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Problem Set 4

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Analytical Problems:

1. In a reversible process, the entropy transfer takes place through heat interactions

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

In an adiabatic process, the system is closed meaning no heat enters or leaves the system

$$q = 0$$

For a reversible adiabatic process $\Delta S = 0$

2. a) Enthalpy (H), internal energy (U), and entropy (S) are state functions. For a cyclic process, the initial and final states are the same. This means that the change in state for a cyclic process is zero so $\Delta H = 0$, $\Delta U = 0$, and $\Delta S = 0$

- b) From step $a \rightarrow b$ T is constant so $\Delta U = 0$
From step $b \rightarrow c$ and $d \rightarrow a$, the process is adiabatic so $q = 0$

The work done by the system is carried out from the heat supplied to the system.

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

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

Heat is absorbed from step $a \rightarrow b$.

c) $w_{total} = w_{ab} + w_{cd} + w_{da} + w_{bc}$

$$w_{total} = -nRT_h \ln\left(\frac{V_b}{V_a}\right) - nRT_c \ln\left(\frac{V_a}{V_b}\right)$$

$$w_{total} = -(T_h - T_c) nR \ln\left(\frac{V_b}{V_a}\right)$$

The total work is negative.

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d) efficiency = $\frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}}$

$$\varepsilon = \frac{-w}{q} = - \frac{[-(T_h - T_c) nRT \ln(V_b/V_a)]}{nRT_h \ln(V_b/V_a)}$$

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

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

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

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

$$\text{Maxwell's Relation: } \left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P = -V\beta$$

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

$$b) \boxed{dS = \frac{C_P}{T} dT - V\beta dP}$$

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

Numerical Problems:

$$\begin{aligned} 1. \Delta H^\circ_{\text{rxn}} &= \sum \Delta H^\circ_{f, \text{prod}} - \sum \Delta H^\circ_{f, \text{react}} \\ &= [(-1364 - 278 - 394) - (-1273)] \text{ kJ/mol} \\ &= -763 \text{ kJ/mol} \end{aligned}$$

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

$$\begin{aligned} \Delta S_{\text{rxn}} &= \sum S^\circ_{\text{prod}} - \sum S^\circ_{\text{react}} \\ &= [(192 + 161 + 213) - (209)] \text{ J/mol}\cdot\text{K} \\ &= 357 \text{ J/mol}\cdot\text{K} \end{aligned}$$

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$$\Delta S_{\text{rxn}} = 357 \text{ J/mol}\cdot\text{K}$$

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

$$\Delta S_{\text{surr}} = 2.56 \times 10^3 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{rxn}} + \Delta S_{\text{surr}} = 357 \text{ J/mol}\cdot\text{K} + 2.56 \times 10^3 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_{\text{univ}} = 2917 \text{ J/mol}\cdot\text{K}$$

This reaction is spontaneous because $\Delta S_{\text{univ}} > 0$.

$$2. \Delta H_m(78.3^\circ\text{C}) = \Delta_{\text{vap}} H_m(25^\circ\text{C}) + \int_{298 \text{ K}}^{351.3 \text{ K}} \Delta C_p dT - 1$$

$$\begin{aligned} \Delta C_p &= C_{p,\text{prod}} - C_{p,\text{react}} = C_p^{\text{prod}} - C_p^{\text{react}} \\ &= (65.6 \text{ J/mol}\cdot\text{K} + 2.38 \times 10^{-4} T \cdot \text{J/mol}\cdot\text{K}) - 112 \text{ J/mol}\cdot\text{K} \\ &= -46.4 \text{ J/mol}\cdot\text{K} + 2.38 \times 10^{-4} T \cdot \text{J/mol}\cdot\text{K} \end{aligned}$$

$$\begin{aligned} \int_{298 \text{ K}}^{351.3 \text{ K}} C_p dT &= \int_{298 \text{ K}}^{351.3 \text{ K}} (-46.4 \text{ J/mol}\cdot\text{K} + 2.38 \times 10^{-4} T \cdot \text{J/mol}\cdot\text{K}) dT \\ &= -46.4 [T] \Big|_{298 \text{ K}}^{351.3 \text{ K}} + \frac{2.38 \times 10^{-4}}{2} [T^2] \Big|_{298 \text{ K}}^{351.3 \text{ K}} \\ &= -46.4 (351.3 - 298) + 1.19 \times 10^{-4} (351.3^2 - 298^2) \\ &= -2473.12 \text{ J/mol} + 4.1183 \text{ J/mol} \\ &= -2469 \text{ J/mol} = -2.469 \text{ kJ/mol} \end{aligned}$$

$$\Delta H_m = -2.469 \text{ kJ/mol}$$

$$\begin{aligned} \Delta_{\text{vap}} H_m(78.3^\circ\text{C}) &= \Delta_{\text{vap}} H_m(25^\circ\text{C}) + \int_{298 \text{ K}}^{351.3 \text{ K}} C_p dT \\ &= 42.3 \text{ kJ/mol} - 2.469 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\Delta_{\text{vap}} H_m = 39.831 \text{ kJ/mol}$$

$$\Delta_{\text{vap}} S_m(78.3^\circ\text{C}) = \frac{\Delta_{\text{vap}} H_m(78.3^\circ\text{C})}{T_B \ln(K)} = \frac{39.831 \text{ kJ/mol}}{351.3 \text{ K}}$$

$$\Delta_{\text{vap}} S_m = 113.38 \text{ J/mol}\cdot\text{K}$$

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Graphical Problems

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

$$\Delta S_{70K \rightarrow 150K} = \frac{(\Delta H_2)}{T_2} - \frac{(\Delta H_1)}{T_1}$$

$$\frac{4450.0}{54.39} - \frac{6815.0}{90.20} = 6.26 \text{ J/K}$$

$$\Delta S_{70K \rightarrow 150K} = 6.26 \text{ J/K}$$

The process is spontaneous because $\Delta S > 0$.