THE COLLEGE OF THE BAHAMAS

EXAMINATION

SEMESTER 01-2009

FACULTY OF PURE AND APPLIED SCIENCES

SCHOOL OF SCIENCES AND TECHNOLOGY

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FREEPORT
EXUMA
ELEUTHERA

DATE AND TIME OF EXAMINATION: Wednesday, April 29, 2009, 7:00 PM in room D2

DURATION: ~~**3 HOURS**~~ 1h.

COURSE NUMBER: CHEM 240

COURSE TITLE: Physical Chemistry

STUDENT NAME:

STUDENT NUMBER:

LECTURER'S NAME

INSTRUCTIONS TO CANDIDATES: This paper has 6 pages and 2 sections. Please follow the instructions given with each section.

Candidates may need the following information: RAM of H = 1.01, He = 4.00, C = 12.0, N = 14.0, O = 16.0
$R = 8.314\ J\ mol^{-1}K^{-1}$, 1.000 atm = 101300, $L = 6.022\times10^{23} mol^{-1}$, $h = 6.626\times10^{34}$, $g = 9.81\times m\ s^{-2}$.

SECTION I: Multiple Choice Questions

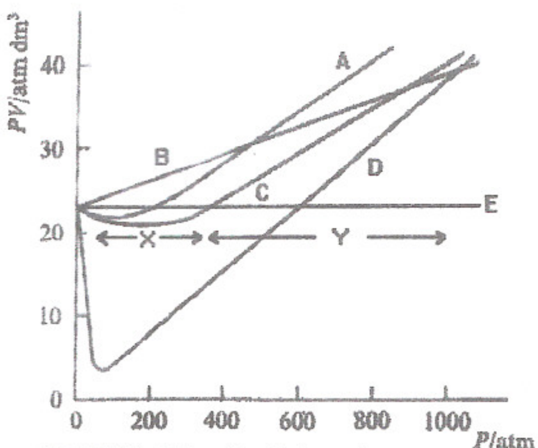
Select the SINGLE best alternative in each of the following cases. Indicate your answer by marking the corresponding letter on the answer sheet provided. Use a cross (X) in soft pencil to make alterations easy. ~~You will need to look at the graphs attached to your question paper.~~ There is a total of 20 marks for this section.

1) Oxygen is collected over water at 25°C and 775 mmHg. What is the partial pressure of oxygen in mmHg if the vapour pressure of water is 23.8 mmHg at 25°C?
   - A 23.8
   - B 750
   - C 751
   - D 775
   - E 799

2) Which of the following statements is NOT true according to the kinetic theory of gases?
   - A molecules occupy zero volume
   - B molecules move randomly
   - C molecules are attracted to one another
   - D molecules suffer elastic collisions
   - E the average kinetic energy of molecules is proportional to temperature.

3) 5 cm^3 of helium (RMM 4.0) effuse through a small hole in 16 minutes. Under the same conditions of temperature and pressure the same volume of sulfur dioxide (RMM 64) would effuse in
   - A 4 minutes.
   - B 16 minutes.
   - C 32 minutes.
   - D 64 minutes.
   - E 256 minutes.

QUESTIONS **4 TO 7** involve Graph 1 which shows plots of PV against P for 1 mol of various gases (A, B, C, D and E) at a certain constant temperature ~~and volume~~.



GRAPH 1: PV against P for various gases

4) Which line shows the behaviour of an ideal gas?
   - A A
   - B B
   - C C
   - D D
   - E E

5) Which line shows the gas with the highest boiling point?
   - A A
   - B B
   - C C
   - D D
   - E E

6) Gas C shows a region X in which the product PV reaches a minimum. Which one of the following best explains this minimum?
   - A The gas is behaving ideally.
   - B Forces of attraction between molecules are at a maximum.
   - C The size of the molecules is appreciable in comparison with the spaces between them.
   - D The molecular motion is at a minimum.
   - E The size of the molecules is at a minimum.

