**PHYSICAL CHEMISTRY 3510**

**EXAM 1**

**September 22, 2017**

*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:

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

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

relative to C = 12, the atomic masses of H and O are 1 and 16

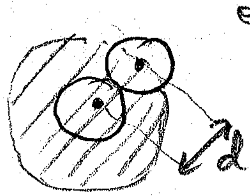
Perfect gas: $pV = nRT$

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

1) *30 points*

a) Kr gas has a van der Waals b parameter of $3 \times 10^{-5}$ m$^3$ mol$^{-1}$. Use this information to estimate the diameter of Kr atoms, assuming they are spherical.
b) 1 mol of a real gas at 230 K and $9 \times 10^6$ Pa has a volume 1.15 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.
c) 0.300 m$^3$ of a perfect gas has a mass of 0.993 kg at $10^5$ Pa and 298 K. What is the molar mass?

a)




excluded volume for 1 molecule $= \frac{4}{3}\pi d^3$

$\therefore$ for 1 mol $= \frac{4}{3}\pi N_A d^3$

but this counts exclusions twice

so $b \approx \frac{2}{3}\pi N_A d^3 = 3 \times 10^{-5}$ m$^3$ mol$^{-1}$

$\therefore d^3 = 3 \times 10^{-5} \text{ m}^3 \cdot \frac{3}{2} \frac{1}{\pi} \cdot \frac{1}{6.02 \times 10^{23}}$

$= 2.38 \times 10^{-29} \text{ m}^3 \quad \therefore \underline{d = 2.88 \times 10^{-10} \text{ m}}.$

b) $Z = \frac{pV}{RT} = 1.15$, If ideal, $V_{ideal} = \frac{RT}{p} = \frac{8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 230 \text{ K}}{9 \times 10^6 \text{ Pa}}$

$= 2.12 \times 10^{-4} \text{ m}^3$

$\therefore V = 1.15 \, V_{ideal} = \underline{2.44 \times 10^{-4} \text{ m}^3}$

$Z > 1$ because intermolecular repulsions dominate at short distances (small volume / high pressure).

c) Molar mass $= M$, mass of gas $= m = nM$.

$pV = nRT \;\therefore\; n = \frac{pV}{RT} \;\therefore\; \frac{pVM}{RT} = m \;\therefore\; M = \frac{mRT}{pV}$

$= \frac{0.993 \text{ kg} \times 8.314 \text{ JK}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{10^5 \text{ Pa} \times 0.300 \text{ m}^3} = \underline{0.082 \text{ kg mol}^{-1}}.$

2) *30 points*

a) Imagine that N molecules of a perfect gas with individual mass m are in a container of volume V at pressure p and temperature T. The mean square speed is $c^2$.
Given that $pV = Nmc^2/3$, deduce that the average kinetic energy of the molecules $\varepsilon$ is given by $\varepsilon = 1.5\, k_B\, T$.

b) Use this result to find $\varepsilon$ for (i) $H_2$ molecules and (ii) $O_2$ molecules at 298 K.

c) What is the ratio $c(H_2)/c(O_2)$ at 298 K?

a) $pV = nRT = \frac{Nmc^2}{3} = \frac{nN_A mc^2}{3} \quad \therefore RT = \frac{N_A mc^2}{3}$

$\therefore mc^2 = \frac{3RT}{N_A} = 3k_BT \quad \therefore \varepsilon = \frac{1}{2}mc^2 = \frac{3}{2}k_BT.$

b) (i) $\varepsilon = 1.5 \times 1.38 \times 10^{-23}\,\mathrm{JK^{-1}} \times 298\,\mathrm{K} = 6.17 \times 10^{-21}\,\mathrm{J}.$

(ii) The same because $\varepsilon$ is independent of mass.

c) $\frac{1}{2}mc^2$ the same so $c^2 \propto \frac{1}{m} \quad \therefore c \propto \frac{1}{\sqrt{m}}$.

$m_{H_2}/m_{O_2} = 2/32 = 1/16 \quad \therefore c_{H_2}/c_{O_2} = \sqrt{16} = 4.$

3) *40 points*

Consider 1 mol of a van der Waals gas.

a) Evaluate $dp/dV$ and $d^2p/dV^2$.

b) Given the information that at the critical point the p-V diagram shows a horizontal inflection, and that the critical volume $V_c = 3b$, prove that the critical temperature $T_c = 8a/(27Rb)$ and the critical pressure $p_c = a/(27b^2)$.

$n=1$

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

$$\frac{dp}{dV} = -RT(V-b)^{-2} + 2aV^{-3} \qquad (1)$$

$$\frac{d^2p}{dV^2} = 2RT(V-b)^{-3} - 6aV^{-4} \qquad (2)$$

b) Horizontal inflection means both derivatives are zero.

Substitute $V_c = 3b$ into (1):

$$\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \therefore \frac{RT_c}{(2b)^2} = \frac{2a}{(3b)^3} \therefore \frac{RT_c}{4b^2} = \frac{2a}{27b^3}$$

$$\therefore T_c = \frac{4b^2}{R} \cdot \frac{2a}{27b^3} = \frac{8a}{R \cdot 27b}.$$

Go back to vderW eqn;

$$p_c = \frac{RT_c}{V_c-b} - \frac{a}{V_c^2} = \frac{8a}{27b} \cdot \frac{1}{2b} - \frac{a}{9b^2}$$

$$= \frac{a}{b^2}\left(\frac{4}{27} - \frac{1}{9}\right)$$

$$= \frac{a}{b^2}\left(\frac{1}{27}\right).$$