2018 Fall Semester Quiz 4
For General Chemistry I (CH101)

Date: November 5 (Mon),   Time: 19:00 ~ 19:45
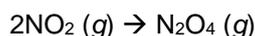
Professor Name	Class	Student I.D. Number	Name
			Solution

The Gas Constant, R

$8.205\ 74 \times 10^{-2}$ L·atm·K^{-1}·mol^{-1}
$8.314\ 47 \times 10^{-2}$ L·bar·K^{-1}·mol^{-1}
$8.314\ 47$ L·kPa·K^{-1}·mol^{-1}
$8.314\ 47$ J·K^{-1}·mol^{-1}
62.364 L·Torr·K^{-1}·mol^{-1}

Avogadro constant (N_A): 6.022 x 10^{23} mol^{-1}

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1. (Total 4 pts) When NO_2 is cooled to room temperature, some of it reacts to form a dimer, N_2O_4, through the reaction

$$2NO_2\ (g) \rightarrow N_2O_4\ (g)$$

Suppose 15.2 g of NO_2 is placed in a 10.0 L flask at high temperature and the flask is cooled to 25 °C. The total pressure is measured to be 0.500 atm. **What partial pressures and mole fractions of NO_2 and N_2O_4 are present?**

Partial pressure		Mole fraction	
P_{NO_2}	$P_{N_2O_4}$	X_{NO_2}	$X_{N_2O_4}$
0.19 atm	**0.31 atm**	**0.38**	**0.62**

Initially, there is 15.2 g/46.01 g mol^{-1} = 0.330 mol NO_2, and therefore, the same number of moles of nitrogen atoms. If at 25°C there are n_{NO_2} moles NO_2 and $n_{N_2O_4}$ moles N_2O_4, then, because the total number of moles of nitrogen atoms is unchanged,

$$n_{NO_2} + 2n_{N_2O_4} = 0.330\ \text{mol} \qquad (a)$$

To find a second relation between n_{NO_2} and $n_{N_2O_4}$, use Dalton's law:

$$P_{NO_2} + P_{N_2O_4} = 0.500\ \text{atm}$$

$$\frac{RT}{V}n_{NO_2} + \frac{RT}{V}n_{N_2O_4} = 0.500\ \text{atm}$$

$$n_{NO_2} + n_{N_2O_4} = 0.500\ \text{atm}\frac{V}{RT}$$

$$= \frac{(0.500\ \text{atm})(10.0\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}$$

$$n_{NO_2} + n_{N_2O_4} = 0.204\ \text{mol} \qquad (b)$$

Subtracting Equation b from Equation a gives

$$n_{N_2O_4} = 0.126\ \text{mol}$$

$$n_{NO_2} = 0.078\ \text{mol}$$

From these results, NO_2 has a mole fraction of 0.38 and a partial pressure of (0.38)(0.500 atm) = 0.19 atm, and N_2O_4 has a mole fraction of 0.62 and a partial pressure of (0.62)(0.500 atm) = 0.31 atm.

Correct answers; +1 pt each. *No partial points will be given for the mistakes in calculation.*
* Partial points: 1 pt (out of 4 pts) will be given if the student calculated partial pressures and mole fractions using the <u>improper</u> gas constant (unit: L <u>bar</u> K^{-1} mol^{-1}). *No partial points will be given for the mistakes in calculation.*

2. (Total 8 pts) According to the Maxwell-Boltzmann distribution, the fraction of molecules, $\Delta N/N$, gives the speed distribution function $f(u)$: $\Delta N/N = f(u)\Delta u$.

$$f(u) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2k_B T}\right)$$

*The molecular weights of O_2, He, and Xe are 32.00 g/mol, 4.00 g/mol, and 131.3 g/mol.

(a) **(2 pts)** $\bar{u}$ for O_2 is 444 m/s. **Calculate $\bar{u}$ for He and Xe at 298 K**
+1 pt each for the correct answers; No partial points.

$$\bar{u} = \sqrt{\frac{8RT}{\pi N_A m}} \propto \sqrt{\frac{1}{m}}$$

$$\therefore \bar{u}(He) = 444 * \sqrt{\frac{32.00\ g/mol}{4.00\ g/mol}} = \mathbf{1260}\ m/s, \quad \bar{u}(Xe) = 444 * \sqrt{\frac{32.00\ g/mol}{131.3\ g/mol}} = \mathbf{219}\ m/s$$

(b) **(2 pts)** u_{mp} for O_2 is 394 m/s. **Calculate u_{mp} for He and Xe at 298 K**
+1 pt each for the correct answers; No partial points.

