**UNIVERSITY OF RUHUNA**
**BACHELOR OF SCIENCE GENERAL DEGREE (LEVEL I) SEMESTER (II)**
**EXAMINATION- JANUARY 2022**

**SUBJECT: Chemistry**
**COURSE UNIT: CHE 1222** **Time: Two (02) hours**

Answer **All** Questions.

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|---|---|---|
| Velocity of light, c | = | $2.997 \times 10^8$ m s$^{-1}$ |
| Avogadro number, $N_A$ | = | $6.022 \times 10^{23}$ mol$^{-1}$ |
| Universal gas constant, $R$ | = | 8.314 J K$^{-1}$ mol$^{-1}$ |
| | = | 0.0821 dm$^3$ atm K$^{-1}$ mol$^{-1}$ |
| Boltzmann constant, $k_B$ | = | $1.381 \times 10^{-23}$ J K$^{-1}$ |
| Faraday constant, $F$ | = | $9.6485 \times 10^4$ C mol$^{-1}$ |
| Electron charge, $e$ | = | $-1.602 \times 10^{-19}$ C |
| Planck's constant, $h$ | = | $6.626 \times 10^{-34}$ J s |
| Proton mass, $m_p$ | = | $1.673 \times 10^{-27}$ kg |
| Electron mass, $m_e$ | = | $9.10 \times 10^{-31}$ kg |
| Atomic mass unit, *amu* | = | $1.6606 \times 10^{-27}$ kg |
| Vacuum permittivity, $\varepsilon_0$ | = | $8.854 \times 10^{-12}$ J$^{-1}$ C$^2$ m$^{-1}$ |
| 1 eV | = | $1.6022 \times 10^{-19}$ J |

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1. Answer **all** parts

(a) Maxwell predicted that the speeds of individual molecules of an ideal gas would be distributed according to the Maxwell distribution of speeds function.

(i) Sketch a graph to show distribution of speeds of gas molecules of an ideal gas at two temperatures $T_1$ and $T_2$ ($T_2 > T_1$).

(05 marks)

(ii) Label the graphs with the temperatures $T_1$ and $T_2$ and mark approximate positions of the most probable speed, $V_{mp}$ and the mean speed, $\tilde{v}$ of molecules on one of the graphs.

(10 marks)

(iii) Write down the expressions for the mean speed and the most probable speed of gas molecules and distinguish between them.

(20 marks)

(iv) Calculate the mean speed of $O_2$ molecules at 298 K.

(15 marks)

(b) Dutch theoretical physicist, Johannes van der Waals (1837-1923) proposed that the ideal gas equation could be corrected to account for the effects that a behavior of a real gas deviates from that of an ideal gas.

(i) Write down the ideal gas equation and the equation proposed by van der Waals for the behavior of real gasses for $n$ moles of gasses. Briefly explain what do the van der Waals constants $a$ and $b$ account for?

(20 marks)

(ii) If one mole of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.00 atm. Use the van der Waals equation to estimate the pressure exerted by 1.000 mol of $Cl_2$ gas in 22.41 L at 0.0 °C. Comment on the values of pressure of the ideal gas and $Cl_2$ gas.

(30 marks)

Note: van der Waals constants for $Cl_2$ gas, $a = 6.49\ L^2\ atm\ mol^{-2}$ and $b = 0.0562\ L\ mol^{-1}$

2. Answer **all** parts

(a) The first law of thermodynamics accounts the total energy change of a system due to two types of energy transformation.

(i) Stating the sign conversion and two types of energy transformations, express the first law of thermodynamics.

(15 marks)

(ii) The volume of a perfect gas in a container was $V_1$ at temperature T and the container volume was changed to $V_2$ keeping the temperature constant at T. If the volume change occurred maintaining the system in equilibrium with surrounding, derive the expression for the work change.

(35 marks)

(b) A 500 $cm^3$ of an ideal gas, which was in the thermodynamic state of 300 K temperature and 100 atm pressure, is expanded isothermally to half of its initial pressure. Calculate the q, $\Delta U$, $\Delta H$ for each of the following expansions.

(i) Irreversible expansion against zero external pressure.

(10 marks)

(ii) Irreversible expansion against 50 atm external pressure.

