

PHYSICAL CHEMISTRY 3510

EXAM 1

September 28, 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:

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

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

$$dU = dq + dw$$

$$H = U + pV$$

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

$$\gamma = C_p/C_v$$

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

$$C_p - C_v = nR$$

1) 30 points

Consider 1 mol of an imaginary gas for which the equation of state is

$$p = \frac{nRT}{V-b} - aV$$

with $b = 6 \times 10^{-3} \text{ m}^3$ and $a = 5 \times 10^5 \text{ m}^3 \text{ Pa}$

a) When 1 mol of this gas has a volume of 0.024 m^3 at 298 K , what is the compression factor? Given your answer, explain if attractive or repulsive intermolecular forces dominate.

b) Determine the work done on the gas when 1 mol of this gas is expanded reversibly and isothermally at 298 K from 0.024 to 0.048 m^3 ?

c) What is the work done on the gas if 1 mol of this gas is expanded from 0.024 to 0.048 m^3 against a constant external pressure of $2 \times 10^4 \text{ Pa}$?

$$\begin{aligned} \text{a) } p &= \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 1 \text{ mol} \times 298 \text{ K}}{(0.024 - 0.006) \text{ m}^3} - 5 \times 10^5 \text{ m}^3 \text{ Pa} \times 0.024 \text{ m}^3 \\ &= (1.376 \times 10^5 - 1.200 \times 10^4) \text{ Pa} = 1.256 \times 10^5 \text{ Pa} \end{aligned}$$

$$Z = \frac{pV}{nRT} = \frac{1.256 \times 10^5 \text{ Pa} \times 0.024 \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 1 \text{ mol} \times 298 \text{ K}} = \underline{\underline{1.217}}$$

This is above 1 so repulsive forces dominate - see notes.

$$\begin{aligned} \text{b) } w &= \int_{V_1}^{V_2} -p_{\text{ext}} dV \text{ and here } p_{\text{ext}} = p \text{ so } w = - \int_{V_1}^{V_2} \left(\frac{nRT}{V-b} - aV \right) dV \\ &= - \left[nRT \ln(V-b) - \frac{1}{2} aV^2 \right]_{V_1}^{V_2} = nRT \ln \left(\frac{V_2-b}{V_1-b} \right) + \frac{1}{2} a (V_2^2 - V_1^2) \\ &= 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln \left(\frac{0.024 - 0.006}{0.048 - 0.006} \right) + \frac{5 \times 10^5}{2} (0.048^2 - 0.024^2) \text{ Pa m}^3 \\ &= -2099 \text{ J} + 432 \text{ J} = \underline{\underline{-1667 \text{ J}}} \end{aligned}$$

$$\begin{aligned} \text{c) } \text{When } p_{\text{ext}} \text{ is constant, } w &= (V_1 - V_2) p_{\text{ext}} = (0.024 - 0.048) \text{ m}^3 \times 2 \times 10^4 \text{ Pa} \\ &= \underline{\underline{-480 \text{ J}}} \end{aligned}$$

2) 40 points

1 mol of CO_2 with $C_p = 37 \text{ J K}^{-1} \text{ mol}^{-1}$ is expanded reversibly and adiabatically from an initial temperature of 298 K and initial volume of 0.02 m^3 to a final volume of 0.03 m^3 . You may treat the CO_2 as a perfect gas and assume the result that pV^γ is constant. Calculate the final temperature and q , w , ΔU , and ΔH .

$$C_p - C_v = R \quad \therefore C_v = C_p - R = 28.686 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\gamma = C_p / C_v = 37 / 28.686 = 1.290$$

