DEPARTMENT OF CHEMISTRY

UNIVERSITY OF SWAZILAND

NOVEMBER 2017 MAIN EXAMINATION

TITLE OF PAPER	**:Transport and Chemical Kinetics**
COURSE NUMBER	**: CHE 341**
TIME	**: 3 Hours**
Important Information	: Each question is equivalent to **25%** of the entire exam. : Answer **questions one (1)** and any other three **(3)** questions in this paper. : Marks for **ALL** procedural calculations will be awarded. : Start each question on a fresh page of the answer sheet. : Diagrams must be large and clearly labelled accordingly. : Additional material: data sheet, graph paper and the periodic table.

You are not supposed to open this paper until permission has been granted by the Chief Invigilator

Question 1 [25 marks]

a) With the aid of an equation/diagram or any other information, explain the following observations;

(i) As the ionic radius increases, the limiting molar conductivity and the ion mobility increases. [4]

(ii) Ionic hydrodynamic radius decreases with an increase of ionic radius. [3]

b) The rate of formation of D in the reaction $2A + B \rightarrow 2C + D$ is 1.6 M/s. Write down the reaction rates and the rates of formation or consumption of A, B and C. [4]

c) Derive the rate law for the decomposition of ozone, using the steady state approximation, in the reaction $2O_3 \rightarrow 3O_2$ having the mechanism; [6]

$$O_3 \rightarrow O_2 + O \qquad k_a$$

$$O_2 + O \rightarrow O_3 \qquad k_a'$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad k_b$$

d) An enzyme catalysed reaction conversion of substrate at 25°C has Michaelis constant of 0.042 mol L^{-1}. The rate of reaction is 2.45x10-4 mol $L^{-1}s^{-1}$ when the substrate concentration is 0.890 mol L^{-1}. Calculate the maximum velocity of the enzyme action governed by the data presented above, clearly showing all steps [8]

Question 2 [25 Marks]

a) For the perchlorate ion ClO_4^- , in water at 25°C, λ_m^0 = 67.2 Scm^2mol^{-1},

(i) Calculate the mobility, u, of ClO_4^- in water. [2]

(ii) Calculate the drift speed , s, of ClO_4^- in water in a field of 24V/cm. [2]

(iii)Calculate the diffusion coefficient of ClO_4^- in water. [2]

b) An enzyme catalysed reaction follows Michaelis-Menten mechanism and has the rate law;

$\frac{d[P]}{dt} = \frac{k_2[S][E]_0}{K_M+[S]}$, where $K_M = \frac{k_1+k_2}{k_1}$

The following data relates to the catalysed reaction;

[S] (mol L^{-1})	0.00125	0.0025	0.0050	0.020
Rate (mol L^{-1} s^{-1})	2.78x10^{-5}	5.00x10^{-5}	8.33x10^{-5}	1.67x10^{-4}

Given that the enzyme concentration is 2.3nM. Calculate;

(i) The maximum rate

(ii) The Michaelis constant

(iii)k_2

(iv)The catalytic efficiency. [16]

c) Give an equation for the diffusion coefficient and show how it varies with the temperature and the collisional cross-section. [3]

Question 3 [25 Marks]

a) Write short notes on the following;

(i) Chain polymerization [3]

(ii) Mean free path (λ) [2]

(iii)Newtonian flow [2]

a) Given that N_2 (N=14.01 g/mol) is in air at 25°C and 1 atm, and its collision cross-section is 45 cm^2,

(i) Determine the number of collisions N_2 has in a second, [4]

(ii) Use two methods to determine the mean free path. [4]

b) For the decomposition of N_2O_5, the following data has been obtained;

T (°C)	25	35	45	55	65
k (s^{-1})	1.72×10^{-5}	6.55×10^{-5}	24.95×10^{-5}	75×10^{-5}	240×10^{-5}

Calculate the activation energy and the pre-exponential factor for this reaction [10].

Question 4 [25 Marks]

a) The rate constant for the first order decomposition of a compound A in the reaction $A \rightarrow P$ is k=2.78x105s-1 at 25°C. If the initial pressure is 32.1 kPa, calculate;

(i) The half-life of A

(ii) The pressure, 10 seconds after the initiation of the reaction. [6]

a) Using an equation of your choice, briefly explain the pre-equilibrium approach. [5]

b) Compare and contrast between weak and strong electrolytes. [3]

c) The alkaline hydrolysis of ethyl benzoate with varying time gave the results in the table below;

t (s)	0	100	300	400	500	600	700	800
[A] (M)	0.05	0.0275	0.0225	0.0185	0.0160	0.0148	0.0148	0.0138

(i) Show that the reaction follows 2nd order kinetics.

(ii) Determine the rate constant of the reaction.

(iii)Calculate the half-life.

