not spontaneous, the reverse process is spontaneous.
- If $\Delta G_r = 0$, the reaction mix. @ equilibrium, and neither direction of Δ is spontaneous.
- For macroscopic changes at constant $V + T$, no nonexpansion work is possible, the condition for spontaneity is $\Delta A_r < 0$ where

$$\Delta A_r = \Delta U_r - T \Delta S_r$$

6.2: The differential forms of U, H, A and G

Differential forms are essential to calculate U, H, A , and G along with P , and T :

$$H = U + PV$$

$$A = U - TS$$

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

The following differentials can be formed:

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdU + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

These natural variables are used because the differential equations are compact.

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

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

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

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

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

These expressions state how U, H, A , and G vary with their natural variables.

4 Maxwell Relations:

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

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

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

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

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

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

S and $P \rightarrow$ positive values.

Devote more to properties of G than A

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

$\Delta S = nR \ln(V_f/V_i)$ at constant T . $P \rightarrow 0, V \rightarrow \infty$ since the volume available to gas is maximized as $V \rightarrow \infty, S \rightarrow \infty, P \rightarrow 0$

Therefore $G = H - TS \rightarrow -\infty$

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

Gibbs Helmholtz Equation:

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

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