

PHYSICAL CHEMISTRY 3510

EXAM 1

September 28, 2015

*Do not turn any pages until told to start. 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:

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

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

$$dU = dq + dw$$

$$H = U + pV$$

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

$$\gamma = C_p/C_v$$

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

$$C_p - C_v = nR$$

$$\text{van der Waals: } p = nRT/(V-b) - a(n/V)^2$$

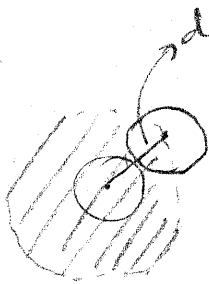
1) 30 points

a) Xe gas has a van der Waals  $b$  parameter of  $5 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ . Use this information to estimate the diameter of a Xe atom.

b) 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  $V$  for a van der Waals gas, and show that they are both zero at the critical point when

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

a)



excluded volume =  $\frac{4}{3}\pi d^3$  for 1 particle, but this double counts so the overall excluded volume per particle is  $\frac{2}{3}\pi d^3$  per molecule or  $\frac{2}{3}\pi N_A d^3$  per mole  $\approx b$ .

$$d^3 = \frac{3b}{2\pi N_A} = \frac{3 \times 5 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}{2\pi \times 6.022 \times 10^{23} \text{ mol}^{-1}} = 3.96 \times 10^{-29} \text{ m}^3$$

$$\therefore d = \underline{3.4 \times 10^{-10} \text{ m}}.$$

b) see notes

$$\frac{dp}{dV} = \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = \frac{-R \cdot 8a}{27Rb} \cdot \frac{1}{(3b - b)^2} + \frac{2a}{(3b)^3}$$

$$= \frac{-8a \cdot 2}{27b \cdot 4b^2} + \frac{2a}{27b^3} = 0$$

$$\frac{d^2p}{dV^2} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = \frac{2R \cdot 8a}{27Rb} \cdot \frac{1}{(3b - b)^3} - \frac{6a}{(3b)^4}$$

$$= \frac{8a \cdot 2R}{27Rb} \cdot \frac{1}{8b^3} - \frac{6a}{81b^4} = \frac{2}{27b^4} - \frac{2}{27b^4} = 0$$

see exercises 106, 107

2) 30 points

One mole of a perfect gas with  $C_V = 30 \text{ J K}^{-1} \text{ mol}^{-1}$  is expanded reversibly and adiabatically from an initial pressure of  $7 \times 10^4 \text{ Pa}$  and an initial temperature of  $298 \text{ K}$  to a final volume of  $0.0668 \text{ m}^3$ . You may assume the result that  $pV^\gamma$  is constant. Calculate  $q$ ,  $\Delta U$ ,  $\Delta H$  and  $w$ .

$$C_p = C_V + R = 38.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\gamma = C_p / C_V = \frac{38.314}{30} = 1.277$$

$$P_1 V_1 = RT_1 \therefore V_1 = \frac{RT_1}{P_1} = \frac{8.314 \times 298}{7 \times 10^4} \text{ m}^3 = 0.0354 \text{ m}^3$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \therefore P_2 = P_1 \left( \frac{V_1}{V_2} \right)^\gamma = 7 \times 10^4 \text{ Pa} \times \left( \frac{0.0354}{0.0668} \right)^{1.277} \\ = 3.11 \times 10^4 \text{ Pa}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \therefore T_2 = T_1 \cdot \frac{P_2 V_2}{P_1 V_1} = \frac{298 \text{ K} \times 3.11 \times 10^4 \times 0.0668}{7 \times 10^4 \times 0.0354} \\ = 250.0 \text{ K}$$

$$\Delta T = -48 \text{ K}$$

$q = 0$  because adiabatic.

$$\Delta U = C_V \cdot \Delta T = 30 \times -48 \text{ J mol}^{-1} = -1440 \text{ J mol}^{-1}$$

$$\Delta H = C_p \cdot \Delta T = 38.314 \times -48 \text{ J mol}^{-1} = -1839 \text{ J mol}^{-1}$$

$$\Delta U = q + w \therefore w = \Delta U - q = \Delta U \text{ here, } -1440 \text{ J mol}^{-1}$$

see exercises 2E2-5

3) 40 points

The enthalpy of combustion of  $C_2H_5OH(l)$  to make  $H_2O(l)$  and  $CO_2(g)$  is  $-1368 \text{ kJ mol}^{-1}$ .

