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Reading # 6

5.12. Using the fact that S Is a State Function to Determine the Dependence of S on V and T

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

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

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

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

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

- $\boxed{dS = \frac{C_V}{T} dT}$, const. V

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

$$\downarrow$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] = 0$$

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

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{\kappa}}$$

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

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

5.13. The Dependence of S on T and P

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

$\cdot\ dU = TdS - \cancel{PdV} = dH - \cancel{PdV} - VdP$

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

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

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

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

$\cdot\ \boxed{dS = \frac{C_P}{T} dT}$

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

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

$$-\left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] = 0$$

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

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

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

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

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6.1. The Gibbs Energy and the Helmholtz Energy

$TdS \geqslant dq$

$\rightarrow TdS \geqslant dU - dw$

$\rightarrow -dU + dw + TdS \geqslant 0$

$\rightarrow -dU - P_{ext.}dV + dw_{nonexpansion} + TdS \geqslant 0$

$\rightarrow -dU + TdS \geqslant -dw_{expansion} - dw_{nonexpansion}$

$\rightarrow d(\underbrace{U - TS}_{\downarrow}) \leq dw_{expansion} - dw_{nonexpansion}$

Helmholtz energy (A)

$\rightarrow dA \leqslant dw_{total} = dw_{expansion} - dw_{nonexpanstion}$

↳ use to calculate the maximum work available through carrying out achemical reaction

$$\Delta A = \Delta U - T\Delta S = \Delta H - \Delta(PV) - T\Delta S = \Delta H - \Delta nRT - T\Delta S$$

- Const. V $\rightarrow dw_{expansion} = 0 = dw_{nonexpansion}$ ↓ not impossible
  $\rightarrow dA \leq 0$
- Const. P and T
  $dU + PdV - TdS \leqslant dw_{nonexpansion}$
  $d(U + PV - TS) \leqslant dw_{nonexpansion}$
  $d(\underbrace{H - TS}_{\downarrow}) \leqslant dw_{nonexpansion}$
  Gibbs energy (G)

$dG - dw_{nonexpansion} \leq 0$

$dG \leq 0$

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

+ Entropic contribution to ΔG_R is greater for higher temp.
+ $\Delta H_R < 0$ (exothermic), $\Delta S_R > 0 \rightarrow$ always spontaneous
+ $\Delta H_R > 0$ (endothermic), $\Delta S_R < 0 \rightarrow$ never spontaneous
+ $\Delta G_R = 0 \rightarrow$ equilibrium
+ Reaction is not spontaneous, reverse reaction is spontaneous

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

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

$$\boxed{\begin{aligned} dU &= TdS - PdV \\ dH &= TdS - VdP \\ dA &= -SdT - PdV \\ dG &= -SdT + VdP \end{aligned}}$$

- $\left(\frac{\partial U}{\partial S}\right) = T$; $\left(\frac{\partial U}{\partial V}\right) = -P$
- $\left(\frac{\partial H}{\partial S}\right) = T$, $\left(\frac{\partial H}{\partial P}\right) = -V$
- $\left(\frac{\partial A}{\partial T}\right) = -S$, $\left(\frac{\partial A}{\partial V}\right) = -P$
- $\left(\frac{\partial G}{\partial T}\right) = -S$, $\left(\frac{\partial G}{\partial P}\right) = V$

Maxwell relations

$$\boxed{\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} \\ -\left(\frac{\partial S}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P = V\beta \end{aligned}}$$

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

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

$$\rightarrow G(T,P) = G^\circ(T,P^\circ) + \int_{P^\circ} V\,d' \approx G^\circ(T,P^\circ) + V(P - P^\circ)$$

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$$G(T,P) = G^\circ(T) + \int_{P^\circ}^{P} V dP' = G^\circ(T) + \int_{P^\circ}^{P} \frac{nRT}{P'} dP'$$

$$G(T,P) = G^\circ(T) + nRT \ln \frac{P}{P^\circ}$$

- $$\left(\frac{\partial (G/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P + G \frac{d[1/T]}{dT}$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} = \frac{-S}{T} - \frac{G}{T^2}$$

$$= -\frac{G+TS}{T^2} = \frac{-H}{T^2}$$

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

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

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

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