Homework Problem Set 4

① an ideal gas (not monoatomic) is expanded reversibly and adiabatically from $(V_i, T_i) \rightarrow (V_F, T_F)$. Prove that $\Delta S = 0$ for the expansion process.

$$\frac{T_F}{T_i} = \left(\frac{V_i}{V_f}\right)^{\gamma} \qquad C_p - C_v = nR$$

reversible process transfer entropy by heat interaction

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

because we have an adiabatic process no heat can enter the system making $\Delta S = 0$

② Given the following reversible Carnot cycle

a) what is $\Delta U, \Delta H,$ and ΔS for entire cycle? $\Delta U, \Delta H$ and $\Delta S \Rightarrow 0$

(state properties)

b) heat is only absorbed in isothermal processes

$$-q_{cycle} = w_{cycle}$$

$$w_{cycle} = -nRT \ln \frac{V_b}{V_a}$$

$$-q_{cycle} = -nRT \ln \frac{V_b}{V_a}$$

c) $T_{hot} V_b^{\gamma-1} = T_{cold} V_c^{\gamma-1}$ and $T_{cold} V_d^{\gamma-1} = T_{hot} V_a^{\gamma-1}$

isothermal compression $w = -nRT_h \ln \frac{V_d}{V_c}$ adiabatic $w = \frac{nR}{1-\gamma}[T_h - T_c]$

expansion $w = -nRT_c \ln \frac{V_b}{V_a}$ " $w = \frac{nR}{1-\gamma}[T_c - T_h]$

$\Rightarrow$

$W = -nRT_c \ln \frac{V_d}{V_c} - nRT_h \ln \frac{V_b}{V_a}$

$T_c V_d^{\gamma-1} = T_h V_a^{\gamma-1}$; $T_c V_c^{\gamma-1} = T_h V_b^{\gamma-1}$

$\left(\frac{V_a}{V_b}\right)^{\gamma-1} = \left(\frac{V_d}{V_c}\right)^{\gamma-1}$

$\frac{V_a}{V_b} = \frac{V_d}{V_c}$

$W = -nRT_c \ln \frac{V_d}{V_c} - nRT_h \ln \frac{V_b}{V_a}$

$= nR(T_c - T_h) \ln \frac{V_b}{V_a}$

Work will be negative ; $T_c < T_h$ and $V_b > V_a$

d) $\varepsilon = \frac{T_h - T_c}{T_h} \times 100$

$\varepsilon = \frac{W}{q} \Rightarrow \frac{nR(T_h - T_c)\ln \frac{V_b}{V_a}}{nRT_h \ln \frac{V_b}{V_a}}$

$= \frac{T_h - T_c}{T_h} \Rightarrow 1 - \frac{T_c}{T_h}$

and $T_c < T_h$ so $\varepsilon < 1$

③ a) $\left(\frac{\partial S}{\partial T}\right)_P$, $\left(\frac{\partial S}{\partial P}\right)_T$

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

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

$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

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

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

b) $dS = \frac{Cp}{T} dT - BK\, dP_{P_2}$

$\Delta S = \int_{Ti}^{Tf} \frac{Cp}{T} dT - \int_{P_1} BK\, dP$

numerical problems

① $C_6H_{12}O_6(s) \longrightarrow CH_3CHOHCOOH(\ell) + C_2H_5OH(\ell) + CO_2(g)$

$\Delta H°rxn = [(-1364) + (-278) + (-394)] - (-1273)$ kJ/mol

$\Delta H°rxn = -2036$ kJ/mol $+ 1273$ kJ/mol

$\Delta H°rxn = -763$ kJ/mol

$\Delta S°rxn = [(192) + (161) + (213)] - 209$ J/(mol K)

$\Delta S°rxn = 357$ J/(mol K)

$\Delta S_{surr} = -\frac{\Delta H°rxn}{298K} \Rightarrow \frac{-(-763\text{ kJ/mol})}{298K} \Rightarrow 2.56$ kJ/mol K

