

Problem Set 4B) Analytical Problems

1) For reversible processes: $\Delta S = \frac{dq}{T}$ adiabatic $\rightarrow dq = 0$

Thus, $\Delta S = \frac{0}{T} = 0$

2) a) Cyclic process $\rightarrow \Delta U = 0, \Delta H = 0, \Delta S = 0$

b) $q = -w$ as $\Delta U = 0$ $w = -nRT \ln \frac{V_b}{V_a}$
 $q = +nRT \ln \frac{V_b}{V_a}$

c) Isothermal Expansion: $W_I = -nRT_{hot} \ln \frac{V_b}{V_a}$
 Adiabatic Expansion: $W_{II} = \frac{nR}{1-\gamma} [T_{cold} - T_{hot}]$

Isothermal Compression: $W_{III} = -nRT_{cold} \ln \frac{V_d}{V_c}$
 Adiabatic Compression: $W_{IV} = \frac{nR}{1-\gamma} [T_{hot} - T_{cold}]$

Given eqs: $T_{hot} V_a^{\gamma-1} = T_{cold} V_d^{\gamma-1}$

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

Substituting $\frac{T_{hot}}{T_{cold}} \left(\frac{V_b}{V_a} \right)^{\gamma-1}$

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

Total work = $nR (T_{cold} - T_{hot}) \ln \frac{V_b}{V_a}$ $V_b > V_a$ $T_{hot} > T_{cold}$

\downarrow
 always negative

d) Efficiency (ϵ) = $\frac{|w|}{\text{heat absorbed}} = \frac{nR (T_{hot} - T_{cold}) \ln \frac{V_b}{V_c}}{nRT_{hot} \ln \frac{V_b}{V_c}} = 1 - \frac{T_{cold}}{T_{hot}}$

$\epsilon < 1$ not 100%

3a) General eqn for dS : $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

To work in molar form, we start with $U = H - PV$

$$dU = TdS - PdV = dH - PdV - VdP$$

$$\downarrow$$

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

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

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

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

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

Numerical Problems

1) $\Delta H_{rxn} = (\sum \Delta H_f^\circ \text{ prod}) - (\sum \Delta H_f^\circ \text{ reactants})$
 $= (-278 - 1364 - 304) - (-1273)$
 $= -760 \frac{\text{kJ}}{\text{mol}}$

$$\Delta S_{rxn} = (\sum S^\circ \text{ prod}) - (\sum S^\circ \text{ react})$$

$$= (192 + 161 + 213) - 209$$

$$= 357 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{sur} = \frac{-\Delta H_{rxn}}{T_{st}} = \frac{-(-760 \frac{\text{kJ}}{\text{mol}} \cdot \frac{1000 \text{ J}}{1 \text{ kJ}})}{298 \text{ K}} = 2560 \frac{\text{J}}{\text{K mol}}$$

$$\Delta S_{uni} = \Delta S_{rxn} + \Delta S_{sur}$$

$$= 2560 + 357 = 2917 \frac{\text{J}}{\text{K mol}}$$

Spontaneous bc ΔH is (-) & ΔS is (+)

2) Kirchhoff equation:

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

$$\Delta C_p = C_p(\text{prod.}) - C_p(\text{react.}) = C_p^g - C_p^l$$

$$= 65.6 \frac{J}{mol K} + 2.38 \times 10^{-4} T \frac{J}{mol K^2} - 117 \frac{J}{mol K}$$

$$= (-46.4 + 2.38 \times 10^{-4} T) \frac{J}{mol K}$$

$$\int_{298}^{351.3} C_p dT = \int_{298}^{351.3} (-46.4 + 2.38 \times 10^{-4} T) dT$$

$$= -46.4 [T]_{298}^{351.3} + \frac{2.38 \times 10^{-4}}{2} [T^2]_{298}^{351.3}$$

$$= -2469 \frac{J}{mol} = -2.5 \frac{kJ}{mol}$$

$$\Delta H_{vap}(351.3K) = 42.3 \frac{kJ}{mol} - 2.5 \frac{kJ}{mol} = 39.8 \frac{kJ}{mol}$$

$$\Delta S_{vap}(351.3K) = \frac{\Delta H_{vap}}{T} = \frac{39.8}{351.3} = 113.4 \frac{J}{mol K}$$

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

$$\Delta S_{70 \rightarrow 150K} = \frac{(\Delta H)_2}{T_2} - \frac{(\Delta H)_1}{T_1}$$

$$= \frac{4450}{84.79} - \frac{6715}{90.2} = 6.26 \frac{J}{K}$$

spontaneous