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Problem Set 4

Analytical Problems

1. Reversible process entropy transfer is taking place by heat interactions

$$\Delta S = \frac{dq_{VA}}{T}$$

- Adiabatic process means the systems is closed + no heat is entered into the system $q \geq 0$ → reversible adiabatic process, $\Delta S = 0$.

2. a.) H, U, S (enthalpy, internal energy + entropy) + state functions, cyclic process initial + final state are same energy / change in state property for cyclic process is zero.

$$\Delta H = 0, \ \Delta S = 0, \ \Delta U = 0$$

b.) Process b → c and d → a are adiabatic process → $q = 0$

During a → b, temp is constant → $\Delta U = 0$.

The work done by the system is being carried out by heat supplied to the system. work done by the system in reversible process = W

$$W = -nRT_h \left| \ln \frac{V_b}{V_a} \right| \Delta U = 0 = q + w \quad q + w = \left(-nR\,T_h \ln\left(\frac{V_b}{V_a}\right)\right)$$

$$q = nRT_h \ln \left(V_b / V_a \right)$$

$$W_{net} = W_{ab} + \cancel{W_{bc}} + W_{cd} + W_{da}$$

$$= -nR\,T_h \ln\left(\frac{V_b}{V_a}\right) - nRT \ln\left(\frac{V_a}{V_b}\right)$$

$$W_{net} = -(T_h - T_l)\, nR \ln\left(\frac{V_b}{V_a}\right)$$

total work done is negative from system point of view

d.) efficiency $(n) = \dfrac{\text{network done by heat engine}}{\text{heat absorbed by heat engine}} = \dfrac{-W}{q}$

$$\frac{[-(T_h - T_c)\, nRT \ln (V_b / V_n)]}{nRT_n \ln (V_b / V_a)} = \frac{T_h - T_c}{T_h} = \frac{1 - T_{cold}}{T_{hot}}$$

3. a.) $S = (P, T)$

Maxwell's relation

$$\boxed{\begin{aligned} dS &= \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P = -\beta V \end{aligned}} \quad \boxed{\left(\frac{\partial S}{\partial P}\right)_P = \frac{C_P}{T}}$$

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right) dP \text{ where } \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \alpha\, P_0 = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

- Equating the mixed second partial derivative, we obtain the following 4 Maxwells 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 dependance of the Gibbs and Helmholtz energies on P, V and T

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

where S and P always take on positive values

- B/C most reactions of interest to chemist are carried out under constant pressure rather than constant volume conditions, we will devote more attention to the properties of G than to those of A.

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

For microscopic change in P at constant T:

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

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

$$G(T,P) = G^\circ(T) + \int_{P_0}^{P} V dP' = G^\circ(T) + \int_{P_0}^{P} \left(\frac{nRT}{P_1}\right) dP' = G^\circ(T) + nRT\ln\frac{P}{P_0}$$

$\Delta S = nR\ln(V_f/V_i)$ at constant T. As $P \to 0$, $V \to \infty$. B/C the volume available to a gas molecule is maximized as $V \to \infty$, $S \to \infty$, $P \to 0$ therefore $G = H - TS \to -\infty$

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

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

Gibbs Helmholtz equation

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

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

b.) $\boxed{dS = \frac{C_P}{T}dT - \beta V dP}$ $\quad \Delta S = \int_{T_1}^{T_2}\frac{C_P}{T}dT - \int_{P_1}^{P_2}\beta V dP$

Numerical problems

a.) $\Delta H_{rxn} = \sum \Delta H^\circ f\ \text{product} - \sum \Delta H^\circ f\ \text{reactant} = [\overset{-1364}{\cancel{}} - 2 + 8 - 394] - 12 + 3$

$\boxed{\Delta H_{rxn} = -763\ KJ/mol}$

$-\Delta S_{rxn} = \sum S\ \text{products} - \sum S\ \text{reactants} \rightarrow [192 + 161 + 213] - [209] = [357\ J/m$

$-\Delta S_{surr} = \frac{-\Delta H_{rxn}}{T} = \frac{-(-763)}{298K} = \boxed{2.56 \times 10^3\ J/mol\cdot K}$

$-\Delta S_{univer} = \Delta S_{rxn} + \Delta S_{surr} = 357 + (2.56 \times 10^3) = \boxed{2917\ J/mol\cdot K}$

- Yes, this action is spontaneous because $\Delta S_{univ} > 0$.

$(78.3°C) = \Delta vap\ H_m\ 25°C + \int_{298K}^{351.3K} \Delta C_P dT$ - ①

$\Delta C_P = C_P(\text{prod}) - C_P(\text{reactants}) \rightarrow C_P - C_P^P = 65.6 + 2.38 \times 10^{-4}) - (112)$

$= 46.4 + 2.38 \times 10^{-4}\ T$

$$\rightarrow \int_{298K}^{351.8K} C_P dt = \int_{298K}^{351.8K}(-46.4 + 2.38\times10^{-4}\ T)\ dT$$

$$\rightarrow -46.4\,[T]_{298K}^{351.8K} + 2.38\times10^{-4}\,[T^2]_{298}^{351.8}$$

$$\rightarrow -46.4\,(351.8 - 298) + 1.19\times10^{-4}\,[(351.3)^2 - (298)^2]$$

$$\rightarrow -2475.12 + 1.19\times10^{-4}\,[123411.69 - 88804]$$

$$= (-2473.12 + 4.11813)$$

$$= -2469\ J/mol = -2.469\ KJ/mol\ [1\ KJ = 1000\ J]$$

Δ Vap Hm = (78.3°C) = Δvap Hm (25°C) + $\int_{298K}^{351.8K}$ Cp d T

42.3 KJ/mol − 2.469 KJ/mol

$\boxed{\text{Vap Hm} = (78.3°C) = 39.831 \text{ KJ/mol}}$

ΔSvap Hm (78.3°C) = $\dfrac{\Delta\text{vap Hm (78.3°C)}}{T_B \text{ (ln K)}} = \dfrac{39.831 \text{ KJ/mol}}{351.3K} = \boxed{113.38 \text{ J/mol K}}$

Graphical Problems

3.) $\Delta H = T\Delta S$

$\Delta S_{70K} - 150K = \left(\dfrac{(\Delta H)_2}{(T_2)}\right) - \left(\dfrac{(\Delta H_1)}{T_2}\right)$

$\dfrac{4450.0}{54.39} - \dfrac{6815.0}{90.2} \rightarrow$ 81.81 − 75.55 = 6.26 JK⁻¹

$\boxed{\Delta S_{70K} + 50K = 6.26 \text{ JK}^{-1}}$