

Homework Problem Set 4

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

$$\frac{T_f}{T_i} = \left(\frac{V_i}{V_f}\right)^\gamma$$

$$C_p - C_v = nR$$

reversible process transfer entropy by heat interaction

$$\Delta S = \frac{dq_{\text{reversible}}}{T}$$

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

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

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

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

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

$$\begin{array}{ll} \text{isothermal compression } w = -nR T_h \ln \frac{V_d}{V_c} & \text{adiabatic } w = \frac{nR}{1-\gamma} [T_h - T_c] \\ \text{expansion } w = -nR T_c \ln \frac{V_b}{V_a} & \text{" } w = \frac{nR}{1-\gamma} [T_c - T_h] \end{array}$$

\Rightarrow

$$W = -nR T_c \ln \frac{V_d}{V_c} - nR T_h \ln \frac{V_b}{V_a}$$

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

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

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

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

$$W = -nR T_c \ln \frac{V_d}{V_c} - nR T_h \ln \frac{V_b}{V_a}$$

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

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

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

$$\mathcal{E} = \frac{W}{Q} \Rightarrow \frac{nR(T_h - T_c) \ln \frac{V_b}{V_a}}{nR T_h \ln \frac{V_b}{V_a}}$$

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

$$\text{and } T_c < T_h \text{ so } \mathcal{E} < 1$$

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

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

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

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

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

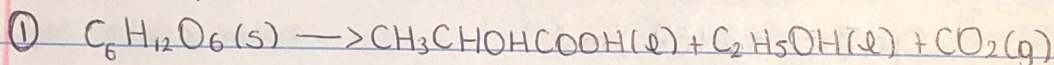
$$dS = \frac{C_P}{T} dT - \beta K dP$$

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

$$b) dS = \frac{C_p}{T} dT - Bk dP_2$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{P_1}^{P_2} Bk dP$$

numerical problems



$$\Delta H^\circ_{rxn} = [(-1364) + (-278) + (-394)] - (-1273) \text{ kJ/mol}$$

$$\Delta H^\circ_{rxn} = -2036 \text{ kJ/mol} + 1273 \text{ kJ/mol}$$

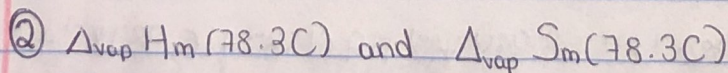
$$\Delta H^\circ_{rxn} = -763 \text{ kJ/mol}$$

$$\Delta S^\circ_{rxn} = [(192) + (161) + (213)] - 209 \text{ J/(mol K)}$$

$$\Delta S^\circ_{rxn} = 357 \text{ J/(mol K)}$$

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

$$\Delta S_{univ}$$



$$\Delta_{vap} H_m(25.0^\circ C) = 42.3 \text{ kJ/mol}^{-1}$$

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

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

$$\Delta_{vap} H_m(78.3^\circ C) = \Delta_{vap} H_m(25.0^\circ C) + \int_{298K}^{351.3} \Delta C_p dT$$

$$\Delta C_p = C_p^g - C_p^l$$

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

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

46.9

$$\begin{aligned}
 \int_{298}^{351.3} \Delta C_p dT &= \int_{298}^{351.3} [(2.38 \times 10^{-4} T) - 46.4] dT \\
 &= \frac{2.38 \times 10^{-4}}{2} [T^2] - 46.4 [T] \\
 &\Rightarrow 1.19 \times 10^{-4} [(351.3)^2 - (298)^2] - 46.4 (351.3 - 298) \\
 &\Rightarrow 4.1183 - 2473.12
 \end{aligned}$$

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

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

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

$$\begin{aligned}
 \Delta_{\text{vap}} S_m(351.3 \text{ K}) &= \frac{\Delta_{\text{vap}} H_m(351.3 \text{ K})}{T} \\
 &= \frac{39.83 \text{ kJ mol}^{-1}}{351.3 \text{ K}} \\
 &\Rightarrow 0.113 \text{ kJ mol}^{-1} \text{ K}^{-1}
 \end{aligned}$$

③ $S_m(70 \text{ K})$, $S_m(150 \text{ K})$, ΔS

$$\begin{aligned}
 S_m(70 \text{ K}) &= \int_{43.76}^{23.66} \frac{C_p dT}{T} + \frac{93.8}{23.66} + \int_{23.66}^{70} \frac{C_p dT}{T} + \frac{743}{43.76} \\
 &+ \int_{43.76}^{54.39} \frac{C_p dT}{T} + \frac{445}{54.39} + \int_{54.39}^{70} \frac{C_p dT}{T}
 \end{aligned}$$

$$\begin{aligned}
 S_m(70 \text{ K}) &= 8.182 \text{ J K}^{-1} + 3.964 \text{ J K}^{-1} + 19.61 \text{ J K}^{-1} + 16.98 \text{ J K}^{-1} + 10.13 \text{ J K}^{-1} \\
 &+ 8.181 \text{ J K}^{-1} + 14.76 \text{ J K}^{-1}
 \end{aligned}$$

$$S_m(70 \text{ K}) \Rightarrow 81.81$$

$$\begin{aligned}
 S_m(150 \text{ K}) &= \int_0^{23.66} \frac{C_p dT}{T} + \frac{93.8}{23.66} + \dots + \int_{54.39}^{90.20} \frac{C_p dT}{T} + \frac{6813}{90.20} + \int_{90.2}^{150} \frac{C_p dT}{T} \\
 &= 8.182 \text{ J K}^{-1} + 3.964 \text{ J K}^{-1} + \dots + 8.181 \text{ J K}^{-1} + \\
 &27.06 \text{ J K}^{-1} + 75.59 \text{ J K}^{-1}
 \end{aligned}$$

$$S_m(150 \text{ K}) \Rightarrow 75.55$$

$$\Delta S_{10 \rightarrow 150} \Rightarrow 81.81 - 75.55$$