**\* Analytical Problems**

Q1  $\Delta S = n \times C_v \times \ln\left(\dfrac{T_f}{T_i}\right) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$   (1)

Adiabatic process in an ideal gas

$$\dfrac{T_f}{T_i} = \left(\dfrac{V_i}{V_f}\right)^{\frac{c_p}{c_v}-1}$$

$$\Rightarrow \ln\dfrac{T_f}{T_i} = \left(\dfrac{C_p}{C_v}-1\right) \times \ln\left(\dfrac{V_i}{V_f}\right)$$   (2)

(1) & (2) $\Rightarrow \Delta S = n \times C_v \times \left(\dfrac{C_p}{C_v}-1\right) \times \ln\left(\dfrac{V_i}{V_f}\right) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$

$$\Rightarrow \Delta S = n \times C_p \times \ln\left(\dfrac{V_i}{V_f}\right) - n \times C_v \times \ln\left(\dfrac{V_i}{V_f}\right) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$$

$$= n \times \ln\left(\dfrac{V_i}{V_f}\right) \times (C_p - C_v) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$$

$$= n \times \ln\dfrac{1}{\left(\dfrac{V_f}{V_i}\right)} \times (C_p - C_v) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$$

$$= n \times \ln 1 \times (C_p - C_v) - n \times \ln\left(\dfrac{V_f}{V_i}\right) \times (C_p - C_v) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$$

since $\ln(1) = 0$ & $C_p - C_v = 0$ " for all gases)

$$\Rightarrow \Delta S = 0 - n \times R \times \ln\left(\dfrac{V_f}{V_i}\right) + n \times R \times \ln\left(\dfrac{V_f}{V_i}\right)$$

$$\Rightarrow \Delta S = 0$$

Q2) a) $\Delta U = 0$, $\Delta H = 0$, $\Delta S = 0$ (a cyclic process)

b) heat is absorbed in the isothermal process

$$\Delta U = q + w \quad \text{(isothermal expansion)}$$

since $\Delta U = 0$ (ideal gas)

$$\Rightarrow q = -w$$

$$\Rightarrow q = nRT_{hot} \ln\left(\frac{V_b}{V_a}\right)$$

for isothermal compression, heat is released

c) work done in isothermal expansion

$$w_I = -nRT_{hot} \ln\left(\frac{V_b}{V_a}\right)$$

work done in isothermal compression:

$$w_{II} = -nRT_{cold} \ln\left(\frac{V_b}{V_a}\right)$$

work done in adiabatic compression $= \dfrac{nR}{1-\gamma}(T_{hot} - T_{cold})$

work done in adiabatic expansion $= \dfrac{nR}{1-\gamma}(T_{cold} - T_{hot})$

Total work done $w = -nRT_{hot} \ln\left(\frac{V_b}{V_a}\right) - nRT_{cold} \ln\left(\frac{V_d}{V_c}\right)$

Now, $T_{hot} V_a^{\gamma-1} = T_{cold} V_d^{\gamma-1}$

$$T_{hot} V_b^{\gamma-1} = T_{cold} V_e^{\gamma-1}$$

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

so $\quad w = -nRT_{hot} \ln\left(\dfrac{V_b}{V_a}\right) - nRT_{cold} \ln\left(\dfrac{V_a}{V_b}\right)$

$\qquad = -nRT_{hot} \ln\left(\dfrac{V_b}{V_a}\right) + nRT_{cold} \ln\left(\dfrac{V_b}{V_a}\right)$

$\qquad = nR(T_{cold} - T_{hot}) \ln\left(\dfrac{V_b}{V_a}\right)$

$\qquad$ since $T_{cold} < T_{hot}$ & $V_b > V_a$

$\Rightarrow$ $w$ is negative

$\Rightarrow$ $w$ done by the system

d) efficiency, $\varepsilon = \dfrac{|w|}{\text{heat absorbed}}$

$\qquad = \dfrac{nR(T_{hot} - T_{cold}) \ln\left(\dfrac{V_b}{V_a}\right)}{nRT_{hot} \ln\left(\dfrac{V_b}{V_a}\right)}$

