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UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2011/12

TITLE OF PAPER: ADVANCED PHYSICAL CHEMISTRY

COURSE NUMBER: C402

TIME: THREE (3) HOURS

INSTRUCTIONS:

THERE ARE **SIX** QUESTIONS. EACH QUESTION IS WORTH 25 MARKS. ANSWER **ANY FOUR** QUESTIONS.

A DATA SHEET AND A PERIODIC TABLE ARE ATTACHED

GRAPH PAPER IS PROVIDED

NON-PROGRAMMABLE ELECTRONIC CALCULATORS MAY BE USED.

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Question 1 (25 marks)

(a) Because of its importance in atmospheric chemistry, the thermal decomposition of nitric oxide, $2\ NO(g) \rightarrow N_2(g) + O_2(g)$, has been studied extensively. The commonly accepted mechanism is:

(1)	$NO + NO \rightarrow N_2O + O$	k_1
(2)	$O + NO \rightarrow O_2 + N$	k_2
(3)	$N + NO \rightarrow N_2 + O$	k_3
(4)	$O + O + M \rightarrow O_2 + M$	k_4
(5)	$O_2 + M \rightarrow O + O + M$	k_4'

(i) Label the steps of the mechanism as initiation, propagation, etc.

(ii) Write down the full expression for the rate of disappearance of NO.

(iii) What does this expression become on the basis of the following assumptions: [N] reaches a steady state, the propagation rate is much faster than the initiation step and that oxygen atoms are in equilibrium with oxygen molecules.

(iv) Find the expression for the effective activation energy for the overall reaction in terms of the activation energies of the individual steps in the reaction. [12]

(b) An enzyme catalysed reaction following the Michaelis-Menten mechanism

$E + S \rightleftharpoons ES \rightarrow P + E$ rate constants are k_1, k_1', k_2

has the rate law $\dfrac{d[P]}{dt} = \dfrac{k_2[S][E]_0}{K_M + [S]}$ where $K_M = \dfrac{k_1' + k_2}{k_1}$

The following data were obtained for the action of ATPase on ATP at 20 °C when the concentration of ATPase was 20 nmol dm^{-3}:

[ATP]/(μmol dm^{-3})	0.60	0.80	1.4	2.0	3.0
Rate/ (μmol dm^{-3} s^{-1})	0.81	0.97	1.30	1.47	1.69

Determine

(i) the maximum velocity of the reaction,

(ii) the Michaelis constant

(iii) the turnover number and

(iv) the catalytic efficiency of the enzyme [13]

Question 2 (25 marks)

(a) Express the activity of a $La_2(SO_4)_3$ solution of molality m in terms of the mean activity coefficient, $\gamma_\pm$ and the molality m. [3]

(b) Use the Debye-Huckel limiting law to estimate the mean activity coefficient of $La_2(SO_4)_3$ in a solution that is 0.002 mol/kg in $La_2(SO_4)_3$ and 0.001 mol/kg K_2SO_4. ($\log \gamma_\pm = -|z_+z_-|AI^{1/2}$, A=0.509 at 25 °C) [4]

(c) Use the standard potentials of the couples Co^{3+}/Co^{2+} $E^\theta = +1.81$ V, Co^{2+}/Co $E^\theta = -0.28$ V and $AgCl/Cl^-,Ag$ $E^\theta = +0.22$V to calculate the E^θ and the equilibrium constant at 298K of the following reaction:

$Co^{3+}(aq) + 3Cl^-(aq) + 3Ag(s) \rightarrow 3AgCl(s) + Co(s)$ [10]

(d) Use the data below to calculate $\Delta_r H^o$ and $\Delta_r G^o$ for the following reaction:

$AgNO_3(aq) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$ [8]

Substance	$\Delta_f H^o$ /kJmol^{-1}	$\Delta_f G^o$ kJmol^{-1}
AgCl(s)	-127.0	-109.8
Ag^+(aq)	+105.6	+77.1
Cl^-(aq)	-167.2	-131.2

Question 3 (25 marks)

(a) Why is the stoichiometry of a reaction generally not sufficient to determine reaction order? When is it possible to infer the reaction order from the stoichiometry? [4]

(b) The data below apply to the formation of urea from ammonium cyanate

$NH_4CNO(aq) \rightarrow NH_2CONH_2(aq)$

Initially 22.9 g of ammonium cyanate was dissolved in enough water to prepare 1.00 dm^3 of solution.

(i) Show that the reaction follows the second order kinetics: $\dfrac{1}{[J]} = \dfrac{1}{[J]} + kt$

(ii) Determine the rate constant.