The enthalpy of combustion of  $CH_3OCH_3(g)$  to make  $H_2O(l)$  and  $CO_2(g)$  is  $-1462 \text{ kJ mol}^{-1}$ .

The enthalpy of formation of  $H_2O(l)$  is  $-286 \text{ kJ mol}^{-1}$ .

The enthalpy of formation of  $CO_2(g)$  is  $-394 \text{ kJ mol}^{-1}$ .

The heat capacities  $C_p$  for  $O_2(g)$ ,  $C_2H_5OH(l)$ ,  $CH_3OCH_3(g)$ ,  $H_2O(l)$  and  $CO_2(g)$  are 29, 112, 66, 75 and  $37 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively. All the data are for 298 K and can be assumed not to vary with T.

Deduce

a)  $\Delta U_{298}$  for the combustion  $C_2H_5OH(l)$ .

b)  $\Delta H$  for the combustion of  $C_2H_5OH(l)$  at 360 K.

c)  $\Delta H_{298}$  for the isomerization of  $C_2H_5OH(l)$  to  $CH_3OCH_3(g)$  [ethanol to dimethyl ether].

d) The temperature of an adiabatic flame of ethanol and pure oxygen.

$$a) H = U + pV \quad \therefore \Delta U = \Delta H - \Delta(pV) \approx \Delta H - RT \Delta n_{\text{gas}}$$



$$\Delta n_{\text{gas}} = 2 - 3 = -1 \text{ mole}$$

$$\Delta U_{298} = \Delta H_{298} + R \cdot 298 \text{ K} = -1368 + \frac{8.314 \cdot 298}{1000} \text{ kJ mol}^{-1}$$

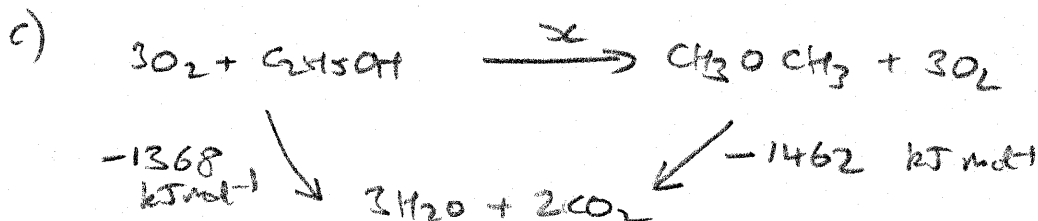
$$= -1366 \text{ kJ mol}^{-1}$$

$$b) \Delta H_{360} = \Delta H_{298} + \int_{298}^{360} \Delta C_p dT = -1368 + \frac{(360 - 298) \cdot 100}{1000} \Delta C_p \text{ kJ mol}^{-1}$$

$$= -1362 \text{ kJ mol}^{-1}$$

$$\Delta C_p = 3 \times 75 + 2 \times 37 - 112 - 3 \times 29 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 100 \text{ J K}^{-1} \text{ mol}^{-1}$$



$$\text{Hess' Law} \quad x - 1462 = -1368 \quad \therefore x = 94 \text{ kJ mol}^{-1}$$

d) Imagine the heat released at 298 K,  $1368 \text{ kJ mol}^{-1}$ , is retained and heats the products to a new temperature  $T^*$ .

$$C_p(\text{products}) = 3 \times 75 + 2 \times 37 \text{ J K}^{-1} \text{ mol}^{-1} = 299 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$1368 \text{ kJ mol}^{-1} = C_p(T - T^*) = \frac{299}{1000} (T^* - 298) \quad \therefore T^* = \underline{4873 \text{ K}}$$