UNIVERSITY OF SWAZILAND
FINAL EXAMINATION 2010/11

TITLE OF PAPER : SEPARATION METHODS

COURSE NUMBER : C611

TIME ALLOWED : THREE(3) HOURS

INSTRUCTIONS : ANSWER ANY FOUR QUESTIONS. EACH QUESTION CARRIES 25 MARKS.

A periodic table and other useful data have been provided with this paper.

DO NOT OPEN THIS QUESTION PAPER UNTIL PERMISSION TO DO SO HAS BEEN GRANTED BY THE CHIEF INVIGILATOR.

Question 1(25 marks)

(a) For the extraction of a weak acid, HB into an organic phase, the acid being monomeric and its anion being insoluble in the organic phase, employ the basic equilibria involved to:

(i) Obtain the expression for the distribution ratio, D, in terms of K_a, K_{DHB} and $[H_30^+]$. (4)

(ii) Show how a linearized form of the expression for D above can be used in evaluating the values of K_a and K_{DHB} graphically. (3)

(b) (i) The distribution coefficient, K_D, of an organic compound between water and an organic solvent is18.0. If 100 mL of an aqueous solution of the compound, buffered at pH 6.00 is extracted three times with 50mL of the organic solvent, calculate the percentage remaining in the aqueous phase ($K_a = 2.0 \times 10^{-6}$). (7)

(ii) What will be the value of D at pH 4? (3)

(iii) Comment on the results of (i) and (ii) above. (1)

(e) A certain metal ion M^{n+} is extracted by a chelating agent. The concentration of the chelating agent is 0.010 M and the following data are obtained:

pH	1	2	3	4	5
D	10^{-8}	10^{-4}	1	10^{4}	10^{8}

From the plot of log D vs. pH obtain the values n and K (collection of constants) (7)

Question 2 (25 marks)

(a) (i). State the expression that relates the net retention volume, V_n, and the specific retention volume, V_g and define the other parameters in it. (2)

(ii) What are the factors that influence the value of Vg, in a solvent and what assumption is made in this respect? (3)

(iii) Assuming an ideal behaviour, how is the net volume affected by an increase in the temperature and volatility of the solutes? (3)

(b). A 5.00 µL sample containing aniline ($C_6H_5NH_2$) and anisole ($C_6H_5OCH_3$) together with other substances was injected into a GC. The heights for the peaks of these two solutes in the resulting chromatogram were 4.22 (aniline) and 7.60 (anisole) chart divisions. Another 5.00 μL sample was injected together with 0.25 μL of pure aniline (all in the same syringe), producing aniline and anisole peak heights of 8.73 and 7.60 chart divisions. Calculate the concentration, in volume %, of the two components under the following assumptions:

(i) The detector responds equally to both compounds. (5)

(ii) The detector response (on a volume basis) is 1.35 times more for anisole than for aniline (4)

(c) (i) Give the two expressions for the resolution, R_s of two adjacent peaks in a chromatogram. Account for the factors that influence its value. (4)

(ii) Using a 2.0 m column, what height of a theoretical plate is needed to achieve a resolution of 1.0? (Given that $\alpha = 1.05$, and $k' = 0.5$) (4)

Question 3 (25 marks)

(a) Draw and label a schematic diagram of a gas chromotograph (4)

(b) For the sample inlet system of the GC

(i) Draw and label a schematic diagram of a flash vapourizer injection port (3)

(ii) Discuss the effect of injection port temperature on the resolution of a mixture (4)

(iii) What measures should be taken, during sample preparation and injection, to ensure accuracy of data and sample preservation (4)

(c) Summarize the ideal features of the solid support and the immobilized liquid (stationary) phase of a gas chromotograph column (5)

(d) A sample containing only the ortho, meta and para isomers of cresol was analysed by the GC. The chromatogram had three peaks with integrated peak areas of 24.6, 30.8, and 9.3 for the ortho, meta and para isomers respectively. If the detector responds equally to the isomers, calculate the percentage of each of the isomers in the sample (5)

Question 4(25 marks).

