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QUALIFICATION: **VARIOUS**	
QUALIFICATION CODE: **VARIOUS**	LEVEL: **6**
COURSE: **PHYSICAL CHEMISTRY**	COURSE CODE: **PCH602S**
DATE: **NOVEMBER 2024**	SESSION: **1**
DURATION: **3 HOURS**	MARKS: **100**

FIRST OPPORTUNITY: EXAMINATION QUESTION PAPER

EXAMINER: ***Prof Habauka Kwaambwa***

MODERATOR: ***Dr Euodia Hess***

INSTRUCTIONS

1. Answer ALL the questions in Sections A and B.
2. Answer all questions on the separate answer sheet.
3. Please write neatly and legibly.
4. Do not use the left side margin of the exam paper. This must be allowed for the examiner.
5. No books, notes and other additional aids are allowed.
6. Mark all answers clearly with their respective question numbers.

PERMISSIBLE MATERIALS

Non-Programmable Calculator

ATTACHMENTS

List of Useful Constants and Equation

THIS QUESTION PAPER CONSISTS OF 8 PAGES (Including this front page and a list of useful constants and equation as an attachment)

SECTION A: MULTIPLE CHOICE QUESTIONS [20]

There are 10 questions in this section. Choose the correct answer. Each question carries 2 marks.

1. A gas sample at 25°C occupies 105 mL at a pressure of 698 Torr. What volume will it occupy at this temperature and a pressure of 1.91 atm?
   A. 50.5 mL
   B. 3.84 L
   C. 59.9 mL
   D. 0.0771 L
   E. None of the above

2. A system suffers an increase in internal energy of 80 J and at the same time has 50 J of work is done on it. What is the heat change of the system?
   A. + 130 J
   B. + 30 J
   C. – 103 J
   D. – 30 J
   E. 0 J

3. The ΔH^{o} for the following reaction at 298 K is - 36.4 kJ.

   $$\frac{1}{2}H_2(g)+\frac{1}{2}Br_2(\ell)\rightarrow HBr(g)$$

   Calculate ΔU^{o} at 298 K.
   A. – 35.2 kJ
   B. + 35.2 kJ
   C. – 36.4 kJ
   D. – 37.6 kJ
   E. + 37.6 kJ

4. The entropy will usually increase when:
   I. Molecule is broken into two or more smaller molecules.
   II. A reaction occurs that results in an increase in the number of moles of gas.
   III. A solid changes to a liquid.
   IV. A liquid change to a gas
   A. I only
   B. II only
   C. III only
   D. IV only
   E. I, II, III, and IV

5. For which of the following reactions would ΔH^{o} for the reaction be equal to ΔH_f^{o} (heat of formation):

   A. $PCl_3(g) + \frac{1}{2}O_2(g) \rightarrow POCl_3(g)$

   B. $\frac{1}{2}N_2O(g) + \frac{1}{4}O_2(g) \rightarrow NO(g)$

   C. $CaO(s) + SO_2(g) \rightarrow CaSO_3(s)$

   D. $2N_2(g) + O_2(g) \rightarrow 2N_2O(g)$

   E. $Al(s) + \frac{3}{2}H_2(g) + \frac{3}{2}O_2(g) \rightarrow Al(OH)_3(s)$

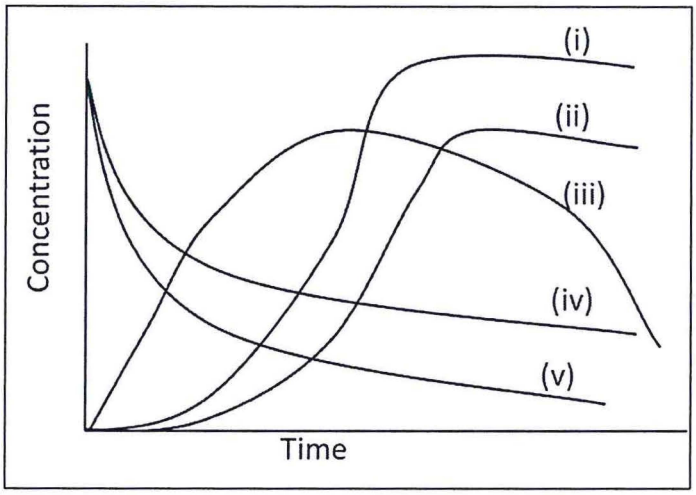
6. Which of the following aqueous solutions has the highest ionic strength (all salts are fully soluble).
   A. 1 M NaCl
   B. 1 M $Ca(NO_3)_2$
   C. 1 M $CuSO_4$
   D. 1 M $Al_2(SO_4)_3$
   E. 1 M Na_3PO_4

