

PHYSICAL CHEMISTRY 3510

EXAM 2

October 12, 2012

Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep any explanations brief and to the point.

Your name: Solutions

SOME POSSIBLY USEFUL INFORMATION:

$$N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$dU = dq + dw$$

$$H = U + pV$$

$$dw = -p_{\text{ex}} dV$$

$$\gamma = C_p/C_v$$

$$\text{Perfect gas: } pV = nRT$$

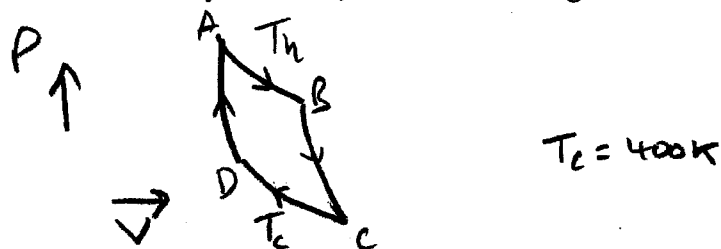
$$C_p - C_v = nR$$

$$\text{Heat engine: } \varepsilon = (T_h - T_c)/T_h$$

$$\text{Adiabat: } pV^\gamma = \text{constant}$$

1) 25 points

Consider the reversible Carnot cycle below, where the working fluid is 1 mol of perfect gas.



- When 50 J of heat is absorbed at T_h , 30 J of work are obtained. Calculate the efficiency and T_h .
- What can you say about the work obtained if the cycle was irreversible?
- What can you say about the sum of the changes in internal energy for the four steps $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$, and why?
- What can you say about the heat transfer in the $B \rightarrow C$ step?

$$a) \quad \epsilon = \frac{|w|}{q_h} = \frac{30 \text{ J}}{50 \text{ J}} = \boxed{0.6}$$

$$= \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} \quad \text{so} \quad \frac{T_c}{T_h} = 0.4$$

$$\text{so } T_h = \frac{T_c}{0.4} = 1000 \text{ K}$$

b) It will be less. Refer to Ch. 3

c) They must sum to zero, as required by the First Law

d) It is adiabatic, so $q = 0$

2) 40 points

1 mol of perfect gas with $C_v = 23 \text{ J K}^{-1} \text{ mol}^{-1}$ is expanded reversibly and adiabatically from an initial temperature of 320 K and initial volume of 0.02 m^3 to a final volume of 0.05 m^3 . Calculate the final temperature and q , w , ΔU , and ΔH .

adiabatic process so $q = 0$

therefore $\Delta U = w = C_v \Delta T$, $\Delta H = C_p \Delta T$

reversible but not isothermal, so

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \left| \quad P_1 = \frac{nRT}{V_1} = \frac{1 \text{ mol } 8.314 \text{ J mol}^{-1} \text{ K}^{-1} 320 \text{ K}}{0.02 \text{ m}^3} \right.$$

$$C_p = C_v + R = 23 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$+ 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 31.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 1.33 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2} = 133 \text{ kPa}$$

$$\gamma = \frac{C_p}{C_v} = \frac{31.314}{23} = 1.36$$

So

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^\gamma = 1.33 \times 10^5 \text{ Pa} \left(\frac{0.02}{0.05} \right)^{1.36} = 38252 \text{ Pa}$$

$$\text{so } T_2 = \frac{P_2 V_2}{nR} = \frac{38252 \text{ Pa} \times 0.05 \text{ m}^3}{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}} = 230 \text{ K}$$

$$\Delta T = 230 \text{ K} - 320 \text{ K} = -90 \text{ K}$$

$$\text{so } \Delta U = 23 \text{ J K}^{-1} \text{ mol}^{-1} \times -90 \text{ K} = -2070 \text{ J mol}^{-1}$$

$$\text{and } \Delta H = 31.314 \text{ J K}^{-1} \text{ mol}^{-1} \times -90 \text{ K} = -2818 \text{ J mol}^{-1}$$

3) 35 points

- a) A reaction has $\Delta C_p = a + bT + c/T^2$. Use this to find ΔH at temperature T_2 , if the value at temperature T_1 is equal to ΔH_1 .
- b) Oxygen has a Joule-Thompson coefficient $\mu = (\partial T/\partial p)_H$ equal to 0.3 K bar^{-1} . If, in an adiabatic system, high-pressure oxygen at 20 bar is expanded through a small nozzle to a final pressure of 1 bar, estimate the change in temperature.

a) C_p is a function of T , so $\Delta H = \int C_p dT$

$$= \int_{T_1}^{T_2} (a + bT + \frac{c}{T^2}) dT$$
$$= \left[aT + \frac{b}{2}T^2 - \frac{c}{T} \right]_{T_1}^{T_2} = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

so $\Delta H_{T_2} = \Delta H_1 + a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

b) $\mu = \left(\frac{\partial T}{\partial p}\right)_H = 0.3 \text{ K bar}^{-1}$ $dp = 1 \text{ bar} - 20 \text{ bar} = -19 \text{ bar}$

$$\mu dp = -19 \text{ bar} \times 0.3 \text{ K bar}^{-1} = \boxed{-5.7 \text{ K} = dT}$$