7) Gas C shows a region Y in which the product PV rises as the pressure increases. Which one of the following best explains this behaviour?
   - A The molecules are being pushed together against forces of repulsion as pressure increases.
   - B The forces of attraction between molecules are becoming larger and larger as pressure increases.
   - C The spaces between molecules are becoming larger and larger as pressure increases.
   - D Both pressure and volume are increasing simultaneously.
   - E The gas is behaving ideally.

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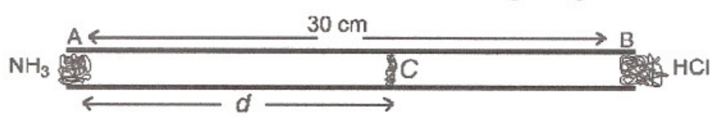
8) Which gas would be expected to have the highest average molecular speed at 300 K?
   - A Hydrogen, H_2
   - B Methane, CH_4
   - C Ethane, C_2H_6
   - D Propane, C_3H_8
   - E Butane, C_4H_{10}

Questions 8 and 9 refer to the following diagram

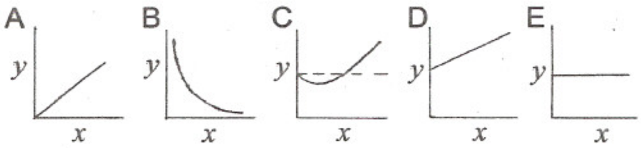


showing a 30 cm glass tube. At one end is placed a piece of glass wool soaked in concentrated hydrochloric acid and at the other end a similar piece soaked in concentrated ammonia. A white band forms at C.

9) The band consists of
   A solid ammonia
   B solid hydrogen chloride
   C solid nitrogen trichloride
   D solid ammonium chloride
   E another substance not mentioned above

10) To 2 significant figures, length *d* is expected to be:
   A 12 cm
   B 1.5 cm
   C 18 cm
   D 20 cm
   E 10 cm

Question 10 to 14 involve the following graphs



In each of the following questions select the graph which best fulfils the requirements.

11) *y* is rate of effusion and *x* is the square root of RMM for an ideal gas at constant pressure and temperature.

12) *y* is *P* and *x* is *1/V* for a fixed number of moles of an ideal gas at constant temperature.

13) *y* is *z (the compressibility factor)* and *x* is *P* for a fixed number of moles of a real gas at constant temperature.

14) *y* is *P* and *x* is the *Celsius* temperature, for an ideal gas at constant temperature and volume.

15) *y* is *R* (the ideal gas constant) and *x* is *P* for a fixed mass of an ideal gas.

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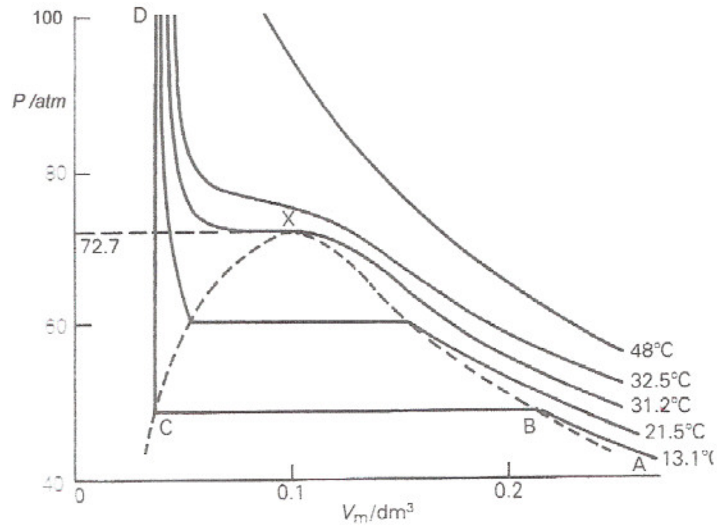
16) One mole of a diatomic gas requires more heat to raise its temperature by a given amount than for a monatomic gas because
   A diatomic molecules are smaller than monatomic ones.
   B diatomic gas molecules possess energy of rotation whereas monatomic ones do not.
   C diatomic gas molecules possess energy of vibration whereas monatomic ones do not.
   D diatomic gas molecules possess energy of vibration as well as rotation whereas monatomic ones do not.
   E diatomic gases have stronger intermolecular forces than monatomic ones.