7. A mixture of aqueous Na_3PO_4 and $ZnSO_4$ (both salts fully soluble) has a certain ionic strength, x. Which ion has the highest activity coefficient according to the Debye-Hückel Limiting Law?
   A. Na^+
   B. SO_4^{2-}
   C. Zn^{2+}
   D. PO_4^{3-}
   E. Insufficient information

8. The following reaction occurs in an electrochemical cell:
   $3Cu^{2+} + 2Cr \rightarrow 2Cr^{3+} + 3Cu$
   The E° for the cell is
   A. 0.40 V
   B. 1.08 V
   C. 0.75 V
   D. 2.50 V
   E. Insufficient information

   Given:
   $E^{\circ}\left(Cu^{2+}/Cu\right) = 0.337V$
   $E^{\circ}\left(Cr^{3+}/Cr\right) = -0.74V$

9. The following graph shows the kinetics curves for the reaction of oxygen and hydrogen to form water.
$O_2(g) + 2H_2(g) \rightarrow 2H_2O(g)$



Which curve represents hydrogen?

A. (i)
B. (ii)
C. (iii)
D. (iv)
E. (v)

10. Match the columns and find out the correct option.

Order of reaction	Units of rate constant, k
(a) Zero order	(P) $Lmol^{-1}s^{-1}$
(b) First order	(Q) $molL^{-1}s^{-1}$
(c) Second order	(R) s^{-1}

A. (a) – (R), (b) – (Q), (c) – (P)
B. (a) – (P), (b) – (Q), (c) – (R)
C. (a) – (Q), (b) – (R), (c) – (P)
D. (a) – (R), (b) – (P), (c) – (Q)
E. None of the above

SECTION B **[80]**

There are **THREEE** questions in this section. Answer **all** Questions.

QUESTION 1 **[31]**

(a) Using **Redlich-Kwong** equation state for a non-ideal gas, answer the following questions:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{T^{\frac{1}{2}}\overline{V}\left(\overline{V} + b\right)}$$

(i) What do the terms **a** and **b** relate to? (2)

(ii) State the condition and show that the equation reduces to an ideal gas equation of state. (4)

(iii) State under what conditions is positive deviation and negative deviation from ideal behaviour of gases observed? (2)

(b) State whether q, w, ΔU and ΔH are positive, negative or zero for adiabatic compression of an ideal gas. (4)

(c) One mole of an ideal gas at 10 bar and 298 K is expanded reversibly isothermally to final pressure of 1 bar. Calculate q, w, ΔU and ΔH for the gas. (7)

(d) The following reactions are being proposed for the green hydrogen production and use in Namibia. For each of the following, deduce if $\Delta H = \Delta U$, $\Delta H < \Delta U$ or $\Delta H > \Delta U$, and the entropy change, ΔS, is greater than zero, less than zero or zero. (4)

(i) $2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$
Green hydrogen production by electrolysis of seawater after desalination (splitting of water)

(ii) $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$
Production of green hydrogen carrier for safer storage and transportation to the European market

(iii) $2NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(l)$
Production of fertiliser, which is then crystallised and dried to produce the final product

(iv) $Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(l)$
One of the reactions in steel production

(e) Use the data below to calculate ΔH°, ΔS°, ΔG° and K_p for the reaction at 298K

$CH_3CH_2CH_2CH_3(g) \leftrightharpoons CH_3CH(CH_3)_2(g)$
Butane 2-Methylpropane

Compound	ΔH_f° / kJmol^{-1}	$S^\circ(298K)$
Butane	-126 kJmol^{-1}	270 JK^{-1}mol^{-1}
2-Methylpropane	-125 kJmol^{-1}	295 JK^{-1} mol^{-1}

(8)

QUESTION 2 **[29]**

(a) Give the equations and **SI** units for the terms **electrolytic conductivity**, κ, and **molar conductivity**, Λ_χ. (2)

(b) Explain briefly the difference between a strong and weak electrolyte and show schematically on the same plot how the molar conductivity of a typical example of each varies with concentration. (4)