Perfect gas law for initial conditions: $pV_1 = nRT_1$

$$\text{so } p_1 = \frac{nRT_1}{V_1} = \frac{1 \times 8.314 \times 298}{0.02} \text{ Pa} = 1.239 \times 10^5 \text{ Pa}$$

$$\begin{aligned} \text{" } pV^\gamma = \text{constant" } \text{ so } p_1 V_1^\gamma &= p_2 V_2^\gamma \quad \therefore p_2 = p_1 \left(\frac{V_1}{V_2} \right)^\gamma \\ &= 1.239 \times 10^5 \text{ Pa} \times \left(\frac{0.02}{0.03} \right)^{1.290} = 7.344 \times 10^4 \text{ Pa} \end{aligned}$$

Perfect gas law for final conditions:

$$p_2 V_2 = nRT_2 \quad \therefore T_2 = \frac{p_2 V_2}{nR} = \frac{7.344 \times 10^4 \text{ Pa} \times 0.03 \text{ m}^3}{8.314 \text{ J K}^{-1}} = \underline{\underline{265.0 \text{ K}}}$$

$q=0$ for an adiabatic process, ideal gas:

$$\Delta U = C_v \Delta T = 28.686 \text{ J K}^{-1} \times (265 - 298) \text{ K} = \underline{\underline{-947 \text{ J}}}$$

$$\Delta H = C_p \Delta T = 37 \text{ J K}^{-1} \times -33 \text{ K} = \underline{\underline{-1221 \text{ J}}}$$

3) 30 points

The enthalpy of combustion of $C_6H_6(l)$ to make $H_2O(l)$ and $CO_2(g)$ is $-3268 \text{ kJ mol}^{-1}$.

The enthalpy of combustion of $C_6H_{12}(l)$ to make $H_2O(l)$ and $CO_2(g)$ is $-4163 \text{ kJ mol}^{-1}$.

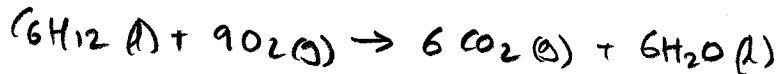
The enthalpy of formation of $H_2O(l)$ is -286 kJ mol^{-1} . All the data are for 298 K.

Deduce

a) ΔU_{298} for the combustion of $C_6H_{12}(l)$.

b) ΔH_{298} for the reaction $C_6H_6(l) + 3 H_2(g) \rightarrow C_6H_{12}(l)$.

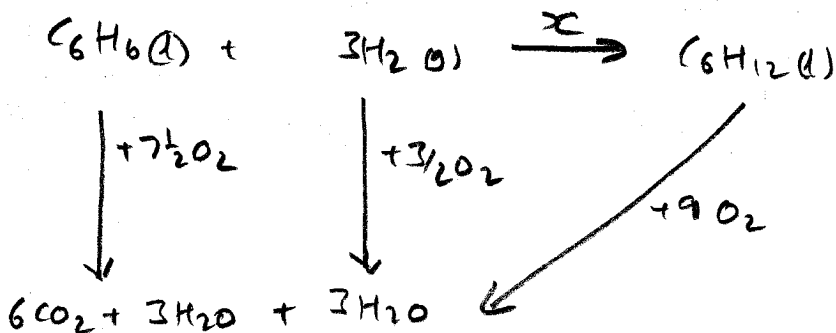
a) $H = U + pV$ so $\Delta U = \Delta H - \Delta(pV) \approx \Delta H - RT \Delta n_{\text{gas}}$



so $\Delta n_{\text{gas}} = -3 \text{ mol}$.

$$\Delta U = -4163 - \frac{8.314 \times 298}{1000} \times -3 \text{ kJ mol}^{-1} \approx \underline{\underline{-4156 \text{ kJ mol}^{-1}}}$$

b) Call $\Delta H_{298} = x$ and make a Hess cycle:



$$\begin{aligned}
 x - 4163 \text{ kJ mol}^{-1} &= -3268 \text{ kJ mol}^{-1} + 3 \times -286 \text{ kJ mol}^{-1} \\
 &= -4126 \text{ kJ mol}^{-1}
 \end{aligned}$$

so $x = \underline{\underline{+37 \text{ kJ mol}^{-1}}}$.