Analytical Problems

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1) $dS = \frac{dq_{rev}}{T}$ $\quad q = 0$ for adiabatic processes

$$\therefore dS = \frac{0}{T} = 0$$

$$\int_i^f dS = \boxed{\Delta S = 0}$$

2) a) $\Delta U = \Delta H = \Delta S = 0$ (state functions)

b) $\underbrace{q_{ab}}_{\Delta T = 0 \rightarrow \Delta U = 0} = -w_{ab} = \boxed{nRT_H \ln \frac{V_b}{V_a}}$, from A to B.

c) $w_T = w_{ab} + w_{bc} + w_{cd} + w_{da} = -nRT_H \ln\frac{V_b}{V_a} + nC_{v,m}(T_c - T_H) - nRT_c \ln \frac{V_d}{V_c} + nC_{v,m}(T_H - T_c)$

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

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

$$\ln \frac{V_d^{\gamma-1}}{V_c^{\gamma-1}} = \ln \frac{\frac{T_H}{T_c} V_a^{\gamma-1}}{\frac{T_H}{T_c} V_b^{\gamma-1}}$$

$$\cancel{(\gamma-1)} \ln \frac{V_d}{V_c} = \cancel{(\gamma-1)} \ln \frac{V_a}{V_b}$$

$= -nRT_H \ln \frac{V_b}{V_a} + nC_{v,m}(T_c - T_H) - nRT_c \ln \frac{V_a}{V_b} + nC_{v,m}(T_H - T_c)$

$= -nRT_H \ln \frac{V_b}{V_a} \cancel{+ nC_{v,m}(T_c - T_H)} + nRT_c \ln \frac{V_b}{V_a} \cancel{- nC_{v,m}(T_c - T_H)}$

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

d) $\varepsilon = \frac{w_{cycle}}{q_{ab}} = \frac{\cancel{n}R(T_H - T_c)\cancel{\ln \frac{V_b}{V_a}}}{\cancel{n}RT_H \cancel{\ln\frac{V_b}{V_a}}} = \frac{T_H - T_c}{T_H} = \boxed{1 - \frac{T_c}{T_H}}$ ← positive

$$\boxed{\therefore \varepsilon \leq 1}$$

3) A) $dU = đq_p + đw = TdS - PdV$

assume constant pressure assume reversibility

$H = U + PV$

$dH = dU + PdV + VdP = \underline{TdS + VdP}$

$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

$$TdS = dH - VdP$$

$$dS = \frac{1}{T}dH - \frac{V}{T}dP = \underbrace{\left(\frac{\partial S}{\partial T}\right)_P}dT + \underbrace{\left(\frac{\partial S}{\partial P}\right)_T}dP$$

$$= \frac{1}{T}\left[C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP\right] - \frac{V}{T}dP = \frac{1}{T}\left[C_p dT + \left(\left(\frac{\partial H}{\partial P}\right)_T - V\right)dP\right]$$

$$= \frac{C_p}{T}dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

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

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial T}\left(\frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\right)\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\left(\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right)_T = \left(\frac{\partial}{\partial P}\left(\frac{1}{T}C_p\right)\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T$$

$$\cancel{\frac{1}{T}}\left[\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\right] = \cancel{\frac{1}{T}}\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T$$

$$\cancel{\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T} - \left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{T}\left(\frac{\partial H}{\partial P}\right)_T + \frac{V}{T} = \cancel{\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T}$$

$$\frac{1}{T}\left(\frac{\partial H}{\partial P}\right)_T - \frac{V}{T} = -\left(\frac{\partial V}{\partial T}\right)_P$$

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

$$= \frac{1}{\cancel{T}}\left[-\cancel{T}\left(\frac{\partial V}{\partial T}\right)_P\right] = -\left(\frac{\partial V}{\partial T}\right)_P$$

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

B) $\boxed{dS = \frac{C_p}{T}dT - V\beta\, dP}$

Numerical Problems

1) $\Delta H^\circ_{rxn} = (-1364 \text{ kJ/mol} - 278 \text{ kJ/mol} - 394 \text{ kJ/mol}) - (-1273 \text{ kJ/mol}) = \boxed{-763 \text{ kJ/mol}}$

$\Delta S^\circ_{rxn} = \left(192 \frac{J}{mol \cdot K} + 161 \frac{J}{mol \cdot K} + 213 \frac{J}{mol \cdot K}\right) - \left(209 \frac{J}{mol \cdot K}\right) = \boxed{+357 \frac{J}{mol \cdot K}}$

$$\Delta S^\circ_{surr} = \frac{-\Delta H^\circ_{rxn}}{T_{surr}} = \frac{+763 \text{ kJ/mol}}{298 \text{ K}} = \boxed{+2,560 \frac{J}{mol \cdot K}}$$

$$\Delta S^\circ_{univ} = \Delta S^\circ_{rxn} + \Delta S^\circ_{surr} = 357 \frac{J}{mol \cdot K} + 2,560 \frac{J}{mol \cdot K} = \boxed{+2,900 \frac{J}{mol \cdot K}}$$

This reaction is spontaneous under standard state conditions because in these conditions, $\Delta S_{univ} > 0$, and $\Delta S_{univ} \geq 0$ is a requirement for spontaneous processes.