$$u_{mp} = \sqrt{\frac{2RT}{N_A m}} \propto \sqrt{\frac{1}{m}}$$

$$\therefore u_{mp}(He) = 394 * \sqrt{\frac{32.00\ g/mol}{4.00\ g/mol}} = \mathbf{1110}\ m/s, \quad u_{mp}(Xe) = 394 * \sqrt{\frac{32.00\ g/mol}{131.3\ g/mol}}$$

$$= \mathbf{195}\ m/s$$

(c) **(2 pts)** Briefly explain why $\bar{u}$ and u_{mp} are different in the Maxwell-Boltzmann distribution.
<u>Full credit (+ 2pts):</u> The Maxwell–Boltzmann distribution is <u>not symmetrical</u> because f(u) depends on u^2 and e^{-u^2}.
* If the student explained <u>the meaning of each speed</u>, <u>full credit (+2 pts)</u> will be also given, for example, $\left[\frac{df(u)}{dv} = 0\right]_{u=u_{mp}}$ or $\bar{u} = \int_0^\infty uf(u)du$.

(d) **(2 pts) Plot the Maxwell-Boltzmann distribution of molecular speeds for He and Xe at 298 K.** You *don't* need to point out the $\bar{u}$ and u_{mp}, obtained from (a-b), in the graph.
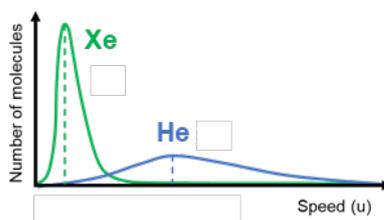
+ 2 pts for the correct plots (distribution-wise).
* If the student did <u>not</u> consider that <u>the total number of the molecules is same</u>, 1 pt will be deducted.

3. (**Total 10 pt**) The underlying assumptions of **the kinetic theory of gases** are simple, (i) A pure gas consists of a large number of identical molecules separated by distances that are great compared with their size; (ii) The gas molecules are constantly moving in random directions with a distribution of speeds; (iii) The molecules exert no forces on one another between collisions, so between collisions they move in straight lines with constant velocities; (iv) The collisions of molecules with the walls of the container are elastic; no energy is lost during a collision.

Suppose that there are **N molecules** in the box and one molecule with **mass of m** collides elastically with a wall of the box with speed of u. **Show that the average kinetic energy per molecule ($\bar{\varepsilon}$) is** $\frac{3}{2}k_BT$. (k_B is Boltzmann constant.) You should write down **_all the calculation process_** to get the full points.

(1)   **Force acted on the original wall by a molecule (+ 3 pts)**

$$\Delta p_{x,mol} = m(-v_x) - mv_x = -2mv_x$$
$$\Delta p_{x,wall} = 2mv_x$$
$$\Delta t = 2\ell/v_x$$
$$f = ma = m\frac{\Delta v}{\Delta t} = \frac{\Delta p_{x,wall}}{\Delta t} = \frac{mv_x^2}{\ell}$$

(2)   **Force acted on the original wall by N molecules   (+ 1 pt)**

$$F = \frac{mv_{x1}^2}{\ell} + \frac{mv_{x2}^2}{\ell} + \frac{mv_{x3}^2}{\ell} + \cdots + \frac{mv_{xN}^2}{\ell} = N\frac{m\overline{v_x^2}}{\ell}, \qquad \text{where } \overline{v_x^2} = \frac{1}{N}\left(v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \cdots + v_{xN}^2\right)$$

(3)   **Pressure on the original wall of area A (+ 1 pt)**

$$P = \frac{F}{A} = \frac{Nm}{A\ell}v_x^2 = \frac{Nm}{V}v_x^2$$

(4)   **The mean-square speed of a molecule with no preferred direction (+ 1 pt)**

$$\overline{u^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$
$$PV = Nmv_x^2 = \frac{1}{3}Nm\overline{u^2}$$

(5)   **Ideal gas law (+ 3 pts)**

$$nRT = \frac{1}{3}Nm\overline{u^2} \;\rightarrow\; RT = \frac{1}{3}N_A m\overline{u^2} \qquad (from\ the\ ideal\ gas\ law)$$

(6)   **Average kinetic energy per molecule (+ 1 pt)**

$$\overline{E} = \frac{1}{2}N_A m\overline{u^2} \;\rightarrow\; \bar{\varepsilon} = \frac{1}{2}m\overline{u^2} = \frac{1}{2}\left(\frac{3RT}{N_A}\right) = \frac{3}{2}k_BT$$

4. (Total 11 pts) Assume that you have 5000 mL flask containing 150 g of CO_2 at 500 K. The molecular weight of CO_2 is 44.0 g/mol.

