

analytical problems

1) Reversible process entropy transfer is taking place by heat interactions

$$\Delta S = \frac{dq_{rev}}{T}$$

adiabatic process, means the system is closed & no heat is entered into the system

$$q = 0$$

→ rev. adiabatic process,  $\Delta S = 0$

2a. H, U, S (enthalpy, internal energy, entropy) are state functions. Cyclic process: initial & final state are same. Change in state property for cyclic process is zero.  $\Delta H = 0$ ,  $\Delta S = 0$ ,  $\Delta U = 0$

2b Process b → c & d → a are adiabatic process →  $q = 0$

during a → b temp is constant →  $\Delta U = 0$

The work done by the system is being carried out by heat supplied to the system. Work done by the system in reversible process =  $w$

$$w = -nRT \ln \left( \frac{V_b}{V_a} \right) \quad \Delta U = 0 = q + w \quad q = -w = -(-nRT \ln \left( \frac{V_b}{V_a} \right))$$

$$q = nRT \ln \left( \frac{V_b}{V_a} \right)$$

$$\begin{aligned} 2c. w_{net} &= w_{ab} + w_{bc} + w_{cd} + w_{da} \\ &= -nRT \ln \left( \frac{V_b}{V_a} \right) - nRT \ln \left( \frac{V_d}{V_c} \right) \\ w_{net} &= -(T_h - T_c) nR \ln \left( \frac{V_b}{V_a} \right) \end{aligned}$$

total work done is negative from system potential view

$$2d \text{ efficiency } (\eta) = \frac{\text{network done by heat engine}}{\text{heat absorbed by heat engine}} = \frac{-w}{q}$$

$$\downarrow$$

$$= \frac{-[-(T_h - T_c) nR \ln \left( \frac{V_b}{V_a} \right)]}{nRT_h \ln \left( \frac{V_b}{V_a} \right)} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_{cold}}{T_{hot}}$$

$$3A. S = S(P, T) \quad ds = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP$$

Maxwell's Relations

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

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

$$ds = \frac{C_P}{T} dT - \beta V dP \quad \text{where } \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \alpha_{P_2} = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

$$3b \quad ds = \frac{C_P}{T} dT - \beta V dP$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \beta V dP$$

Numerical problems

$$1A \quad \Delta H_{rxn} = \sum \Delta H_f^\circ \text{ prod} - \sum \Delta H_f^\circ \text{ reactants} = -[1364 - 2 + 8 - 394] - 1273$$

$$\Delta H_{rxn} = -763 \text{ kJ/mol}$$

$$\Delta S_{rxn} = \sum S_{products} - \sum S_{reactants} \rightarrow [192 + 161 + 213] - [209]$$

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