

# Mid-Term Exam

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- 1 The internal energy does not change ( $\Delta U = 0$ ), which implies that  $\Delta T = 0$ .  
 Therefore, the process is adiabatic.

$$T_1 = T_2 = T \cancel{\text{H}}$$

Since it's adiabatic,  $q=0$  and  $PV^\gamma = \text{constant}$

↳ no degradation of energy occurs, since it's reversible  $\therefore \Delta S = 0 \cancel{\text{H}}$

2a  $dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{C_p}{T} \left(\frac{\partial T}{\partial V}\right)_P$   
 $\therefore \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$

From a Maxwell relationship:  $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$

So:  $\left(\frac{\partial T}{\partial P}\right)_S = \frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{-\alpha V}{C_p/T} = -\frac{\alpha V T}{C_p} \cancel{\text{H}}$

2b  $\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -C_p^{-1} \left(\frac{\partial H}{\partial P}\right)_T$

$$dH = TdS + VdP$$

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

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left(V - T\alpha V\right) = \frac{V}{C_p} \left(1 - T\alpha\right) \cancel{\text{H}}$$

$$2c) H = H(T, V)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_V dT + \left(\frac{\partial H}{\partial V}\right)_T dV$$

$$\text{at constant volume: } \left(\frac{\partial H}{\partial S}\right)_V = \left(\frac{\partial H}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$

$$\text{from cyclostatic rates: } \left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V = \frac{C_V}{T} \left(\frac{\partial T}{\partial P}\right)_V \quad \text{if } S = S(P, V)$$

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

$$\text{from enthalpy } H = U + PV$$

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial PV}{\partial T}\right)_V \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{P}{\alpha} \quad \text{and } C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\left(\frac{\partial H}{\partial T}\right)_V = C_V + \frac{\alpha V}{\beta}$$

$$\text{So: } \left(\frac{\partial H}{\partial S}\right)_V = \left[ C_V + \frac{\alpha V}{\beta} \right] \left[ \frac{T}{C_V} \right] = T + \frac{T\alpha V}{\beta} = T \left[ 1 + \frac{\alpha V}{\beta} \right]$$

$$\text{But } \beta = K_T C_V$$

$$\left(\frac{\partial H}{\partial S}\right)_V = T \left[ 1 + \frac{\alpha V}{K_T C_V} \right]$$

$$3) dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = +S \quad @ \text{constant pressure}$$

$$\text{if } G = RT \ln\left(\frac{aP}{(RT)^{5/2}}\right) \Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -\frac{5}{2}R + R \ln\left(\frac{aP}{(RT)^{5/2}}\right) = -S$$

$$\text{So: } S = \frac{5}{2}R + R \ln\left(\frac{aP}{(RT)^{5/2}}\right)$$

$$\text{Then: } S = S(T, P)$$

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

$$\text{at constant pressure, the 1st law gives: } \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

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

$$\left(\frac{\partial S}{\partial T}\right)_P = R \frac{5}{2T}$$

$$\text{So: } C_p = T \left( R \frac{5}{2T} \right) = \frac{5}{2} R //$$

4]  $U = k \frac{S^3}{V}$

Say  $U = U(P, T)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{P,T} dn$$

4a]  $J = \frac{(JK^{-1})^3}{m^3} \text{ k-units}$  as  $S$  is in J per Kelvin

$$\text{k-units} = \frac{J K^3 m^3}{J^3} = \frac{K^3 m^3}{J^2} //$$

4c]  $U = k \frac{S^3}{V}$  where  $U = nC_v T$

$$nC_v T = K \frac{S^3}{V}$$

$$\frac{nRT}{1-\gamma} = \frac{KS^3}{V} \text{ for an ideal gas}$$

$$PV = KS^3$$

$$\frac{1-\gamma}{1-\gamma} = \frac{V}{V}$$

$$P = \frac{(1-\gamma)KS^3}{V^2} //$$

$$U = \frac{KS^3}{V} \quad S = nC_p T$$

$$\frac{nRT}{1-\gamma} = \frac{K(nC_p T)^3}{V} \quad \text{with } C_p = \frac{R\gamma}{1-\gamma}$$

$$\frac{nRT}{1-\gamma} = \frac{K(nT R \gamma)^3}{V(1-\gamma)}$$

$$\frac{nRT}{1-\gamma} = \frac{Kn^3 T^3 R^3 \gamma^3}{V(1-\gamma)}$$

$$\frac{nR V (1-\gamma)^3}{(1-\gamma) Kn^3 R^3 \gamma^3} = \frac{T^3}{T} \Rightarrow T^2 = \frac{(1-\gamma)^2 V}{n^2 K R^2 \gamma^3}$$

$$T = \sqrt{\frac{V(1-\gamma)^2}{n^2 R^2 K \gamma^3}} //$$

4b The adiabats of the ideal gas is  $PV^\gamma = \text{constant}$

So, from P and V from 4c

$$\left[ \frac{(1-\gamma)kS^3}{V^2} \right] \left[ \frac{V(1-\gamma)^2}{n^2 R^2 k \gamma^3} \right]^{\gamma} = \text{constant}$$

$\underbrace{P}_{\text{P}} \quad \underbrace{V}_{\text{V}} \quad \cancel{\text{H}}$

4d  $dU = dq + dw$

$$dU = TdS - PdV$$

$$dU = TdS - \frac{(1-\gamma)kS^3}{V^2} dV \cancel{\text{H}}$$

5a The work is defined by  $\rightarrow \text{H}_2\text{O molecular weight} = 18.015$

$$w = PdV$$

$$w = (1 \text{ atm}) \left( \frac{18.015}{0.9998 \text{ g/cm}^3} - \frac{18.015}{0.917 \text{ g/cm}^3} \right) (0.001 \text{ L})$$

$$w = -1.63 \text{ L atm}$$
$$= -0.16 \text{ J} \cancel{\text{H}}$$

5c  $q = 6.01 \text{ kJ} \rightarrow$  as it's the heat of melting,

$$\Delta S = \frac{q}{T} = \frac{6.01 \text{ kJ}}{0^\circ\text{C}} = 22.002 \frac{\text{J}}{\text{K}} \cancel{\text{H}}$$

5b  $\Delta U = q - w = 6.01 \text{ kJ} - (-0.16 \text{ J})$

$$\Delta U = 6010.16 \text{ J} \cancel{\text{H}}$$

References:

- [1] Stolen, S., Grönbech, T., & Neill L., A. (2004). Chemical Thermodynamics of Materials - Macroscopic and Microscopic Aspects. (J. W. & S. Inc., Ed.). John Wiley & Sons Ltd.
- [2] B. Gaskell, D., & E. Laughlin, D. (2018). Introduction to the Thermodynamics of Materials. (C. Press Ed.). Taylor & Francis Group
- [3] Mortimer G., R. (2013). Mathematics for Physical Chemistry. (A. P. of Elsevier, Ed.) (4th ed.) Amsterdam: British Library Cataloguing in Publication Data