

PHYSICAL CHEMISTRY 3510

EXAM 1

September 28, 2018

*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: Key

SOME POSSIBLY USEFUL INFORMATION:

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

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

$$k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

relative to C = 12, the atomic masses of He and Ar are 4 and 40

Perfect gas: $pV = nRT$

van der Waals gas: $p = nRT/(V-b) - a(n/V)^2$

1) 20 points

a) Ar gas has a van der Waals b parameter of $1.5 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Use this information to estimate the diameter of Ar atoms, assuming they are spherical.

b) 1 mol of a real gas at 220 K and $3 \times 10^6 \text{ Pa}$ has a volume 0.85 times that expected from the perfect gas equation of state. Calculate the compression factor Z and the volume V , and explain qualitatively what the magnitude of Z tells us about intermolecular forces in this system.

$$a.) \frac{2}{3} \pi d^3 N_A = 1.5 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$\frac{2}{3} \pi d^3 = 2.49 \times 10^{-29} \text{ m}^3$$

$$d^3 = 1.19 \times 10^{-29} \text{ m}^3$$

$$d = 2.28 \times 10^{-10} \text{ m} = 2.28 \text{ \AA}$$

$$b.) T = 220 \text{ K} \quad P = 3 \times 10^6 \text{ Pa}$$

If ideal, volume would be

$$\frac{nRT}{P} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 220 \text{ K}}{3 \times 10^6 \text{ Pa}} = 6.10 \times 10^{-4} \text{ m}^3$$

So volume here is

$$0.85 \times 6.10 \times 10^{-4} \text{ m}^3 = 5.185 \times 10^{-4} \text{ m}^3$$

$$Z = \frac{PV}{nRT} = 0.85$$

\therefore Attractive forces dominate
(see notes for further explanation)

2) 30 points

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

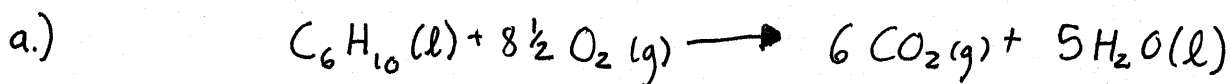
The enthalpy of combustion of $C_6H_{10}(l)$ to make $H_2O(l)$ and $CO_2(g)$ is $-3910 \text{ kJ mol}^{-1}$.

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

For the standard conditions of 298 K and 10^5 Pa , deduce

a) ΔU_{298} for the combustion of $C_6H_{10}(l)$.

b) ΔH_{298} for the reaction $C_6H_6(l) + 2 H_2(g) \rightarrow C_6H_{10}(l)$.



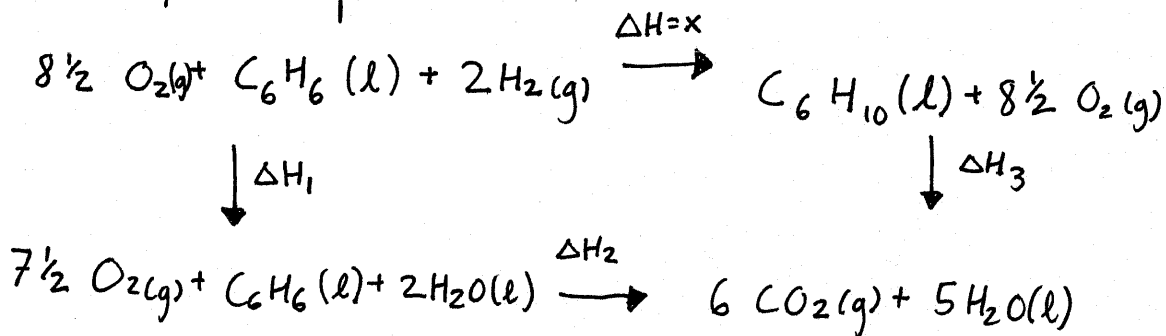
$$H = U + pV \quad \therefore \Delta U = \Delta H - \Delta(pV) \approx \Delta H - RT\Delta n_{\text{gas}}$$

$$= \Delta H - RT \times (-2.5)$$

$$\Delta U = -3910 + \frac{8.314 \times 298 \times 2.5}{1000} \text{ kJ mol}^{-1}$$

$$= -3910 + 6 \text{ kJ mol}^{-1} = -3904 \text{ kJ mol}^{-1}$$

b.) Make a Hess cycle. One option is:



$$\Delta H_1 + \Delta H_2 = \Delta H_3 + x$$

$$\Delta H_1 = 2 \times \Delta_f H(H_2O(l)) = -572 \text{ kJ mol}^{-1}$$

$$\Delta H_2 = \Delta_{\text{combust}} H(C_6H_6(l)) = -3268 \text{ kJ mol}^{-1}$$

$$\Delta H_3 = \Delta_{\text{combust}} H(C_6H_{10}(l)) = -3910 \text{ kJ mol}^{-1}$$

$$x = \Delta H_1 + \Delta H_2 + (-\Delta H_3) = +70 \text{ kJ mol}^{-1}$$

3) 20 points

Assuming ideal behavior, explain what you expect for the ratio of the average molecular kinetic energy in Ar compared to He at 300 K, and the ratio of the root mean square molecular velocity in Ar compared to He at 300 K.

Average molecular KE = $\frac{3}{2} kT$ independent of mass

$$\text{so } \underline{\underline{KE(\text{Ar}) = KE(\text{He})}}$$

KE = $\frac{1}{2} m c^2$ and is constant (at fixed T) so $c^2 \propto \frac{1}{m}$

$c \propto \frac{1}{\sqrt{m}}$. Ar has mass 10x that of He

$$\therefore \cancel{c(\text{Ar})}$$
$$c(\text{Ar}) = c(\text{He})/\sqrt{10} \approx 0.32 c(\text{He})$$

4) 30 points

Consider $n = 1$ mol of a real gas which has a new equation of state:

$$p = \frac{nRT}{V-nb}$$

where $b = 6 \times 10^{-3} \text{ m}^3$

a) What is the work done on the gas if 1 mol of this gas is expanded irreversibly from 0.024 to 0.040 m^3 against a constant external pressure of $5 \times 10^4 \text{ Pa}$?

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 0.040 m^3 ?

a.) $dw = -p_{\text{ex}} dV$

$$w = \int dw = - \int_{V_1}^{V_2} p_{\text{ex}} dV \quad \text{For constant } p_{\text{ex}}, w = -p_{\text{ex}} (V_2 - V_1)$$

$$= -5 \times 10^4 \text{ Pa} \times (0.040 - 0.024) \text{ m}^3 = -800 \text{ J}$$

b.) Reversible so ~~$p_{\text{ex}} = P$~~ $p_{\text{ex}} = p$

$$w = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} \right) dV = - \left[nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) \right]$$

$$= - \left[2478 \text{ J} \times \ln \left(\frac{0.034}{0.018} \right) \right]$$

$$= -1576 \text{ J}$$