$\qquad = \dfrac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \dfrac{T_{cold}}{T_{hot}}$

$\qquad$ since $T_{hot} > T_{cold}$ $\Rightarrow$ $\varepsilon < 1$

Q3)

a) $\quad dS = \left(\dfrac{\partial S}{\partial P}\right)_T dP + \left(\dfrac{\partial S}{\partial T}\right)_P dT \qquad (1)$

$\qquad$ since: $\left(\dfrac{\partial S}{\partial P}\right)_T = \left(\dfrac{\partial V}{\partial T}\right)_P = \beta V$

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

$(1) \Rightarrow dS = \dfrac{C_P}{T} dT - \left(\dfrac{\partial V}{\partial T}\right)_P dP \qquad (2)$

b) since $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

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

(a) $\Rightarrow$ $dS = \frac{C_p}{T} dT - \beta V dP$

$$\Delta S = \int_{T_i}^{T_s} \frac{C_p}{T} dT - \int_{P_i}^{P_s} \beta V dP$$

* Numerical Problems

Q1)

$\Delta H^\circ_{rxn} = \Delta H^\circ_f [CH_3 CHOH COOH] + \Delta H^\circ_f [C_2H_5OH] + \Delta H^\circ_f [CO_2] - \Delta H^\circ_f [C_6H_{12}O_6]$

$= -1364 + 278 - 394 + 1273 = -763 \, kJ/mol$

$\Delta S^\circ_{rxn} = S^\circ(\text{lactic acid}) + S^\circ(\text{ethanol}) + S^\circ(CO_2) - S^\circ(\text{glucose})$

$= 192 + 161 + 213 - 209 = 357 \, J/(mol \, K)$

$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T \cdot S^\circ_{rxn}$

$= -763 \times 10^3 \, J/mol - 298.15 K \times 357 \, J/(mol \, K)$

$= -86.94 \, kJ/mol \quad < 0$

$\rightarrow$ The reaction is spontaneous

$\Delta S_{surr} = \frac{-\Delta H^\circ_{rxn}}{T} = \frac{-763 \times 10^3 \, J/mol}{298.15 K}$

$= 2560.4 \, J/(mol \, K)$

$\Delta S_{univ} = \Delta S^\circ_{rxn} + \Delta S^\circ_{surr}$

$= 357 + 2560.4 = 2917.4 \, J/(mol \, K)$

Q2) $T_1 = 300K$      $T_2 = 351.3K$

$dH = C_p \, dT$

$$\Rightarrow \int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p \, dT = \int_{300K}^{351.3K} 65.6 \, J/(mol \, K) + 2.38 \times 10^{-4} \, TJ/(mol \, dT$$

$H_2 - H_1 = 65.6 (351.3 - 300)K + 2.84 \times 10^{-4} \left[ T^2 \right]_{300}^{351.3}$

$J/(mol \, K)$

$H_2 - 42.3 \, kJ/mol = 65.6 \sqrt{} \times 51.3K + 2.38 \times 10^{-4} \, J/(mol \, K^2) \times 96645 \, K$

$= 3.36 \, kJ/mol + 23 J/mol$

$= 3.383 \, kJ/mol$

$\Rightarrow H_2 = 45 \, kJ/mol$

     $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T_{boiling}} \rightarrow = 42.3 \, kJ/mol$

                $= 357.3K$

$$\Rightarrow \Delta S_{vap} = 0.1204 \, kJ/(mol \, k)$$
$$= 120.4 \, J/(mol \, K)$$

* Graphical problem

Q3)

$$\Delta S_{70K \rightarrow 150K} = \left( \frac{\Delta H_2}{T_2} \right) - \left( \frac{\Delta H_1}{T_1} \right) = \frac{4450}{54.39} - \frac{6815.0}{90.2}$$

                                      $= 6.26 \, J/(mol \, K)$

$S_m (70K) = \dfrac{\Delta H}{T} = \dfrac{4450}{54.39} = 81.82 \, J/(mol \, K)$

$S_m (150K) = \dfrac{6815}{90.2} = 75.55 \, J/(mol \, K)$