UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2007

TITLE OF PAPER: INTRODUCTORY CHEMISTRY II

COURSE NUMBER: C112

TIME: THREE (3) HOURS

INSTRUCTIONS:

There are **six** questions. Each question is worth 25 marks. Answer **any four** questions.

Non-programmable electronic calculators may be used.

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Question 1 (25marks)

a) The rate of decrease in N_2H_4 partial pressure in a closed reaction vessel from the reaction $N_2H_4(g) \rightarrow 2\ NH_3(g)$ is 63 Torr/h. What are the rates of change of NH_3 partial pressure and total pressure in the vessel? [4]

b) The reaction $ClO_2(aq) + 2\ OH^-(aq) \rightarrow ClO_3^-(aq) + H_2O(l)$ was studied and the following results were obtained:

Expt	$[ClO_2]$, M	$[OH^-]$, M	Rate, M/s
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

(i) Determine the rate law for the reaction

(ii) Calculate the rate constant.

(iii) Calculate the rate when $[ClO_2] = 0.010$ M and $[OH^-] = 0.025$ M. [6]

c) The gas phase decomposition of SO_2Cl_2,
$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$, is first order in SO_2Cl_2. The rate constant for the decomposition at 660 K is $4.5 \times 10^{-2}\ s^{-1}$.

(i) If the initial pressure of SO_2Cl_2 375 Torr, what will be its partial pressure after 65 s?

(ii) At what time will the partial pressure of SO_2Cl_2 decline to one-tenth its initial value? [6]

d) (i) What factors determine whether a collision between two molecules will lead to a chemical reaction?
(ii) According to the collision theory, why does temperature affect the value of the rate constant? [4]

e) The activation energy of a reaction is 65.7 kJ/mol. How many times faster will the reaction occur at 50 °C than at 0 °C? [5]

Question 2 (25marks)

a) Consider the following equilibrium, for which $K_p = 0.0752$ at 480 °C:

$$2\ Cl_2(g) + 2\ H_2O(g) \rightleftharpoons 4\ HCl(g) + O_2(g)$$

(i) What is the value of K_p for the reaction

$$4\ HCl(g) + O_2(g) \rightleftharpoons 2\ Cl_2(g) + 2\ H_2O(g)?$$

(ii) What is the value of K_p for the reaction

$$Cl_2(g) + H_2O(g) \rightleftharpoons 2\,HCl(g) + \tfrac{1}{2}O_2(g)$$

(iii) What is the value of K_c for the reaction in (ii)? [7]

b) For the reaction $I_2(g) + Br_2(g) \rightleftharpoons 2\,IBr(g)$, $K_c = 280$ at 150 °C. Suppose that 0.500 mol IBr in a 1.00 L flask is allowed to reach equilibrium at 150 °C, what are the equilibrium concentrations of IBr, I_2 and Br_2? [7]

c) Consider the equilibrium, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$. A gas vessel is charged with a mixture of the three gases which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are $P_{PCl_3} = 0.124\,\text{atm}$, $P_{Cl2} = 0.157\,\text{atm}$, and $P_{PCl_5} = 1.30\,\text{atm}$. What is the value of K_p at this temperature? [5]

d) For the following reaction, $\Delta H^o = +\,2816$ kJ:

$$6\,CO_2(g) + 6\,H_2O(l) \rightleftharpoons C_6H_{12}O_6(s) + 6\,O_2(g)$$

How is the equilibrium yield of $C_6H_{12}O_6$ affected by

(i) increasing the partial pressure of CO_2
(ii) increasing the temperature
(iii) removing CO_2
(iv) decreasing the total pressure
(v) removing some of the $C_6H_{12}O_6$
(vi) adding a catalyst? [6]

Question 3 (25 marks)

a) Carbon dioxide in the atmosphere dissolves in rainwater to produce carbonic acid (H_2CO_3), causing the pH of clean unpolluted rain to range from about 5.2 to 5.6. What are the ranges of $[H^+]$, $[OH^-]$ in the raindrops? [4]

b) Phenylacetic acid ($HC_8H_7O_2$) is one of the substances that accumulates in the blood of people with phenylketonuria, an inherited disorder that can cause mental retardation or even death. A 0.085 M solution of $HC_8H_7O_2$ is found to have a pH of 2.68. Calculate K_a value of this acid. [5]

c) Calculate the molar concentration of OH^- ion in a 1.15 M solution of hypobromite ion (BrO^-) given its K_b is 4.0×10^{-4}. What is the pH of this solution [6]

d) Predict whether aqueous solutions of the following compounds are acidic, basic, or neutral. In each case write a supporting equation. [5]

(i) $CrBr_3$ (ii) LiI (iii) K_3PO_4 (iv) NH_4Cl (v) $KHSO_4$.

e) The molar solubility of $PbBr_2$ at 25 °C is 1.0×10^{-2} mol/L. Calculate its $K_{sp.}$ [5]

Question 4 (25 marks)

a) Sodium bromide is formed from its elements at 298 K according to the equation

$$Na(s) + \tfrac{1}{2}Br_2(l) \rightleftharpoons NaBr(s).$$

(i) Construct a Born-Haber cycle for sodium bromide.

