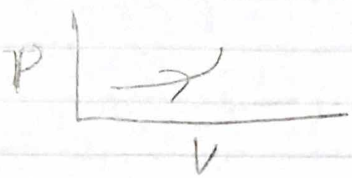
George Paxos   Problem Set 4

Analytical Problems:

reversible, adiabatic process, not monoatomic Ideal gas

1. Prove $\Delta S = 0$ for the expansion process



$$\oint dS = \oint \frac{\delta q_{rev}}{T}$$

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

$$\Delta S = 0$$

2a ΔU, ΔH, and ΔS are all equal to zero

2b q = "+" for $a \to b$ $q_{cycle} = -w_{cycle}$
q = "−" for $c \to d$

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

$\Delta U_{cycle} = 0$

$w + q = u$

$-w = q$

$$\frac{V_b}{V_A} = \frac{V_c}{V_D} \qquad \frac{V_D}{V_A}$$

$$w_{cycle} = \left(-nRT_{hot} \ln \frac{V_b}{V_a}\right) + \left(nC_{v,m}(T_{cold} - T_{hot})\right) + \left(-nRT_{cold} \ln \frac{V_a}{V_b}\right) + \left(nC_{v,m}(T_{hot} - T_{cold})\right)$$

total work is "−"

d

$$\text{Efficercy} = \frac{w}{q_{ab}} = \frac{q_{ab} + q_{cd}}{q_{ab}} = 1 + \frac{q_{cd}}{q_{ab}}$$

Efficercy always less than 1

3a+b

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

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

$\frac{dS}{1} = \frac{T}{dH}$

$dS = \frac{dH}{T}$

$dS = \frac{C_P dT}{T}$

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

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

part a

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

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

part B → $$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} - \beta V \int_{P_i}^{P_f} dP$$

Numerical Problems:

1. $\Delta H^o_{rxn} = [(-1364 \frac{kJ}{mol}) + (-278 \frac{kJ}{mol}) + (-394 \frac{kJ}{mol})] - [-1273 \frac{kJ}{mol}]$
$= -763 \frac{kJ}{mol}$

$\Delta S^o_{rxn} = [(192 \frac{J}{molK}) + (161 \frac{J}{molK}) + (213 \frac{J}{molK})] - [209 \frac{J}{molK}]$
$= 357 \ J mol^{-1} K^{-1}$

$\Delta S^o_{rxn} = \Delta S_{sys}$

$$\Delta S_{rxn} - \frac{\Delta H_{rxn}}{T_{surr}} = \Delta S_{univ}$$

Assume $T_{surr} \approx T_{sys}$

$$.357 \frac{kJ}{molK} - \frac{-763 \ kJ mol^{-1}}{273 K} = 3.152 \ kJ/molK$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

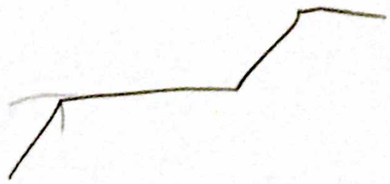
$$3152 \ J/molK = 357 \frac{J}{molK} + \Delta S_{surr}$$

$$\Delta S_{surr} = 2795 \ J mol^{-1} K^{-1}$$

Spontaneous because

$[\Delta G = \underbrace{\Delta H}_{“-”} - \underbrace{T\Delta S}_{“+”}]$ is true

$\Delta G = -$



$T = 78.3°C$

(2.) $\Delta H_{vap,m} = ?$

$\Delta S_{vap,m} = ?$

$$\Delta H_{vap,m}(351.3K) = \Delta H_{vap,m}(298K) + \int_{298K}^{351.3K} \Delta C_p \, dT$$

$$= 42.3\ kJ\,mol^{-1} +$$

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

$$\int_{298K}^{351.3K} \left[(65.6\ J\,mol^{-1}K^{-1} + 2.38E\text{-}4\,T\ J\,mol^{-1}K^{-2}) - 112\ J\,mol^{-1}K^{-1} \right] dT$$

$$\left[(65.6\ J\,mol^{-1}K^{-1})\Delta T + \left(\frac{2.38E\text{-}4}{2}\frac{J}{mol K^2}\right) T^2 \right] - 112 \frac{J}{mol K} \Delta T$$

$$65.6 \frac{J}{mol K}(53.3K) + 1.19E\text{-}4 \frac{J}{mol K^2}(351.3^2 - 298^2)K - 112 \frac{J}{mol K}(53.3K)$$

$$3496.48 \frac{J}{mol} + 4.1183 \frac{J}{mol} - 5969.6$$

$$\int_{298}^{351.3} \Delta C_p \, dT = -2469 \frac{J}{mol}$$

$$\Delta H_{vap,m}(351.3K) = 42.3 \frac{kJ}{mol} + \left(-2.469 \frac{kJ}{mol}\right)$$

$$\Delta H_{vap,m}(351.3K) = 39.831 \frac{kJ}{mol}$$

$$\Delta S_{vap,m}(351.3K) = \frac{\Delta H_{vap,m}(351.3K)}{T_b} = \frac{39.831 \frac{kJ}{mol}}{351.3K}$$

$$= .11338 \frac{kJ}{mol} = 113.38 \frac{J}{mol K}$$

Graphical Problems

(3) $S_m(70K)$, $S_m(150K)$ and $\Delta S_{70K \to 150K}$

$$S_m(70K) = \left(\int_0^{23.66K} .9\frac{J}{K^2 mol}dT + \frac{93.8\frac{J}{mol}}{23.66K}\right) \text{ solid III} \to \text{solid II} \to 25.26\frac{J}{molK}$$

$$+$$

$$\left(\int_{23.66K}^{43.76K} 1.05\frac{J}{K^2 mol}dT + \frac{743\frac{J}{mol}}{43.76K}\right) \text{ Solid II} \to \text{Solid I} \to 38.1\frac{J}{molK}$$

$$\left(\int_{43.76K}^{54.39K} .85\frac{J}{K^2 mol}dT + \frac{4450\frac{J}{mol}}{54.39K}\right) \text{ solid I} \to \text{liquid} \to 90.85\frac{J}{molK}$$

$$\left(\int_{54.39K}^{70K} .75\frac{J}{K^2 mol}dT\right) \to 11.71\frac{J}{molK}$$

$$S_m(70K) = (25.26 + 38.1 + 90.85 + 11.71)\frac{J}{molK} = 165.92\frac{J}{molK}$$

$$S_m(150K) = S_m(70K) + \left(\int_{70K}^{90.2K} .35\frac{J}{molK^2}dT + \frac{6815\frac{J}{mol}}{90.2K}\right) \to 82.6\frac{J}{molK}$$

$$+$$

$$\left(\int_{90.2K}^{(150K)} .2\frac{J}{molK^2}dT\right) = 11.96\frac{J}{molK}$$

$$S_m(150K) = (165.92 + 82.6 + 11.96)\frac{J}{molK} = 260.5\frac{J}{molK}$$

$$\Delta S_{m\,70K \to 150K} = 94.58\frac{J}{molK}$$