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

most important idea: no phase changes / chemical reactions occur to a single phase system of a liquid, solid, gas that undergoes a transformation from initial T_i, V_i , to T_f, V_f .

Idea Diagram:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V - \left(\frac{\partial V}{\partial T}\right)_P \\ \left(\frac{\partial S}{\partial T}\right)_V &= \frac{C_V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{F} \left[P + \left(\frac{\partial P}{\partial V}\right)_T \right] \\ \Delta S &= \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{B}{T} dV \end{aligned}$$

Thermodynamic Law: N/A

5.13) Dependence of S on T and P

most important idea: only applies to a single phase system of pure liquid, solid, gas that undergoes transformation from $T_i, P_i \rightarrow T_f, P_f$

Idea Diagram:

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

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

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

Thermodynamic Law: N/A

6.1) The Gibbs Energy and the Helmholtz Energy

Most important idea: Maximum nonexpansion work can be applied to calculate electrical work produced by a reaction in an electrochemical cell

Idea Diagram:

$$d(U-TS) \leq dW_{\text{expansion}} + dW_{\text{nonexpans}}$$

$$\downarrow dA - dW_{\text{expansion}} - dW_{\text{nonexpansion}} \leq 0$$

$$\downarrow dG - dW_{\text{expansion}} \leq 0$$

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

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

Thermodynamic Law: N/A

6.2) The Differential forms of U, H, A and G

most important idea: The four relations are very useful for transforming obscure partial derivatives in other partial derivatives that can be directly measured

Idea Diagram

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

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

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

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

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Thermodynamic Law: N/A

6.3) Dependence of the Gibbs and Helmholtz energies on P, V, and T

most important idea: Helmholtz energy of a pure substance decreases as either temperature increases or decreases

Idea Diagram:

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

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

$$\int_{P_0}^P \delta G = G(T, P) - G^{\circ}(T, P^{\circ}) = \int_{P_0}^P V dP'$$

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

Thermodynamic Law: N/A