Questions 17 and 18 involve the following diagram showing the variation of pressure with volume for a real gas at the indicated temperatures.



17) The critical temperature of the gas is:
   A 13.1°C
   B 21.5°C
   C 31.2°C
   D 32.5°C
   E 48°C

18) Within area ABXC there exists:
   A Only gas.
   B Gas and liquid
   C Only liquid
   D A supercritical fluid
   E A fourth state of matter

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19) ΔU, the change is internal energy of a system, is given by:
   A q
   B q + w
   C w
   D ΔH
   E nRT

20) A *closed system* is one where:
   A Neither energy nor matter is exchanged with the surroundings.
   B Matter but not energy is exchanged with the surroundings.
   C Energy but not matter is exchanged with the surroundings.
   D Both matter and energy are exchanged with the surroundings.
   E Both heat and work are exchanged with the surroundings.

SECTION II: STRUCTURED QUESTIONS

INSTRUCTIONS: Answer ALL questions from this section in the spaces provided on the question paper. There is a total of ** marks for this section. INDICATE NUMERICAL ANSWERS CLEARLY BY UNDERLINING.

1) This question concerns various aspects of ideal and real gases.

a) Account for the following observations in terms of the kinetic molecular theory of gases.

i) The volume of a gas can readily be reduced by increasing the applied pressure. (2)

There are wide spaces between the molecules (1) Hence the molecules can easily be pushed closer together and crammed into a smaller volume (1)

ii) The pressure exerted by a gas increases as the temperature is raised at constant volume (3)

As the temperature is raised the molecules move faster (1) Hence they impact the wall more frequently (1) and more violently (1) giving a higher pressure

b) This part of the question concerns the *Van der Waals equation*

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

which is sometimes used to describe the behaviour of real gases.

i) What aspect of a real gas does parameter a account for? (1)

"a" accounts for the attractive forces between molecules.

ii) What aspect of a real gas does parameter *b* account for? (1)

b accounts for the finite size of of the molecules / repulsive forces between molecules (1)

iii) In which one of the following gases would you expect *a* to be the largest: He, H_2, CO_2, O_2, N_2? Explain your choice. (Note the boiling points of these compounds are 4, 20, 195, 90, 77 K.) (3)

CO_2 (1) It is clear from the b.p.'s (1) that the attractive forces between the molecules is largest here (1)

iv) In which one of the following gases would you expect *b* to be the largest: He, CO_2, NH_3, $CH_3CH_2CH_2CH_3$, HCl, PH_3? Explain your choice. (2)

$CH_3CH_2CH_2CH_3$ (1) since the molecules are clearly the largest. (1)

 FBBfbb

(12)

2) This questions concerns the Kinetic theory of gases.

a) There are various ways of expressing the speed of the molecules of a gas. The root mean square speed $\sqrt{u^2}$ is given by $\sqrt{\frac{3RT}{M}}$. The average speed $\bar{u}$ of the molecules of a gas is given by $\sqrt{\frac{8RT}{\pi M}}$ and the most probable speed $\hat{u}$ is given by $\sqrt{\frac{2RT}{M}}$.

i) Calculate the ratio between these quantities for a given gas under the same conditions of temperature, and so rank them in increasing order, smallest first. (Your calculation should not be specific for any value of T or M.) (4)

$$\sqrt{u^2} : \bar{u} : \hat{u} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}} \ (1)$$

$$= \sqrt{3} : \sqrt{8/\pi} : \sqrt{2} \ (1) = 1.732 : 1.596 : 1.414 \ (1)$$

(for 4 sig figs) Hence $\sqrt{u^2} > \bar{u} > \hat{u}$ (1)

ii) Evaluate $\sqrt{u^2}$ for oxygen gas at 100°C. (3)

