

**PHYSICAL CHEMISTRY 3510**

**EXAM 1**

**September 30, 2013**

*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:**

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

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

$$dU = dq + dw$$

$$H = U + pV$$

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

$$\gamma = C_p/C_v$$

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

$$C_p - C_v = nR$$

1) 21 points

The van der Waals equation of state for 1 mol of gas is  $p = RT/(V-b) - a/V^2$ .

At the critical point, where  $T = T_c$ ,  $p = p_c$  and  $V = V_c$ , there is a horizontal inflection on a plot of  $p$  versus  $V$ . Obtain equations for the first and second derivatives of  $p$  as a function of  $V$ , and show that they are both zero at the critical point when

$$V_c = 3b, \quad p_c = a/(27b^2), \quad T_c = 8a/(27Rb).$$

$$p = RT(V-b)^{-1} - aV^{-2}$$

$$\frac{dp}{dV} = -RT(V-b)^{-2} + 2aV^{-3}$$

substitute  $T = T_c$  and  $V = V_c$  so  $V-b = 2b$

$$\begin{aligned} \frac{dp}{dV} &= \frac{-R \cdot 8a}{27Rb} \cdot \frac{1}{(2b)^2} + \frac{2a}{(3b)^3} \\ &= \frac{-2a}{27b^3} + \frac{2a}{27b^3} = 0 \end{aligned}$$

$$\begin{aligned} \frac{d^2p}{dV^2} &= \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \\ &= \frac{2R \cdot 8a}{27Rb (2b)^3} - \frac{6a}{(3b)^4} \\ &= \frac{2a}{27b^4} - \frac{2a}{81b^4} = 0 \end{aligned}$$

2) 28 points

One mole of a perfect gas with  $C_V = 35 \text{ J K}^{-1} \text{ mol}^{-1}$  is expanded reversibly and adiabatically from an initial pressure of  $8 \times 10^4 \text{ Pa}$  and initial volume of  $0.04 \text{ m}^3$  to a final volume of  $0.05 \text{ m}^3$ . You may assume the result that  $pV^\gamma$  is constant. Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ .

$$\gamma = C_p/C_V = \frac{35 + 8.314}{25} = 1.238$$

$$\begin{aligned} P_1 V_1^\gamma &= P_2 V_2^\gamma \quad \therefore P_2 = P_1 \left( \frac{V_1}{V_2} \right)^\gamma \\ &= 8 \times 10^4 \text{ Pa} \cdot \left( \frac{0.04}{0.05} \right)^{1.238} = 0.759 \times 8 \times 10^4 \text{ Pa} \\ &= 6.07 \times 10^4 \text{ Pa} . \end{aligned}$$

$$T_1 = \frac{P_1 V_1}{nR} = \frac{8 \times 10^4 \text{ Pa} \times 0.04 \text{ m}^3}{1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} = 385 \text{ K} .$$

$$T_2 = \frac{P_2 V_2}{nR} = 365 \text{ K} . \quad \Delta T = T_2 - T_1 = -20 \text{ K} .$$

Adiabatic so  $q = 0$  .

$$\Delta U = C_V \cdot \Delta T = \underline{-700 \text{ J}} = q + w \quad \therefore \underline{w = -700 \text{ J}} .$$

$$\Delta H = C_p \cdot \Delta T = \underline{-866 \text{ J}} .$$

3) 30 points

The enthalpy of combustion of  $C_4H_4(g)$  to make  $H_2O(l)$  and  $CO_2(g)$  is  $-2340 \text{ kJ mol}^{-1}$ .

The enthalpy of combustion of  $C_4H_8(g)$  to make  $H_2O(l)$  and  $CO_2(g)$  is  $-2760 \text{ kJ mol}^{-1}$ .

The enthalpy of formation of  $H_2O(l)$  is  $-286 \text{ kJ mol}^{-1}$ . All the data are for  $298 \text{ K}$ .

The heat capacities  $C_p$  for  $O_2(g)$ ,  $C_4H_4(g)$ ,  $C_4H_8(g)$ ,  $H_2O(l)$  and  $CO_2(g)$  are 29, 61, 71, 75 and  $37 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

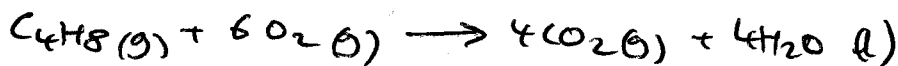
Deduce

a)  $\Delta U_{298}$  for the combustion of  $C_4H_8(g)$ .

b)  $\Delta H$  for the combustion of  $C_4H_8(g)$  at  $900 \text{ K}$ .

c)  $\Delta H_{298}$  for the reaction  $C_4H_4(g) + 2 H_2(g) \rightarrow C_4H_8(g)$ .

a)  $H = U + pV \therefore \Delta U = \Delta H - \Delta(pV) = \Delta H - RT \Delta n_{\text{gas}}$   
 (neglecting liquid volumes)



$$\Delta n_{\text{gas}} = 4 - 6 = -2$$

$$\Delta U = -2760 \text{ kJ mol}^{-1} - \frac{8.314 \times 298}{1000} \times -2 \text{ kJ mol}^{-1}$$

$$= -2753 \text{ kJ mol}^{-1}$$

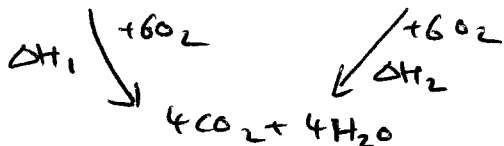
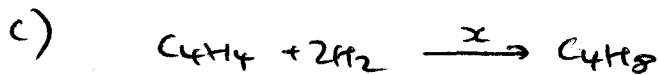
b)  $\Delta H_{900} = \Delta H_{298} + \int_{298}^{900} \Delta C_p \cdot dT$

$$\Delta C_p = (4 \times 37 + 4 \times 75 - 6 \times 29 - 71) \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 203 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{900} = -2760 \text{ kJ mol}^{-1} + \frac{203 (900 - 298)}{1000} \text{ kJ mol}^{-1}$$

$$= -2638 \text{ kJ mol}^{-1}$$



Hess' Law:  $x + \Delta H_2 = \Delta H_1$

$$\Delta H_1 = \Delta_c H(C_4H_4) + 2 \Delta_f H(H_2O)$$

$$= -2340 - 2 \times 286 \text{ kJ mol}^{-1}$$

$$= -2912 \text{ kJ mol}^{-1}$$

$$x = \Delta H_1 - \Delta H_2 = -152 \text{ kJ mol}^{-1}$$

4) 21 points

Nitrogen has a Joule-Thomson coefficient of  $\mu = (\partial T/\partial p)_H = 2 \times 10^{-6} \text{ K/Pa}$ . If  $\text{N}_2$  at 300 K and  $3 \times 10^7 \text{ Pa}$  expands through a porous plug until the pressure is  $1 \times 10^5 \text{ Pa}$ , estimate its final temperature. Is the  $\text{N}_2$  behaving like a perfect gas? Explain whether attractive or repulsive intermolecular forces dominate here.

$$\left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} \quad \text{so} \quad \Delta T \approx 2 \times 10^{-6} \text{ K Pa}^{-1} \cdot (1 \times 10^5 - 3 \times 10^7) \text{ Pa} \\ = -59.8 \text{ K}.$$

A perfect gas would have  $\mu = 0$  because there are no intermolecular forces.

Here, reducing  $p$  increases the average separation between the molecules and this takes work (so  $U$  and the temperature decrease) to overcome intermolecular attraction.