(25 marks)

(iii) Reversible expansion

(15 marks)

3. Answer **all** parts

(a) The thermodynamics relations derived relating fundamental thermodynamics quantities could be used only under the specific conditions for a given system. Give the specific conditions related to each of the following thermodynamics expressions.

(i) $\Delta U = nC_{v,m}\Delta T$

(ii) $\Delta H = nC_{p,m}\Delta T$

(iii) $pV^{\gamma} = K$, $TV^{(\gamma-1)} = K$, and $T^{\gamma}p^{(1-\gamma)} = K$, where K is a constant

(iv) $w = -nRTln\, \frac{p_1}{p_2}$

(v) $dS = \frac{dq_{rev}}{T}$

(30 marks)

(b) Explain the use of the appropriate relations and information from above part (a) with other fundamental relations to derive the relationship, $TV^{(\gamma-1)} = K$.

(40 marks)

(c) A system containing 3 moles of an ideal monoatomic gas at 340 K and 8 atm pressure undergoes an adiabatic expansion to half of its initial pressure reversibly. Calculate q, ΔT, ΔU, ΔH and w for the process. $C_{v,m}$ and $C_{p,m}$ for the monoatomic gas are 3R/2 and 5R/2, respectively.

(30 marks)

4. Answer **all** parts

(a) The entropy is a measure of the randomness of a system and its change can be calculated using the heat transfer between the system and the surrounding at the reversible condition. $dS = \frac{dq_{rev}}{T}$. State the thermodynamics conditions and relations used in the derivations of expressions given below.

(i) $\Delta S = nC_{v,m}\ln\frac{T_2}{T_1}$ (20 marks)

(ii) $\Delta S = nC_{p,m}\ln\frac{T_2}{T_1}$ (10 marks)

(iii) $\Delta S_{Trans} = \frac{\Delta H_{Trans}}{T_{Trans}}$ (10 marks)

(b) 10 moles of a monoatomic gas, which is in the initial state of 25 °C and 10 atm pressure, was expanded adiabatically to a final state of 4 atm pressure. When the expansion was against a 4 atm external pressure, the final temperature was 227 K while it was 207 K for the reversible expansion. Calculate the entropy changes in the system, surrounding, and the universe for both expansions.

(60 marks)

5. Answer **all** parts

(a) NO and $O_2$ gases were mixed in a reaction container of volume V at 293 K. When the concentration of $O_2$ was doubled, the rate of the reaction doubled. When the concentrations of both NO and $O_2$ were doubled, the rate of the reaction increased by a factor of 8.

(i) Find the order of the reaction with respect to each species and hence the overall order of the reaction.

(30 marks)

(ii) The numerical value of the rate constant ($k$) was found to be $8.92 \times 10^6$, what is the unit of the rate constant, $k$?

(05 marks)

(iii) *What is the change of the reaction rate if the volume of the container is reduced to* one third of the original volume, V?

(10 marks)

(iv) What is the change of the reaction rate if the volume of the container is doubled?

(10 marks)

(b) The reaction between NO and $O_2$ [above part (a)] is $2NO + O_2 \rightleftharpoons 2NO_2$, and the proposed mechanism is

Step 1 $\qquad NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

Step 2 $\qquad N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$

Show that the rate constant, $k = \frac{k_1 k_2}{k_{-1}}$

(45 marks)

6. Answer **all** parts

(a) The four commonly studied colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure.

(i) State the assumption(s) on which the colligative properties are based.

(10 marks)

(ii) Briefly discuss the *following statement.*

"All of the colligative properties result from lowering of the chemical potential of the solvent in the presence of a solute."

(15 marks)

(iii) Calculate the concentration of a urea ($NH_2CONH_2$) solution that has an osmotic pressure of 30.0 atm at 25 °C.

(15 marks)

(b) Raoult's law is a law of physical chemistry with implications in thermodynamics.

(i) State the Raoult's law and give the molecular interpretation for the same.

(20 marks)

(ii) The vapour pressure of a 500 g sample of benzene was 400 torr and it was lowered to 386 Torr when 19.06 g of a nonvolatile organic compound was dissolved in it. Calculate the molar mass of the compound. (The molar mass of benzene is 78.11 g)

(30 marks)

(iii) State the assumption(s) you made in above part (b)-ii.

(10 marks)

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