(a) Discuss the factors that influence the number of theoretical plates of a GC column, stating specifically how N is affected in each case. (3)

(b) Using the Van Deemter equation, discuss the three major factors that cause band broadening of a GC column. (7)

(c) What are the advantages of open tubular columns over packed columns in GC? (3)

(d) Identical portions of a substance were chromatographed on a 100 - m column at the following velocities:

Sample	Flow Velocity (cms^{-1})	Retention time, t_r (s)	Peak width at half height, $w^{1/2}$ (s)
1	7.0	625	7.9
2	10.0	438	5.2
3	15.0	292	3.2
4	25.0	175	1.9
5	40.0	110	1.2
6	60.0	73	0.8
7	80.0	61	0.7

With the aid of a Van Deemter plot;

(i) Determine the optimum flow velocity.

(ii) Calculate N, the number of theoretical plates at optimum flow velocity. (12)

Question 5(25 marks)

(a) Define the following terms and discuss the factors that influence their values:

(i) Electrophoretic mobility.

(ii) Electroosmotic flow velocity. (6)

(b) Give a brief account of the principles of capillary zone electrophoresis (CZE). What is its main limitation and how is it overcome by the micelar electrokinetic chromatography (MEKC)? (7)

(c) Discuss the efficiency and solute resolution of capillary electrophoresis, indicating the parameters that influence them. (6)

(d) CZE was employed for the analysis of $N0_3^-$ in aquarium water, using 10_4^- as an internal standard. Standard solutions of 30.0 ppm $N0_3^-$ and 20.0 ppm of 10_4^- gave peak heights (arbitrary units), of 190.0 and 200.2 respectively. A 2.50 mL water sample from an aquarium was transferred into a 250.0 mL volumetric flask and then diluted to volume after adding sufficient internal standard to make its concentration 10.00 ppm. Analysis gave signals of 29.2 and 105.8 $N0_3^-$ and 10_4^-, respectively. Estimate the concentration of $N0_3^-$ in the aquarium sample in ppm.
(6)

Question 6 (25 marks)

(a). Describe the basic principles of 'Size Exclusion Chromatography', citing any feature differentiating it from the other HPLC techniques.
(5)

(b). Define the terms: 'The Exclusion Limit' and 'The Inclusion or Permeation Limit'. Illustrate the two on a single diagram. (5)

(c). Give three advantages, one disadvantage and one application of 'Size Exclusion Chromatography'. (5)

(d). What is a supercritical fluid mobile phase? Illustrate its meaning with the aid of a phase diagram and give one common example.
(4)

(e). The size exclusion chromatography was used to analyze a series of polyvinylpyridine standard of varying molecular weights. The data obtained are tabulated below:

Formula Weight	100,000	20,000	600,000	3,000	Unknown
Retention Vol. (mL)	7.98	9.30	6.42	10.94	8.45

(i). Calculate the 'Formula Weight' for the unknown.
(ii). What is the retention volume for a polyvinylpyridine with F.W. = 80,000 ? (6)

PERIODIC TABLE OF ELEMENTS

GROUPS

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

TRANSITION ELEMENTS

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VII
1	1.008 H 1																
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	18.9 F 9
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	35.4 Cl 17
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	79.9 Br 35
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. I 53
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	(21 At 85
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. 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.