(iv)Find the relaxation time. [11]

Question 5 [25 Marks]

a) Compute the root mean square speed the mean speed and the most probably speed for O_2 at 300K. [10]

b) At what temperature would the mean speed for H_2 be equal to that of O_2 at 300K? [4]

c) Give the law of the independent migration of ions explaining the terms. [3]

d) Estimate the effective radius of sucrose in water at 25°C given the diffusion coefficient is 5.2×10^{-10} m^2s^{-1} and that the viscosity of water is 1cP. [4]

e) Explain the purpose of a catalyst in a reaction, with an aid of a diagram. [4]

Question 6 [25 Marks]

a) A solution of LiCl was electrolyzed in a Hittorf cell. A current of 0.77 A had been passed for two hours, the mass of LiCl in the anode compartment had decreased by 0.793 g. Calculate the transport numbers of the Li^+ and Cl^- ions. [6]

b) List the three assumptions of the Kinetic model . [3]

c) Calculate the mean free path of argon ($\sigma = 0.36\ nm^2$) at 0.3 atm. [3]

d) Use the kinetic theory of gases to explain how the diffusion coefficient varies wit

(i) An increase in Molar mass, [2]

(ii) An increase in collisional cross-section . [2]

e) The charge of Mg^{2+} is twice that of Na^+, and from the equation $u = \frac{ze}{6\pi\eta a}$ one might conclude that Mg^{2+} (aq) have a much greater mobility than Na^+ (aq). Actually, these ions have similar mobilities. Explain why. [4]

f) Bearing in mind distinctions between the mechanisms of stepwise and chain polymerization, describe ways in which it is possible to control the molar mass of a polymer by manipulating the kinetic parameters of polymerization. [5]

The end

Data Sheet

$$pV = \frac{1}{3} nMc^2$$

$$z = \sigma \hat{c}_{rel} \aleph$$

$$s = uE$$

$$z = \frac{\sigma c_{rel} P}{kT}$$

$$\lambda = \frac{kT}{\sigma P}$$

$$Z_w = \frac{P}{(2\pi mkT)^{\frac{1}{2}}}$$

$$\Lambda_m = K/c$$

$$\Lambda_m = \Lambda_m^0 - K\sqrt{c}$$

$$\lambda = zuF$$

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\,924\,58 \times 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\,177 \times 10^{-19}$ C
Faraday constant	$F = N_A e$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = N_A k$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		6.2364×10 L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\,08 \times 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\,57 \times 10^{-34}$ J s
Avogadro constant	N_A	$6.022\,14 \times 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\,54 \times 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\,39 \times 10^{-31}$ Kg
proton	m_p	$1.672\,62 \times 10^{-27}$ Kg
neutron	m_n	$1.674\,93 \times 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_0 = 1/c^2\mu_0$	$8.854\,19 \times 10^{-12}$ J^{-1} C^{2} m^{-1}
	$4\pi\varepsilon_0$	$1.112\,65 \times 10^{-10}$ J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_0	$4\pi \times 10^{-7}$ J s^{2} C^{-2} m^{-1}
		$4\pi \times 10^{-7}$ T^{2} J^{-1} m^{3}
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Rydberg constant	$R_\infty = m_e e^4/8h^3 c\varepsilon_0^{\,2}$	$1.097\,37 \times 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\,65$ m s^{-2}
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1×10^{-7} J
1 eV	=	$1.602\,2 \times 10^{-19}$ J	1 eV/molecule	=	96 485 kJ mol^{-1}

Prefixes

f	p	n	μ	m	c	d	k	M	G
femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

PERIODIC TABLE OF ELEMENTS

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 H 1																	4.003 He 2
2	6.941 Li 3	9.012 Be 4											10.811 B 5	12.011 C 6	14.007 N 7	15.999 O 8	18.998 F 9	20.180 Ne 10
3	22.990 Na 11	24.305 Mg 12				TRANSITION ELEMENTS							26.982 Al 13	28.086 Si 14	30.974 P 15	32.06 S 16	35.453 Cl 17	39.948 Ar 18
4	39.098 K 19	40.078 Ca 20	44.956 Sc 21	47.88 Ti 22	50.942 V 23	51.996 Cr 24	54.938 Mn 25	55.847 Fe 26	58.933 Co 27	58.69 Ni 28	63.546 Cu 29	65.39 Zn 30	69.723 Ga 31	72.61 Ge 32	74.922 As 33	78.96 Se 34	79.904 Br 35	83.80 Kr 36
5	85.468 Rb 37	87.62 Sr 38	88.906 Y 39	91.224 Zr 40	92.906 Nb 41	95.94 Mo 42	98.907 Tc 43	101.07 Ru 44	102.91 Rh 45	106.42 Pd 46	107.87 Ag 47	112.41 Cd 48	114.82 In 49	118.71 Sn 50	121.75 Sb 51	127.60 Te 52	126.90 I 53	131.29 Xe 54
6	132.91 Cs 55	137.33 Ba 56	138.91 *La 57	178.49 Hf 72	180.95 Ta 73	183.85 W 74	186.21 Re 75	190.2 Os 76	192.22 Ir 77	195.08 Pt 78	196.97 Au 79	200.59 Hg 80	204.38 Tl 81	207.2 Pb 82	208.98 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	223 Fr 87	226.03 Ra 88	(227) **Ac 89	(261) Rf 104	(262) Ha 105	(263) Unh 106	(262) Uns 107	(265) Uno 108	(266) Une 109	(267) Uun 110								

Atomic mass → 10.811; Symbol → B; Atomic No. → 5

*Lanthanide Series	140.12 Ce 58	140.91 Pr 59	144.24 Nd 60	(145) Pm 61	150.36 Sm 62	151.96 Eu 63	157.25 Gd 64	158.93 Tb 65	162.50 Dy 66	164.93 Ho 67	167.26 Er 68	168.93 Tm 69	173.04 Yb 70	174.97 Lu 71
**Actinide Series	232.04 Th 90	231.04 Pa 91	238.03 U 92	237.05 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

( ) indicates the mass number of the isotope with the longest half-life.