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2) $dH = C_p dT \longrightarrow \Delta H_{m,vap}(78.3°C) = \Delta H_{m,vap}(25.0°C) + \int_{25.0°C}^{78.3°C} \Delta C_p \, dT$

$$\Delta C_p = C_p^g - C_p^l = 65.6 \frac{J}{mol \cdot K} - 112 \frac{J}{mol \cdot K} + 2.38 \times 10^{-4} T \frac{J}{mol \cdot K^2} = -46.4 \frac{J}{mol \cdot K} + 2.38 \times 10^{-4} T \frac{J}{mol \cdot K^2}$$

$$\Delta H_{m,vap}(351.45 K) = \Delta H_{m,vap}(298.15 K) + \int_{298.15 K}^{351.45 K} \left(-46.4 \frac{J}{mol \cdot K} + 2.38 \times 10^{-4} T \frac{J}{mol \cdot K^2}\right) dT$$

$$= 42.3 \frac{kJ}{mol} + \left[-46.4 T \frac{J}{mol \cdot K} + 1.19 \times 10^{-4} T^2 \frac{J}{mol \cdot K^2}\right]_{298.15 K}^{351.45 K}$$

$$= 42.3 \frac{kJ}{mol} + \left[\left(-16.293 \frac{kJ}{mol}\right) - \left(-13.824 \frac{kJ}{mol}\right)\right] = \boxed{39.8 \frac{kJ}{mol} = \Delta_{vap} H_m (78.3°C)}$$

$$\Delta_{vap} S_m (78.3°C) = \frac{\Delta_{vap} H_m (78.3°C)}{351.45 \text{ K}} = \frac{39.8 \frac{kJ}{mol}}{351.45 \text{ K}}$$

$$\boxed{\Delta_{vap} S_m (78.3°C) = 113 \frac{J}{mol \cdot K}}$$

<u>Graphical Problem</u>

$$3)\ S_m(T) = \cancel{S_m(0K)}^{\,0} + \sum_{\text{phases}} \int_0^{T_f} \frac{C_{p,m}^{\text{phase}}}{T}\,dT + \sum_{\text{changes}} \frac{\Delta H_{\text{change}}}{T_{\text{change}}}$$

$$S_m(70K) = \int_{0K}^{23.66K} \frac{C_{p,m}^{\text{solid III}}}{T}\,dT + \frac{93.8\ \text{J/mol}}{23.66\ \text{K}} + \int_{23.66K}^{43.76K} \frac{C_{p,m}^{\text{solid II}}}{T}\,dT + \frac{743\ \text{J/mol}}{43.76\ \text{K}} + \int_{43.76K}^{54.39K} \frac{C_{p,m}^{\text{solid I}}}{T}\,dT + \frac{4450.0\ \text{J/mol}}{54.39\ \text{K}} + \int_{54.39K}^{70K} \frac{C_{p,m}^{\text{liquid}}}{T}\,dT$$

$$\approx \frac{1}{2}(23.66\,\cancel{K})\left(0.90\,\frac{\text{J}}{\text{mol K}^{\cancel{2}}}\right) + 3.96\,\frac{\text{J}}{\text{mol K}} + \frac{1}{2}\left((0.94+1.05)\frac{\text{J}}{\text{mol K}^{\cancel{2}}}\right)(20.1\,\cancel{K}) + 16.98\,\frac{\text{J}}{\text{mol K}} + \frac{1}{2}\left((1.05+0.85)\frac{\text{J}}{\text{mol K}^{\cancel{2}}}\right)(10.63\,\cancel{K}) + 81.82\,\frac{\text{J}}{\text{mol K}}$$

$$+ \frac{1}{2}\left((0.97+0.80)\frac{\text{J}}{\text{mol K}^{\cancel{2}}}\right)(15.61\,\cancel{K}) \boxed{= 157\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}$$

$$S_m(150K) \approx \underbrace{S_m(70K) - \int_{59.39K}^{70K} \frac{C_{p,m}^{\text{liquid}}}{T}\,dT}_{} + \int_{59.39K}^{90.20K} \frac{C_{p,m}^{\text{liquid}}}{T}\,dT + \frac{6815.0\ \text{J/mol}}{90.20\ \text{K}} + \int_{90.20K}^{150K} \frac{C_{p,m}^{\text{gas}}}{T}\,dT$$

$$\approx 143.1\,\text{J/mol K} + \frac{1}{2}\left((0.97+0.60)\,\text{J/mol K}^{\cancel{2}}\right)(35.81\,\cancel{K}) + 75.55\,\text{J/mol K} + \frac{1}{2}\left((0.32+0.20)\frac{\text{J}}{\text{mol K}^{\cancel{2}}}\right)(59.8\,\cancel{K})$$

$$\boxed{= 262\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}$$

$$\boxed{\Delta S_{70K\to150K} \approx 105\,\frac{\text{J}}{\text{mol}\cdot\text{K}}}$$