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	$F = eN_A$	9.6485×10^{4} C mol^{-1}
Boltzmann constant	k	$1.380\,66 \times 10^{-23}$ J K^{-1}
Gas constant	$R = kN_A$	$8.314\,51$ J K^{-1} mol^{-1}
		$8.205\,78 \times 10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
		62.364 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 of		
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 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}
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}
Bohr magneton	$\mu_B = e\hbar/2m_e$	$9.274\,02 \times 10^{-24}$ J T^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\,79 \times 10^{-27}$ J T^{-1}
Electron g value	g_e	$2.002\,32$
Bohr radius	$a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$	$5.291\,77 \times 10^{-11}$ m
Rydberg constant	$R_\infty = m_e e^4/8h^3c$	$1.097\,37 \times 10^{5}$ cm^{-1}
Fine structure constant	$\alpha = \mu_0 e^2 c/2h$	$7.297\,35 \times 10^{-3}$
Gravitational constant	G	$6.672\,59 \times 10^{-11}$ N m^{2} kg^{-2}
Standard acceleration of free fall†	g	$9.806\,65$ m s^{-2}

† Exact (defined) values

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}

APPENDIX C POTENTIALS OF SELECTED HALF-REACTIONS AT 25 °C

A summary of oxidation/reduction half-reactions arranged in order of decreasing oxidation strength and useful for selecting reagent systems.

Half-reaction		E° (V)
$F_2(g) + 2H^+ + 2e^-$	$= 2HF$	3.06
$O_3 + 2H^+ + 2e^-$	$= O_2 + H_2O$	2.07
$S_2O_8^{2-} + 2e^-$	$= 2SO_4^{2-}$	2.01
$Ag^{2+} + e^-$	$= Ag^+$	2.00
$H_2O_2 + 2H^+ + 2e^-$	$= 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^-$	$= MnO_2(s) + 2H_2O$	1.70
$Ce(IV) + e^-$	$= Ce(III)$ (in 1*M* $HClO_4$)	1.61
$H_5IO_6 + H^+ + 2e^-$	$= IO_3^- + 3H_2O$	1.6
Bi_2O_4 (bismuthate) $+ 4H^+ + 2e^-$	$= 2BiO^+ + 2H_2O$	1.59
$BrO_3^- + 6H^+ + 5e^-$	$= \frac{1}{2}Br_2 + 3H_2O$	1.52
$MnO_4^- + 8H^+ + 5e^-$	$= Mn^{2+} + 4H_2O$	1.51
$PbO_2 + 4H^+ + 2e^-$	$= Pb^{2+} + 2H_2O$	1.455
$Cl_2 + 2e^-$	$= 2Cl^-$	1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$= 2Cr^{3+} + 7H_2O$	1.33
$MnO_2(s) + 4H^+ + 2e^-$	$= Mn^{2+} + 2H_2O$	1.23
$O_2(g) + 4H^+ + 4e^-$	$= 2H_2O$	1.229
$IO_3^- + 6H^+ + 5e^-$	$= \frac{1}{2}I_2 + 3H_2O$	1.20
$Br_2(l) + 2e^-$	$= 2Br^-$	1.065
$ICl_2^- + e^-$	$= \frac{1}{2}I_2 + 2Cl^-$	1.06
$VO_2^+ + 2H^+ + e^-$	$= VO^{2+} + H_2O$	1.00
$HNO_2 + H^+ + e^-$	$= NO(g) + H_2O$	1.00
$NO_3^- + 3H^+ + 2e^-$	$= HNO_2 + H_2O$	0.94
$2Hg^{2+} + 2e^-$	$= Hg_2^{2+}$	0.92
$Cu^{2+} + I^- + e^-$	$= CuI(s)$	0.86
$Ag^+ + e^-$	$= Ag$	0.799
$Hg_2^{2+} + 2e^-$	$= 2Hg$	0.79
$Fe^{3+} + e^-$	$= Fe^{2+}$	0.771
$O_2(g) + 2H^+ + 2e^-$	$= H_2O_2$	0.682
$2HgCl_2 + 2e^-$	$= Hg_2Cl_2(s) + 2Cl^-$	0.63
$Hg_2SO_4(s) + 2e^-$	$= 2Hg + SO_4^{2-}$	0.615
$Sb_2O_5 + 6H^+ + 4e^-$	$= 2SbO^+ + 3H_2O$	0.581
$H_3AsO_4 + 2H^+ + 2e^-$	$= HAsO_2 + 2H_2O$	0.559
$I_3^- + 2e^-$	$= 3I^-$	0.545
$Cu^+ + e^-$	$= Cu$	0.52
$VO^{2+} + 2H^+ + e^-$	$= V^{3+} + H_2O$	0.337
$Fe(CN)_6^{3-} + e^-$	$= Fe(CN)_6^{4-}$	0.36
$Cu^{2+} + 2e^-$	$= Cu$	0.337
$UO_2^{2+} + 4H^+ + 2e^-$	$= U^{4+} + 2H_2O$	0.334

