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$\boxed{\text{Problem set \# 4}}$

Analytical Problems

1)

$$\Delta S = nR\ln\frac{V_f}{V_i} + nC_{v,m}\ln\frac{T_f}{T_i}$$

- Reversibly expansion $\rightarrow V_f = V_i \rightarrow \ln\frac{V_f}{V_i} = \ln(1) = 0$
- Adiabatically $\rightarrow$ const. $T \rightarrow \ln\frac{T_f}{T_i} = \ln(1) = 0$

$\Rightarrow \Delta S = 0$

2)

a) $\Delta U = 0$

$\Delta H = 0$

$\Delta S = 0$

b) $q_{cycle} = \underset{\text{(absorbed)}}{q_{ab}} + \cancel{q_{bc}}^{\,0} + \underset{\text{(released)}}{q_{cd}} + \cancel{q_{da}}^{\,0}$

$q_{absorbed} = q_{ab} = -w_{ab} = nRT_{hot}\ln\frac{V_b}{V_a}$

Step $a \rightarrow b$

c) $w_{ab} = -nRT_{hot}\ln\frac{V_b}{V_a}$

$w_{bc} = nC_{v,m}(T_{cold} - T_{hot})$

$w_{cd} = -nRT_{cold}\ln\frac{V_d}{V_c} = -nRT_{cold}\ln\frac{V_a}{V_b}$

(because $T_{hot}V_b^{\gamma-1} = T_{cold}V_c^{\gamma-1}$, $T_{hot}V_a^{\gamma-1} = T_{cold}V_d^{\gamma-1}$)

$w_{da} = nC_{v,m}(T_{hot} - T_{cold})$

$\rightarrow w_{total} = -nR\underbrace{(T_{hot} - T_{cold})}_{>0}\underbrace{\ln\frac{V_b}{V_a}}_{>0} < 0$

Total work is negative

d)

$$\varepsilon = \frac{|w_{total}|}{q_{ab}} = \frac{\cancel{nR}(T_{hot} - T_{cold}) \cancel{\ln \frac{V_b}{V_a}}}{\cancel{nR} T_{hot} \cancel{\ln \frac{V_b}{V_a}}} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

$$= 1 - \underbrace{\frac{T_{cold}}{T_{hot}}}_{<1} > 0$$

3)

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

$$dU = TdS - \cancel{PdV} = dH - \cancel{PdV} - VdP$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

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

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

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

B)

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

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

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

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

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$$-\frac{1}{T}\left(\frac{\partial V}{\partial T}\right) - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] = 0$$

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

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

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

Numerical Problems

1)

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

$$= -763\ \text{kJ/mol}$$

$$\Delta S^\circ_R = 192\ \text{J/molK} + 161\ \text{J/molK} + 213\ \text{J/molK} - 209\ \text{J/molK}$$

$$= 357\ \text{J/molK}$$

$$\Delta S^\circ_{surr} = -\frac{\Delta H^\circ_R}{T_{surr}} = -\frac{(-763\times10^3\ \text{J/mol})}{298\ \text{K}} = 2560.4\ \text{J/molK}$$

$$\Delta S^\circ_{univ} = 357\ \text{J/molK} + 2560.4\ \text{J/molK}$$

$$= 2917.4\ \text{J/molK}$$

2)

$$\Delta H_{m,vap}(78.3°C) = \Delta H_{m,vap}(25.0°C) + \int_{298K}^{351.3K} (C_P^g - C_P^l)\,dT$$

$$= 42.3\ \text{kJ/mol} + \int_{298K}^{351.3K} (65.6\ \text{J mol}^{-1}\text{K}^{-1} + 2.38\times10^{-4}\,T\ \text{J mol}^{-1}\text{K}^{-2} - 112\ \text{J mol}^{-1}\text{K}^{-1})\,dT$$

$$= 42.3\times10^3\ \text{J/mol} - 46.4\,T\Big|_{298K}^{351.3K}\ \text{J molK}^{-1} + 2.38\times10^{-4}\,\frac{T^2}{2}\Big|_{298K}^{351.3K}\ \text{J mol}^{-1}\text{K}^{-2}$$

$$= 39830.99832\ \text{J}$$

$$\Delta S_{m,vap}(78.3°C) = \frac{39831.0\ \text{J/mol}}{351.3\ \text{K}} = 113.4\ \text{J/molK}$$