(ii) Use the data below and the Born-Haber cycle in (i) to calculate the enthalpy of vaporization of liquid bromine. [10]

Standard enthalpies	ΔH^o /kJ mol^{-1}
ΔH^o_f formation of NaBr(s)	-361
ΔH^o_{ea} electron addition to Br(g)	-325
ΔH^o_{sub} sublimation of Na(s)	+107
ΔH^o_{ion} bond dissociation of Br_2(g)	+194
ΔH^o_{ion} first ionization of Na(g)	+498
ΔH^o_L lattice dissociation of NaBr(s)	+753

b) Draw Lewis structures of the following species. Identify those that do not obey the octet rule and explain why they do not.

(i) SO_3^{2-} (ii) AlH_3 (iii) SbF_5 [9]

c) Give the VSEPR model shape of the species in (iii) [6]

Question 5 (25 marks)

a) Write five methods by which alkyl halides can be converted to alkanes and write equation(s) to illustrate each method. [[7½]

b) An alkane has seven carbon atoms per molecule. Write the structures of any seven isomers of the alkane and name them. [7]

c) Write the names of any five fractions that can be obtained from fractional distillation of crude oil and for each fraction give its use. [5]

d) (i) What is a polymer?
   (ii) Write the names and formulae of any three polymers and for each polymer named, write the formula of its monomer. [5½]

Question 6 (25 marks)

a) Write the names of any six classes of organic compounds and for each class write its general molecular formula and its functional group. [9]

(b) Define the following terms and illustrate with equation or structure where possible.

(i) Substitution reaction
(ii) Hydrolysis
(iii) Dehalogenation
(iv) Inductive effect
(v) Markownikoff's rule [10]

b) Outline by equations only, steps in the conversion of limestone to vinyl chloride. [6]

The end

General data and fundamental constants

Quantity	Symbol	Value
Speed of light	c	$2.997\ 924\ 58 \text{ X } 10^{8}$ m s^{-1}
Elementary charge	e	$1.602\ 177 \text{ X } 10^{-19}$ C
Faraday constant	$F = N_Ae$	$9.6485 \text{ X } 10^{4}$ C mol^{-1}
Boltzmann constant	k	$1.380\ 66 \text{ X } 10^{-23}$ J K^{-1}
Gas constant	$R = N_Ak$	$8.314\ 51$ J K^{-1} mol^{-1}
		$3.205\ 78 \text{ X } 10^{-2}$ dm^3 atm K^{-1} mol^{-1}
		$6.2364 \text{ X } 10$ L Torr K^{-1} mol^{-1}
Planck constant	h	$6.626\ 08 \text{ X } 10^{-34}$ J s
	$\hbar = h/2\pi$	$1.054\ 57 \text{ X } 10^{-34}$ J s
Avogadro constant	N_A	$5.022\ 14 \text{ X } 10^{23}$ mol^{-1}
Atomic mass unit	u	$1.660\ 54 \text{ X } 10^{-27}$ Kg
Mass		
electron	m_e	$9.109\ 39 \text{ X } 10^{-31}$ Kg
proton	m_p	$1.672\ 62 \text{ X } 10^{-27}$ Kg
neutron	m_n	$1.674\ 93 \text{ X } 10^{-27}$ Kg
Vacuum permittivity	$\varepsilon_o = 1/c^2\mu_o$	$8.854\ 19 \text{ X } 10^{-12}$ J^{-1} C^2 m^{-1}
	$4\pi\varepsilon_0$	$1.112\ 65 \text{ X } 10^{-10}$ J^{-1} C^2 m^{-1}
Vacuum permeability	μ_o	$4\pi \text{ X } 10^{-7}$ J s^2 C^{-2} m^{-1}
		$4\pi \text{ X } 10^{-7}$ T^2 J^{-1} m^3
Magneton		
Bohr	$\mu_B = e\hbar/2m_e$	$9.274\ 02 \text{ X } 10^{-24}$ J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	$5.050\ 79 \text{ X } 10^{-27}$ J T^{-1}
g value	g_e	$2.002\ 32$
Bohr radius	$a_o = 4\pi\varepsilon_o\hbar/m_ee^2$	$5.291\ 77 \text{ X } 10^{-11}$ m
Fine-structure constant	$\alpha = \mu_oe^2c/2h$	$7.297\ 35 \text{ X } 10^{-3}$
Rydberg constant	$R_\infty = m_ee^4/8h^3c\varepsilon_o^2$	$1.097\ 37 \text{ X } 10^{7}$ m^{-1}
Standard acceleration of free fall	g	$9.806\ 65$ m s^{-2}
Gravitational constant	G	$6.672\ 59 \text{ X } 10^{-11}$ N m^2 Kg^{-2}

Conversion factors

1 cal	=	4.184 joules (J)	1 erg	=	$1 \text{ X } 10^{-7}$ J
1 eV	=	$1.602\ 2 \text{ X } 10^{-19}$ 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.

TRANSITION ELEMENTS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
PERIODS	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											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.