TABLE 9.3

van der Waals Constants of Several Gases

Name	Formula	a (atm L^2 mol^{-2})	b (L mol^{-1})
Ammonia	NH_3	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO_2	3.592	0.04267
Hydrogen	H_2	0.2444	0.02661

(a) (**3 pts**) Calculate the pressure (atm) of the sample using the **ideal gas law**. Show all the calculation process.

$$PV = nRT$$

$$n = \frac{150 \text{ g}}{44.0 \text{ g/mol}} = 3.41 \text{ mol}$$

$$P = \frac{nRT}{V} = \frac{(3.41 \text{ } mol)(0.08206 \text{ } L \text{ } atm \text{ } mol^{-1}K^{-1})(500 \text{ } K)}{5.00 \text{ } L} = 28.0 \text{ atm}$$

Ideal gas law, + 1 pt
Correct answer, + 2 pts; No partial points for the wrong answer.

(b) (**3 pts**) Calculate the pressure (atm) of the sample using the **van der Waals equation**. Show all the calculation process.

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

$$n = \frac{150 \text{ g}}{44.0 \text{ g/mol}} = 3.41 \text{ mol}$$

$$P = \frac{(3.41 \text{ } mol)(0.08206 \text{ } L \text{ } atm \text{ } mol^{-1}K^{-1})(500 \text{ } K)}{5.00 \text{ } L - (3.41 \text{ } mol)(0.04267 \text{ } L \text{ } mol^{-1})}$$

$$- (3.592 \text{ atm } L^2 \text{ } mol^{-2})\frac{(3.41 \text{ } mol)^2}{(5.00 \text{ } L)^2} = 28.9 \text{ } atm - 1.67 \text{ } atm$$

$$= 27.2 \text{ } atm$$

Van der Waals equation, + 1 pt
Correct answer, + 2 pts; No partial points for the wrong answer.

(c) (**5 pts**) On the basis of the effects of van der Waals constants on the pressure, explain the reason why P_{ideal} and $P_{van \text{ } der \text{ } Waals}$, you obtained in (a) and (b), are different. Do attractive or repulsive forces dominate?

$P_{van \text{ } der \text{ } Waals}$ in (b) is less than P_{ideal} in (a). Different from the ideal gas, the real gas has unneglectable volume and attraction between molecules. Both factors can affect the pressure.

The effect of the **b** term in the van der Waals equation is related to the **excluded volume of particles (repulsive forces)**, increasing P from 28.0 atm to 28.9 atm. On the other hand, the **a** term in the van der Waals equation is related to the **intermolecular attraction**, decreasing P by 1.67 atm. The **a term is more influential** than the b term; thus, **attractive forces dominate** in (b).

[Keywords]

- Meaning of **a and b** term → **1.5 pt each**
- **Attractive** forces are dominate → **2 pts**

5. (3 pts) State which attractive intermolecular forces does play the most dominant role in the following molecular pairs.
+0.5 pt each for correct answers.

(a) **Sodium ion – water**
Ion – dipole force

(b) **Hydroxide ion – water**
Ion – dipole force

(c) **Carbon dioxide gas – water**
Induced dipole force (Dipole – induced dipole force)

(d) **Methanol – ethanol**
Hydrogen bonding

(e) **Chloride ion – hexane(C_6H_{14})**
Induced dipole force (Ion – induced dipole force / Charge – induced dipole force)

(f) **Octane (C_8H_{18}) – hexane (C_6H_{14})**
Induced dipole – induced dipole force (London dispersion force / Van der Waals force)

6. (4 pts) The following table gives several important points on the pressure 0 temperature diagram of ammonia:

Sketch the phase diagram of ammonia using this information. You should indicate _where triple point, critical point, normal boiling point, and normal melting point are_ in the graph. In addition, point out the _phases (solid / liquid / gas)_ in the graph.
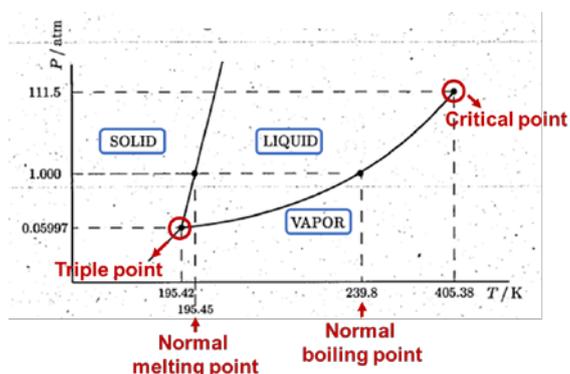
Shape of the phase diagram; +0.5 pt
Triple point, critical point, normal boiling point, and normal melting point; +0.5 pt each
Phases; +0.5 pt each