(continued)

APPENDIX C (*continued*)

Half-reaction		$E°$ (V)
$Hg_2Cl_2(s) + 2e^-$	$= 2Hg + 2Cl^-$	0.2676
$BiO^+ + 2H^+ + 3e^-$	$= Bi + H_2O$	0.32
$AgCl(s) + e^-$	$= Ag + Cl^-$	0.2222
$SbO^+ + 2H^+ + 3e^-$	$= Sb + H_2O$	0.212
$CuCl_3^{2-} + e^-$	$= Cu + 3Cl^-$	0.178
$SO_4^{2-} + 4H^+ + 2e^-$	$= SO_2(aq) + 2H_2O$	0.17
$Sn^{4+} + 2e^-$	$= Sn^{2+}$	0.15
$S + 2H^+ + 2e^-$	$= H_2S(g)$	0.14
$TiO^{2+} + 2H^+ + e^-$	$= Ti^{3+} + H_2O$	0.10
$S_4O_6^{2-} + 2e^-$	$= 2S_2O_3^{2-}$	0.08
$AgBr(s) + e^-$	$= Ag + Br^-$	0.071
$2H^+ + 2e^-$	$= H_2$	0.0000
$Pb^{2+} + 2e^-$	$= Pb$	−0.126
$Sn^{2+} + 2e^-$	$= Sn$	−0.136
$AgI(s) + e^-$	$= Ag + I^-$	−0.152
$Mo^{3+} + 3e^-$	$= Mo$	*approx.* −0.2
$N_2 + 5H^+ + 4e^-$	$= H_2NNH_3^+$	−0.23
$Ni^{2+} + 2e^-$	$= Ni$	−0.246
$V^{3+} + e^-$	$= V^{2+}$	−0.255
$Co^{2+} + 2e^-$	$= Co$	−0.277
$Ag(CN)_2^- + e^-$	$= Ag + 2CN^-$	−0.31
$Cd^{2+} + 2e^-$	$= Cd$	−0.403
$Cr^{3+} + e^-$	$= Cr^{2+}$	−0.41
$Fe^{2+} + 2e^-$	$= Fe$	−0.440
$2CO_2 + 2H^+ + 2e^-$	$= H_2C_2O_4$	−0.49
$H_3PO_3 + 2H^+ + 2e^-$	$= HPH_2O_2 + H_2O$	−0.50
$U^{4+} + e^-$	$= U^{3+}$	−0.61
$Zn^{2+} + 2e^-$	$= Zn$	−0.763
$Cr^{2+} + 2e^-$	$= Cr$	−0.91
$Mn^{2+} + 2e^-$	$= Mn$	−1.18
$Zr^{4+} + 4e^-$	$= Zr$	−1.53
$Ti^{3+} + 3e^-$	$= Ti$	−1.63
$Al^{3+} + 3e^-$	$= Al$	−1.66
$Th^{4+} + 4e^-$	$= Th$	−1.90
$Mg^{2+} + 2e^-$	$= Mg$	−2.37
$La^{3+} + 3e^-$	$= La$	−2.52
$Na^+ + e^-$	$= Na$	−2.714
$Ca^{2+} + 2e^-$	$= Ca$	−2.87
$Sr^{2+} + 2e^-$	$= Sr$	−2.89
$K^+ + e^-$	$= K$	−2.925
$Li^+ + e^-$	$= Li$	−3.045