UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2016

TITLE OF PAPER : ENVIRONMENTAL CHEMISTRY

COURSE NUMBER : CHE 612/ERM 640

TIME ALLOWED : 3 HRS

INSTRUCTIONS : THIS EXAMINATION HAS SIX (6) QUESTIONS

: ANSWER ANY FOUR QUESTIONS

: EACH QUESTION HAS 25 MARKS

: THIS EXAMINATION HAS A TOTAL OF 100 MARKS

: DATA SHEETS ARE PROVIDED WITH THIS EXAMINATION PAPER

DO NO TOPEN THIS PAPER UNTIL THE CHIEF INVIGILATOR
INSTRUCTS YOU TO DO SO

Question 1 (25 Marks)

a) Using diagrams, examples and or equations write short notes on the Octanol / water partition coefficient, K_{ow}, as applied in environmental chemistry.

In each highlight the environmental relevance, methods of determination and where applicable give methods of estimation using Quality Structure Activity Relationships (QSAR's)   [15]

b)   A model environmental has 6 major phases; air, water, soil, sediments, suspended solids and biota. It has an area of 1 km^2 and an atmosphere of 10 km high. Soil to depth of 3 cm covers 30% of the surface, while the rest is covered with water to an average depth of 10m. Water has a 3-cm layer of sediment, contains 5 ml of suspended solids per cubic meter, and $0,5mlm^{-3}$ of biota. All phases are homogeneous. 100 moles. Pp-DDT is discharged from a factory to this environment until steady concentrations in each phase are reached at $25^{O}C$.

pp-DDT has the following characteristics at $25^{O}C$.
K_{sorb} (soil, 2% organic carbon)	1,700
K_{sorb}(sediment, suspend solids, 4% organic carbon)	25,400
K_B (fish, 5% lipid)	77,400
K_{OW}	1,,555,000
H	2.3 $mole^{-1}$ m^3 Pa

i)   Determine Henry's constant, Z values for water, soil, fish and sediment, and suspended solids, respectively. [5]

ii)   Establish the overall distribution of the pollutant in this environment using the fugacity concept. [3]

iii)   In which phase is DDT dominant, explain. [2]

Question 2 (25 Marks)

a) Using any of the pollutants and sorbents given below, write short notes on any two of the following mechanisms of Soil Sorption as an environmental fate property.

      (i).   Ligand exchange   [5]
      (ii).   Surface complexation   [5]
      (iii).   Protonation and Ion exchange [5]

COOH

PARAQUAT

H_3AsO_4

ATRAZINE

$Fe(OH)_3$

DISSOLVED ORGANIC, HUMIC ACID
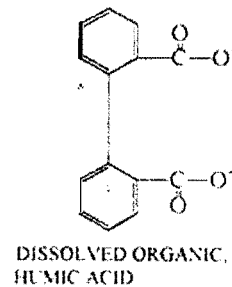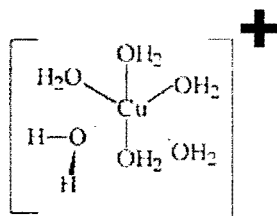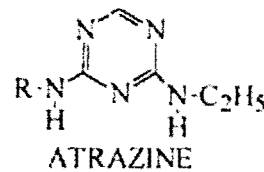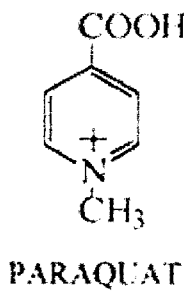
b) Using thermodynamic assumptions derive the Freundlich adsorption equation.

[3]

$$\Gamma = KC_{eq.}^{N}$$

c) The sorption of phenol on a slit loam yielded the following results:

Equilibrium Concentration mg/1	Toluene Sorbed ($\mu g/g$)
0.08	12
0.20	33
0.32	49
0.40	67
0.53	83

    i) Verify whether or not this sorption follows a one site Langmuir or the Freundlich Sorption Isotherm. [3]
    ii) Determine the appropriate constants and comment on their magnitude.   [4]

iii) Given that the solubility and vapour pressure for toluene is 67000 mM L^{-1} and 0.2 mm Hg, respectively, using mobility and retardation values determine whether or not it poses any risk for ground water contamination if the soil bulk density is 1.7, porosity is 0.25 and fractional organic carbon is 0.2%. [5]

Useful relations:

$$\Gamma = KC_{eq}^N \qquad \Gamma = \frac{\Gamma_\infty KC_{equil.}}{1 + KC_{equil.}} \qquad \Delta H = \log\left[\frac{S \cdot P_v}{K}\right]$$

ISOTHERM	RETARDATION FACTOR
LINEAR $\Gamma = K_d C$	$R_f = 1 \cdot \frac{\rho_b}{\eta} K_d$
FREUNDLICH $\frac{X}{m} = K_d C_e^{1/n}$	$R_f = 1 + \frac{\rho_b N K_d C^{N-1}}{\eta}$
LANGMUIR $\Gamma = \frac{\Gamma' K' C_{eq}}{1 + \Gamma' C_{eq}}$	$R_f = 1 + \frac{\rho_b}{\eta}\left(\frac{K_d \Gamma'}{(1 + K_d C)^2}\right)$

Question 3 [25 Marks]

a) Using short notes compare and contrast advection and dispersion as forms of pollutant transport in aquatic environments. [15]

b) A truck which is carrying water containing 1275 mg/L benzene overturns and spills a volume of water sufficient to saturate a thin acquifer over an area 5 m^2. The acquifer conatins ground flowing with an average linear velocity of 0.45 m/day. Assume that DL and DT are 2.1 m^2/day and 0.21 m^2/day repsectively.