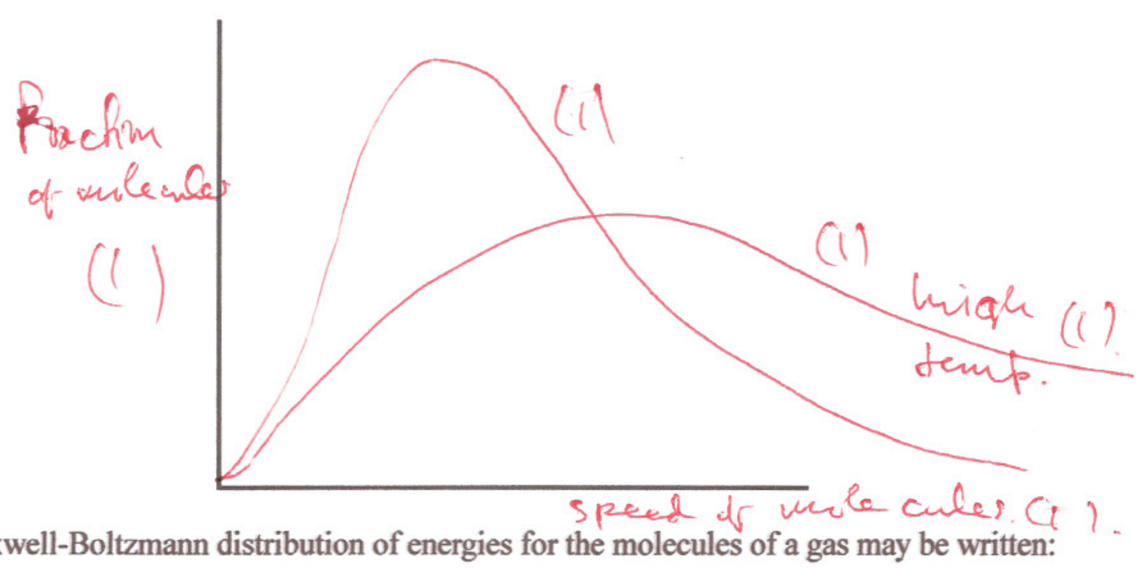
$$\sqrt{u^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times (273+100)}{(2 \times 16.0 \times 10^{-3})}} \ (1)(1) = 5.39 \times 10^2 \ ms^{-1}$$

$\simeq$ 539 ms^{-1} for 3 sig figs (1)

~~iii) Compare your value of $\sqrt{u^2}$ for oxygen with the escape velocity for the Moon (2.38 km s^{-1}) and comment on your result. (Note: the surface temperature of the moon regularly exceeds 100°C.) (2)~~

more space

b) Sketch a graph showing the Maxwell-Boltzmann distribution of speeds for the molecules of a gas at two different temperatures on the axes below: Make sure you label your axes and indicate which line shows the gas at the higher temperature. (5)



(12)

c) The Maxwell-Boltzmann distribution of energies for the molecules of a gas may be written:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-(E_2 - E_1)/(kT)}$$

where N_2/N_1 indicates the relative populations of the energy states E_2 and E_1.

i) Explain the meaning of the terms g_1 and g_2. (2)

ii) Assuming that $g_2/g_1 = 1$, calculate the relative populations of energy states which differ firstly by 0.5kT J and secondly by 100 kT J at around room temperature. (2)

iii) The first two electronic energy states of molecules (the *ground state* and the *first excited state*) differ by about 100 kT at room temperature. What can you conclude from this about the electronic energy state of the molecules in a gas at room temperature? (1)

i) These are the degeneracies of the energy states (1) ie. the number of possible states a molecule may have but still have the same energy (or 1)

1 { g_2 is the degeneracy of the state with energy E_2.
g_1 " " " " " " " " E_1.

ii) $\frac{N_2}{N_1} = 1 e^{-0.5kT/kT}$ (1) $= e^{-0.5} = 0.6065...$ (½)

$\frac{N_2}{N_1} = e^{-100} = 3.72 \times 10^{-44}$ (½)

iii) All the molecules are in their ground state.