Raunak Manji

Problem Set 4

Analytical Problems:

1. The reversible process for entropy transfer takes place by heat interactions

$$\left[\Delta S = \frac{dq_{VA}}{T}\right]$$

The adiabatic process defines the system is closed and no heat will enter the system $q \geq 0$

The reversible adiabatic process is $\Delta S = 0$

2 a. The values of ΔH, ΔS, ΔU is zero since it is a state function and cyclic processes.

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

b. The process $b \to c$, and $d \to a$ are adiabatic process $q = 0$

In process $a \to b$, temperature is constant, therefore $\Delta U = 0$

The work done by the system is carried out by heat supplied to the system, and is a reversible process $= w$.

$W = -nRT_h \left(\ln \frac{V_b}{V_a}\right) \mid \Delta U = 0 = q + w \mid q + w = \left(nRT_h \ln\left(\frac{V_b}{V_a}\right)\right)$

$q = nRT_h \ln\left(\frac{V_b}{V_a}\right)$

c. The total work done is negative.

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

$= -nRT_h \ln\left(\frac{V_b}{V_a}\right) = nRT \ln\left(\frac{V_a}{V_b}\right)$

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

d. Efficiency $(\eta) = \dfrac{\text{network done by the heat engine}}{\text{heat absorbed by heat engine}} = \dfrac{-w}{q}$

$= \left[\dfrac{-(T_h - T_c)\, nRT \ln(V_b/V_a)}{nRT_h \ln(V_b/V_a)}\right] = \dfrac{T_h - T_c}{T_h} = 1 - \dfrac{T_{cold}}{T_{hot}}$

3a.

$S = (P, T)$

Maxwell's Relation

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

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

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

$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right) dp$ where $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ $\partial p_0 = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

b.

$$\boxed{dS = \frac{C_P}{T} dT - \beta V dP} \qquad \boxed{\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \beta V dp}$$

Numerical Problems:

1.a. $\Delta H_{rxn} = \sum \Delta H_f^\circ \text{product} - \sum \Delta H_f^\circ \text{reactants}$

$= [-1364 - 2 + 8 - 394] - 1273]$

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

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

$= [357 \text{ J/mol k}]$

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

$- \Delta S_{univ.} = \Delta S_{rxn} + \Delta S_{surr} = 357 + (2.56 \times 10^3) = \boxed{2917 \text{ J/mol k}}$

This action is spontaneous because the value of $\Delta S_{univ} > 0$.

2.

$\Delta H_m (78.3C) = \Delta Vap\, H_m\, 25°C + \int_{298k}^{351.3k} \Delta C_p dT - 1$

$\Delta C_p = C_p(\text{product}) - C_p(\text{reactants})$

$\rightarrow C_p - C_p^{r} = (65.6 + 2.38 \times 10^{-4}) - (112)$

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

$\int_{298k}^{351.3k} C_p dT = \int_{298k}^{351.3k} (-46.4 + 2.38 \times 10^{-4} T)\, dT$

$-46.4 [T]_{298k}^{351.3k} + 2.38 \times 10^{-4} [T^2]_{298}^{351.3}$

$-46.4 (351.3 - 298) + 1.19 \times 10^{-4} [(351.3)^2 - (298)^2]$

$-2475.12 + 1.19 \times 10^{-4} [123411.69 - 88404]$

$-2473.12 + 4.11813$

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

$\Delta Vap\, H_m = (78.3°C) = \Delta Vap H_m (25°C) + \int_{298k}^{351.3k} C_p dT$

$= 42.3\ kJ/mol - 2.469\ kJ/mol$

$$\boxed{Vap\, H_m = (78.3°C) = 39.831\ kJ/mol}$$

$\Delta S\ vap\ H_m (78.3°C) = \frac{\Delta Vap\ H_m (78.3°C)}{T_B (\ln k)} = \frac{39.831\ kJ/mol}{351.3K}$

$$\boxed{= 113.38\ J/mol\,K}$$

3. ~~3a~~ Graphical Problems

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

$\Delta S_{70k - 150k} = \left(\frac{\Delta H_2}{T_2}\right) - \frac{(\Delta H_1)}{T_2}$

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

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