ΔS_{univ}

② $\Delta_{vap} Hm(78.3C)$ and $\Delta_{vap} Sm(78.3C)$

$\Delta_{vap} Hm(25.0C) = 42.3$ kJ mol^{-1}

$C_p^g = 65.6$ J mol^{-1} K^{-1} $+ 2.38 \times 10^{-4}$ T J mol^{-1} K^{-2}

$C_p^l = 112$ J mol^{-1} K^{-1}

$\Delta_{vap} Hm(78.3°C) = \Delta_{vap} Hm(25.0°C) + \int_{298K}^{351.3} \Delta Cp\, dT$

$\Delta Cp = C_p^g - C_p^\ell$

$\Delta Cp \Rightarrow (65.6\text{ J mol}^{-1}\text{ K}^{-1} + 2.38 \times 10^{-4}\text{ T J mol}^{-1}\text{ K}^{-2}) - (112\text{ J mol}^{-1}\text{ K}^{-1})$

$\Delta Cp \Rightarrow -46.4$ J mol^{-1} K^{-1} $+ 2.38 \times 10^{-4}$ T J mol^{-1} K^{-2}

46.9

$$\int_{298K}^{351.3} \Delta C_p \, dT = \int [(2.38\times10^{-4} T) - 46.4] \, dT$$

$$= \frac{2.38\times10^{-4}}{2}[T^2] - 46.4[T]$$

$$\Rightarrow 1.19\times10^{-4}[(351.3)^2 - (298)^2] - 46.4(351.3 - 298)$$

$$\Rightarrow 4.1183 - 2473.12$$

$$\int \Delta C_p dT \Rightarrow -2469 \text{ J mol}^{-1}$$

$$\Delta_{vap} H_m(351.3K) = 42.3 \text{ kJ mol}^{-1} - 2.469 \text{ kJ mol}^{-1}$$

$$\Delta_{vap} H_m(351.3K) = 39.83 \text{ kJ mol}^{-1}$$

$$\Delta_{vap} S_m(351.3K) = \frac{\Delta_{vap} H_m(351.3K)}{T}$$

$$= \frac{39.83 \text{ kJ mol}^{-1}}{351.3K}$$

$$\Rightarrow 0.113 \text{ kJ mol}^{-1} K^{-1}$$

③ $S_m(70K)$, $S_m(150K)$, ΔS

$$S_m(70K) = \int_{0}^{23.66} \frac{C_p dT}{T} + \frac{93.8}{23.66} + \int_{2366}^{4376} \frac{C_{p,m} dT}{T} + \frac{743}{43.76} + \int_{4376}^{5439} \frac{C_{p,m} dT}{T} + \frac{445}{54.39} + \int_{54.39}^{70} \frac{C_{p,m} dT}{T}$$

$$S_m(70K) = 8.182 \text{ J K}^{-1} + 3.964 \text{ J K}^{-1} + 19.61 \text{ J K}^{-1} + 16.98 \text{ J K}^{-1} + 10.13 \text{ J K}^{-1} + 8.181 \text{ J K}^{-1} + 4.76 \text{ J K}^{-1}$$

$$S_m(70K) \Rightarrow 81.81$$

$$S_m(150K) = \int_{0}^{2366} \frac{C_{p,m} dT}{T} + \frac{93.8}{23.66} + \ldots + \int_{54.39}^{90.20} \frac{C_{p,m} dT}{T} + \frac{6815}{90.20} + \int_{90.2}^{150} \frac{C_{p,m} dT}{T}$$

$$= 8.182 \text{ J K}^{-1} + 3.964 \text{ J K}^{-1} + \ldots + 8.181 \text{ J K}^{-1} + 27.06 \text{ J K}^{-1} + 75.59 \text{ J K}^{-1}$$

$$S_m(150K) \Rightarrow 75.55$$

$$\Delta S_{70 \to 150} \Rightarrow 81.81 - 75.55$$