(iii) Determine the mass of ammonium cyanate left after 300 minutes. [9]

t/min	0	20.0	50.0	65.0	150
Mass of urea/g	0	7.0	12.1	13.8	17.7

(c) The reactant 1,3 cyclohexadiene can be photochemically converted to cis hexatriene. In an experiment, 2.5 mmol of cyclohexadiene are converted to cis hexatriene when irradiated with 100 W of 280 nm light for 27 s. All the light is absorbed by the sample. What is the quantum yield for this photochemical process? [5]

(d) The second order rate constant for the reaction of oxygen atoms and benzene have been measured and found to be 1.44 x 10^7 $dm^3mol^{-1}s^{-1}$ at 300.3 K and 6.9 x 10^7 $dm^3mol^{-1}s^{-1}$ at 392.2 K. Find the pre-exponential factor and the activation energy of the reaction. [7]

Question 4 (25 marks)

(a) Define the mean free path. How does this quantity vary with number density, particle diameter and the mean particle speed? [3]

(b) Calculate the mean free path of argon (σ = 0.36 nm^2) at 298 K at (i) 0.3 atm and (ii) $5x10^{-6}$ atm. [6]

(c) A thermopane window consists of two sheets of glass separated by a volume filled with air (which we will model as N_2 where κ= 0.0240 J K^{-1} m^{-1} s^{-1}). If the window is 1 m^2 in area with a separation between glass sheets of 3 cm, what is the loss of energy when:

(i) The exterior of the window is at a temperature of 10 °C and the interior of the window is a temperature of 22 °C?

(ii) The same temperature differential as in (i) is used, but now the window is filled with Ar (κ = 0.0163 J K^{-1} m^{-1} s^{-1}) rather than N_2? [6]

(d) Gas cylinders of CO_2 are sold in terms of weight of CO_2. A cylinder contains 22.7 kg of CO_2. Use Poiseuille's formula $\left(\frac{dV}{dt} = \frac{(P_1^2 - P_2^2)\pi r^4}{16 l \eta p_0}\right)$ to determine for how long can this cylinder be used in an experiment that requires flowing CO_2 at 293 K (η = 146 μP) through a 1.00 m long tube (diameter 0.75 mm) with input pressure of 1.05 atm and output pressure of 1.00 atm? The flow is measured at the tube output. [6]

(e) A solid surface with dimensions 3.5 mm x 4.0 cm is exposed to helium gas at 111 Pa and 1500 K. How many collisions do the He atoms make with this surface in 10s? (Collision frequency $Z_w = \frac{p}{(2\pi mkT)^{1/2}}$ [4]

Question 5 (25 marks)

(a) A certain solid sample adsorbs 0.44 mg of CO when the pressure of the gas is 26.0 kPa and the temperature is 300 K. The amount adsorbed when the pressure is 3.0 kPa and temperature 300 K is 0.19 mg. The Langmuir isotherm, $\theta = \frac{Kp}{1+Kp}$, is known to describe the adsorption. Find the fractional coverage at the surface at the two pressures. [10]

(b) Hydrogen iodide is very strongly adsorbed on gold but only slightly adsorbed on platinum. If the adsorption follows the Langmuir isotherm on both surfaces, predict the order of the HI decomposition on each of the two surfaces. [6]

(c) In an experiment on the adsorption of ethene on iron it was found that the same volume of gas desorbed in 1856 s at 873 K and 8.44 s at 1012 K. What is the activation energy desorption? How long would it take for the same amount of ethene to desorb at (i) 298 K, (ii) 1500 K? [9]

Question 6 (25 marks)

(a) Use the kinetic theory of gases to explain how the diffusion coefficient varies with
   (i) an increase in molar mass
   (ii) an increase in collisional cross-section [6]

(b) A manometer was connected to a bulb containing nitrogen (molar mass 28.02 g/mol) under slight pressure. The gas was allowed to escape through a small pinhole, and the time for the manometer reading to drop from 65.1 cm to 42.1 cm was 18.5 s. When the experiment was repeated using a fluorocarbon gas, the same fall took 82.3 s. Calculate the molar mass of the fluorocarbon. [7]

(c) Myogloblin is a protein that participates in oxygen transport in blood. For myogloblin in water at 20 °C, the diffusion coefficient, D, is 1.13 x 10^{-10} m^2 s^{-1}, specific volume, $\overline{V}$ = 0.740 cm^3 g^{-1}. The viscosity of water is 1.002 cP at this temperature

   (i) Estimate the size of a myogloblin molecule. [6]
   (iii) Estimate the molecular mass of myogloblin? [6]

(Useful data: volume of a sphere = $\frac{4}{3}\pi r^3$ and diffusion coefficient D= $\frac{kT}{6\pi\eta a}$)

General data and fundamental constants

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

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	1 X 10^{-7} J
1 eV	=	1.602 2 X 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

Atomic mass →, Symbol →, Atomic No. →

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								

*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.