PHYSICAL CHEMISTRY 5200
QUIZ 1
September 24, 2020

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

SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

N_A or $L = 6.022 \times 10^{23}$ mol^{-1} $\qquad\qquad$ $R = 8.314$ J K^{-1} mol^{-1}

k or $k_B = R/N_A$

$dU = dq + dw$ $\qquad\qquad\qquad$ $H = U + pV$

$dw = -p_{ex}\, dV$ $\qquad\qquad\qquad$ $\gamma = C_p/C_v$

Perfect gas: $pV = nRT$ $\qquad$ and $\qquad$ $C_p - C_v = nR$

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

1)   *20 points*
a) The compression factor for ethylene is about 1.3 at p = 300 bar, about 0.6 at p = 100 bar, tends to 1 as p tends to zero. Explain this, briefly, in terms of molecular properties, and use pictures if they would help.
b) The excluded volume b for NH_3 is 3.7 x 10^{-2} dm^3 mol^{-1}. Justify the idea that, per molecule, the excluded volume is (16/3) πr^3 where r is the molecular radius. Use this result to estimate the radius of NH_3 molecules.

a) see notes (slide 22)

b)
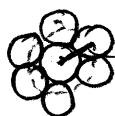
at closest approach, internuclear distance is $2r$

∴ excluded volume for 1 molecule is $\frac{4}{3}\pi(2r)^3$

$= \frac{4}{3}\pi 8r^3 = \frac{32}{3}\pi r^3$.

For many molecules, excluded volume $= N \cdot \frac{32}{3}\pi r^3 \times \frac{1}{2}$

$\frac{1}{2}$ because when molecule #1 excludes #2, likewise #2 excludes #1, so the $\frac{1}{2}$ avoids double counting. So, on a per molecule basis,

excluded volume $= \frac{16}{3}\pi r^3$.

3.7×10^{-2} dm^3 $mol^{-1} = 3.7 \times 10^{-2} \times 10^{-3}$ m^3 mol^{-1}

$= \frac{3.7 \times 10^{-2} \times 10^{-3}}{6.022 \times 10^{23}}$ m^3 molecule^{-1}

$= 6.14 \times 10^{-29}$ m^3 molecule^{-1}

$= \frac{16}{3}\pi r^3$

∴ $r^3 = 3.67 \times 10^{-30}$ m^3 ∴ $r = 1.54 \times 10^{-10}$ m.

(see homework 1C6 and 1C7)

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2) 15 *points*

Consider samples of He (4 g/mol) and Ar (40 g/mol) at 298 K and 10^5 Pa. Calculate
i) The average kinetic energies of the He and Ar atoms.
ii) The ratio of the root mean square velocities c_{He}/c_{Ar}.
iii) In effusion experiments, under the same conditions, and unknown molecule effuses 2.5 times more slowly than Ar. Estimate the molar mass of the unknown molecule.

i) Average KE is $E_K = \frac{3}{2} k_B T$ independent of mass so same for He and Ar.

$$E_K = 1.38 \times 10^{-23} \, J K^{-1} \times 298 K \times 1.5$$
$$= 6.17 \times 10^{-21} \, J.$$
$$(or \ 3.71 \ kJ \ mol^{-1})$$

ii) $E_K = \frac{1}{2} m c^2$ $\therefore$ $m_{He} c_{He}^2 = m_{Ar} c_{Ar}^2$

$$\therefore \frac{c_{He}^2}{c_{Ar}^2} = \frac{m_{Ar}}{m_{He}} = 10 \quad \therefore \frac{c_{He}}{c_{Ar}} = \sqrt{10}.$$

iii) Rate of effusion $\propto c \propto \frac{1}{\sqrt{m}}$

$$\therefore m \ unknown = 40 g \, mol^{-1} \times 2.5^2$$
$$= 250 \ g \, mol^{-1}.$$

3)   *15 points*

The enthalpy of combustion of propanal C_2H_5CHO*(l)* to make H_2O*(l)* and CO_2*(g)* is -1817 kJ mol^{-1}.

The enthalpy of combustion of propanone (acetone) CH_3COCH_3*(l)* to make H_2O*(l)* and CO_2*(g)* is -1769 kJ mol^{-1}.

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

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

All the data are for 298 K and can be assumed not to vary with T.

Use the above data to deduce

a) ΔU_{298} for the combustion of C_2H_5CHO*(l)*.

b) $\Delta_f H_{298}$ for propanone, CH_3COCH_3*(l)*.

c) ΔH_{298} for the isomerization of C_2H_5CHO*(l)* to CH_3COCH_3*(l)*.

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

$$C_2H_5CHO(l) + 4O_{2(g)} \longrightarrow 3H_2O(l) + 3CO_{2(g)}$$

$\therefore \Delta n_{gas} = 0 + 3 - 4 - 0 = -1$
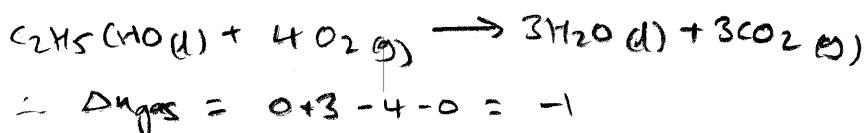
$\therefore \Delta U = \Delta H + RT$ here

$= -1817 \text{ kJ mol}^{-1} + \dfrac{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{1000 \text{ (J/kJ)}}$

$= -1814.5 \text{ kJ mol}^{-1}$.

(b) In terms of $\Delta_f H$, with x the unknown for propanone,

$$CH_3COCH_3(l) + 4O_{2(g)} \longrightarrow 3CO_{2(g)} + 3H_2O(l)$$
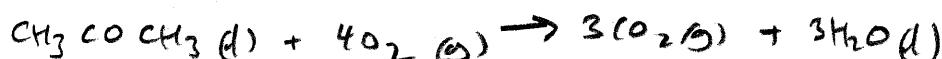
$\Delta H_{298} = -1769 \text{ kJ mol}^{-1} = 3\Delta_f H(H_2O) + 3\Delta_f H(CO_2) - 4\Delta_f H(O_2) - x$

$= 3x - 286 - 3 \times 394 - 4 \times 0 - x \quad \text{kJ mol}^{-1}$

$\therefore x = -(-1769 + 3 \times 286 + 3 \times 394 \text{ kJ mol}^{-1}) = -271 \text{ kJ mol}^{-1}$

(c)

$$C_2H_5CHO + 4O_2 \xrightarrow{\;x\;} CH_3COCH_3 + 4O_2$$

$-1817 \text{ kJ mol}^{-1} \searrow \quad 3CO_2 + 3H_2O \quad \nearrow -1769 \text{ kJ mol}^{-1}$
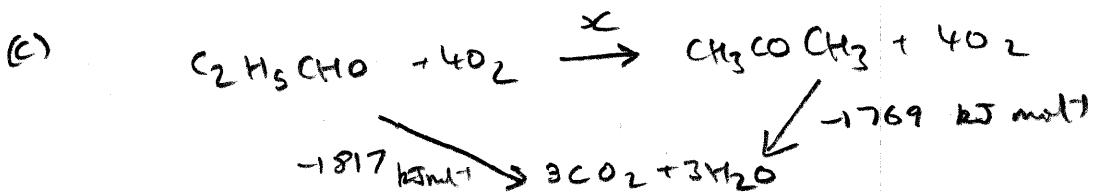
$x - 1769 \text{ kJ mol}^{-1} = -1817 \text{ kJ mol}^{-1} \quad \therefore x = -48 \text{ kJ mol}^{-1}$.

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