Graphing Problems

1)

- $0K < T < 12.97K$

① $\frac{C_{p,m}(T)}{Jmol^{-1}K^{-1}} = 2.11 \times 10^{-8} \frac{T^3}{K^3}$

- $12.97K < T < 23.66K$

② $\frac{C_{p,m}(T)}{Jmol^{-1}K^{-1}} = -5.666 + 0.6927\frac{T}{K} - 5.191 \times 10^{-3}\frac{T^2}{K^2} + 9.943 \times 10^{-4}\frac{T^3}{K^3}$

- $23.66K < T < 43.76K$

③ $\frac{C_{p,m}(T)}{Jmol^{-1}K^{-1}} = 31.70 - 2.038\frac{T}{K} + 0.08384\frac{T^2}{K^2} - 6.685 \times 10^{-4}\frac{T^3}{K^3}$

- $43.76K < T < 54.39K$

④ $\frac{C_{p,m}(T)}{Jmol^{-1}K^{-1}} = 46.094$

- $54.39K < T < 90.20K$

⑤ $\frac{C_{p,m}(T)}{Jmol^{-1}K^{-1}} = 81.268 - 1.1467\frac{T}{K} + 0.01516\frac{T^2}{K^2} - 6.407 \times 10^{-5}\frac{T^3}{K^3}$

- $90.20K < T < 298.15K$

⑥ $\frac{C_{p,m}(T)}{Jmol^{-1}K^{-1}} = 32.71 - 0.04093\frac{T}{K} + 1.545 \times 10^{-4}\frac{T^2}{K^2} - 1.819 \times 10^{-7}\frac{T^3}{K^3}$

- $$S^\circ_m(70K) = \int_{0K}^{12.97K} \frac{C_{p,m}①}{T}dT + \int_{12.97K}^{23.66K} \frac{C_{p,m}②}{T}dT + \frac{93.80J}{23.66K} + \int_{23.66K}^{43.76K} \frac{C_{p,m}③}{T}dT + \frac{743J}{43.76K} + \int_{43.76K}^{54.39K} \frac{C_{p,m}④}{T}dT + \frac{445.0J}{54.39K} + \int_{54.39K}^{70K} \frac{C_{p,m}⑤}{T}dT$$

$$= 1.53JK^{-1} + 6.65JK^{-1} + 3.96JK^{-1} + 19.62JK^{-1} + 16.98JK^{-1} + 10.02JK^{-1} + 8.18JK^{-1} + 13.43JK^{-1}$$

$$= 80.37JK^{-1}mol^{-1}$$

- $$S^\circ_m(150K) = 1.53JK^{-1} + 6.65JK^{-1} + 3.96JK^{-1} + 19.62JK^{-1} + 16.98JK^{-1} + 10.02JK^{-1} + 8.18JK^{-1} + \int_{54.39K}^{90.20K} \frac{C_{p,m}⑤}{T}dT + \frac{6815J}{90.20K} + \int_{90.20K}^{150K} \frac{C_{p,m}⑥}{T}dT$$

$$= 66.94JK^{-1} + 27.06JK^{-1} + 75.55JK^{-1} + 15.14JK^{-1}$$

$S^{\circ}_{m}(150K) = 184.69\ JK^{-1} mol$

$$\Delta S^{\circ}_{m}(70K \rightarrow 150K) = 184.69\ JK^{-1}mol^{-1} - 80.37\ JK^{-1}mol^{-1}$$
$$= 104.32\ JK^{-1}mol^{-1}$$