(c) Compare and contrast the conductometric titration graphs of (i) a strong acid with a strong base; (ii) a weak acid with a strong base; and (iii) mixture of a strong acid and weak acid with a strong base. (4)

(d) The limiting molar conductivities (in Sm^2mol^{-1}) of sodium chloride, sodium formate (HCOONa) and hydrochloric acid are 1.264×10^{-2}, 1.046×10^{-2} and 4.261×10^{-2}, respectively. The conductivity of 0.0100 $moldm^{-3}$ formic acid (HCOOH) at 25°C is 5.07×10^{-2} Sm^{-1}. Calculate the dissociation constant of 0.01 $moldm^{-3}$ formic acid. (6)

(e) Use the Debye-Hückel limiting law for the mean activity coefficient of an electrolyte:

$$\log_{10}\gamma_{\pm} = -A\left|z_+ z_-\right|\sqrt{I}$$

to calculate the mean activity coefficient for 0.010 $molkg^{-1}$ $CuCl_2$ in:

(i) water, and;

(ii) 0.010 $molkg^{-1}$ NaCl, given that A = 0.509 $mol^{-1/2}\,kg^{1/2}$. (6)

(f) Two platinum electrodes were immersed in aqueous solution of a nitrate $M(NO_3)_2$, where M is a metal which forms a divalent ion. After passing a current of 0.501 amps for 63 minutes, 1.10 g of the metal M had been deposited on the platinum cathode. Using Faradays laws of electrolysis, calculate the molar mass of the metal M. (3)

(g) In the cell

Pt | Fe^{2+}, Fe^{3+} | | Hg_2^{2+} | Hg

the standard emf of the half-cells are:

E^o (Fe^{3+}, Fe^{2+}) = +0.771 V and E^o(Hg_2^{2+} | Hg) = +0.789 V.

Deduce the overall reaction of cell. Will the reaction occur spontaneously as written in the cell? (4)

QUESTION 3 **[20]**

(a) Nitrogen pentoxide (N_2O_5) gas decomposes according to the reaction

$2N_2O_5 \rightarrow 4NO_2 + O_2$

At 328K, the rate of the reaction under certain conditions is 0.75×10^{-4} mol $L^{-1}s^{-1}$. Assuming that none of the intermediates have appreciable concentrations, calculate the values of the following: (6)

(i) $\dfrac{d[N_2O_5]}{dt} =$

(ii) $\dfrac{d[NO_2]}{dt} =$

(iii) $\frac{d[O_2]}{dt} =$

(b) Consider a reaction A $\xrightarrow{k}$ P. The integrated rate law for the reaction is:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

(i) State the two reaction requirements needed in order to derive the equation above. (1)

(ii) What is the order of the reaction? What are the units of the rate constant if the rate is in mol L^{-1} min^{-1}? (2)

(iii) What plot would you construct the plot to determine the rate constant, k, for the reaction? Label the axes on diagram and sketch the graph that you would expect. How would you get k from the graph? (2)

(iv) Derive the half-life expression for this reaction. (3)

(c) The table below gives experimental data for the half-lives, $t_{0.5}$, of different reactions as a function of the initial reactant concentration, C_o. Determine the order of each of the three reactions. (6)

	$t_{0.5}$ / min		
C_o / moldm^{-3}	Reaction 1	Reaction 2	Reaction 3
4	5	120	100
2	5	60	200

END OF EXAMINATION QUESTION PAPER

LIST OF USEFUL EQUATION AND CONSTANTS

Van der Waals eqⁿ. $P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$

Universal Gas constant	R	=	8.314 J K^{-1} mol^{-1}
Boltzmann's constant,	k	=	1.381 x 10^{-23} J K^{-1}
Planck's constant	h	=	6.626 x 10^{-34} J s
Debye-Hückel's constant,	A	=	0.509 $(mol\ dm^{-3})^{1/2}$ or $mol^{-0.5}kg^{0.5}$
Faraday's constant	F	=	96485 C mol^{-1}
Mass of electron	m_e	=	9.109 x 10^{-31} kg
Velocity of light	c	=	2.998 x 10^8 m s^{-1}
Avogadro's constant	N_A	=	6.022 x 10^{23}
1 electron volt (eV)		=	1.602 x 10^{-19} J

1 atm = 101325 Pa = 760 mmHg = 760 torr; 1 bar = 10^5 Pa