There is a nearby private well at a seasonal cottage. If the center of the spill is located at Xo=0 and Yo=0, then the location of the well is x= 72 m and y=5.5 m. The owners of the Private well are away for the season and will not return for another 200 days. If there is no degradation or retardation of benzene as it moves through the acquifer, what will the concentration of benzene be in the well when the owners return ? [10]
Useful relation.

$$C = \frac{C_0 A}{2(\sqrt{\pi})^2 (2D_x t)(2D_y t)^{1/2}} \, exp\left[-\frac{1}{2}\left\{\frac{(x - x_0 - u_x t)^2}{2D_x t} + \frac{(y - y_o - u_y t)^2}{2D_y t}\right\}\right]$$

Question 4 [25 Marks]

a) Using an example of your choice define the term "risk". [5]

b) You are an environmental consultant and have been asked to conduct a risk assessment on a site on the outskirts of a city selected for domestic housing development. Outline diagrammatically the steps you would take in this evaluation. [15]

c) Daily intake values and reference dose for Cu, Zn, Cd, inorganic arsenic and organic Hg from oysters are as follows:

Cu	40	373	909
Zn	300	531	129.3
Cd	0.5	0.340	0.832
As	0.3	0.484	11.8
Hg	0.1	0.056	0.178

Evaluate the risk associated with these elements at a maximum daily oyster intake of 139 g/day for an adult weight of 65 kg and comment on your results. [5]

Useful relation:

$$HQ = \frac{EFr \times ED_{tot} \times SFI \times MCS}{RFDo \times BWa \times ATn}$$

Where:
Efr: Exposure frequency (350 day/yr)
EDtot: exposure duration (30 yrs)
SFI: sea food ingestion g/day
RFDo: Reference dose, oral (mg/kg/day) (TDI)
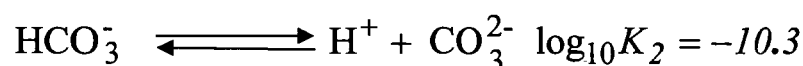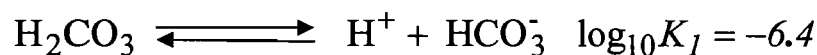MCS: metal concentration in edible portion of food
ATn: average time (30 yrs)
BW: Body weight.

Question 5 [25 Marks]

a) With the aid of diagrams, examples and appropriate reaction equations, write short notes on the following terms [10]
   i) Chemical speciation
   ii) Sediment stratification

b) Given the following equilibrium equations for carbon dioxide in water,using charge balance calculate the fraction dissociated at pH 6.8 for the following species:
   i) H_2CO_3 [2]
   ii) HCO_3^- [2]
   iii) CO_3^{2-} [2]

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad \log_{10}K_1 = -6.4$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad \log_{10}K_2 = -10.3$$

c) The diagram and equilibria given below illustrate some oxidation/reduction chemistry of mercury.
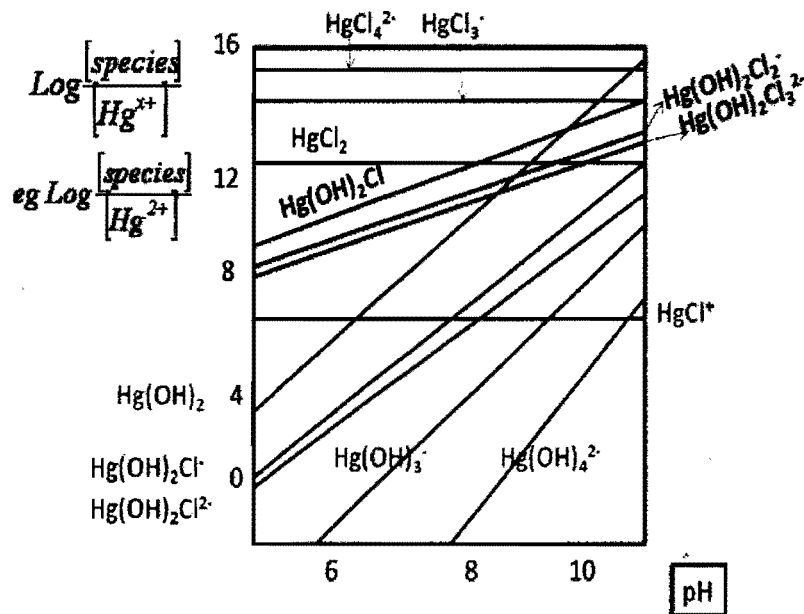
Chlorination complexes

1. $Hg^{2+} + Cl^- \rightleftharpoons HgCl^+$

2. $HgCl^+ + Cl^- \rightleftharpoons HgCl_2$

3. $HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-$

4. $HgCl_3 + Cl^- \rightleftharpoons HgCl_4^{2-}$ $Log k = 15.2$

Hydroxyl complexes

5. $Hg^+ + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+$ $Log K = -6$

6. $HgCl^+ + OH^- \rightleftharpoons HgOHCl$

Using equation 4 and 5 show the equilibrium lines represented by

i) $Log \dfrac{\left[Hg(OH)_2 \right]}{\left[Hg^+ \right]}$ [2]

iii) $Log \dfrac{\left[HgCl_4^{2-} \right]}{\left[Hg^{2+} \right]}$ [2]

iv) Using the speciation diagram for mercury discuss the aqueous chemistry of mercury in surface water systems. [5]

Question 6 [25 Marks]

a) With the aid of the ^{12}C-NMR and infra-red spectra below and any other pertinent facts compare and contrast humic and fulvic acids. [15]

CPMAS ^{13}C-NMR spectra of the fulvic acid *"fractions"* and the humic acids from three soil types.
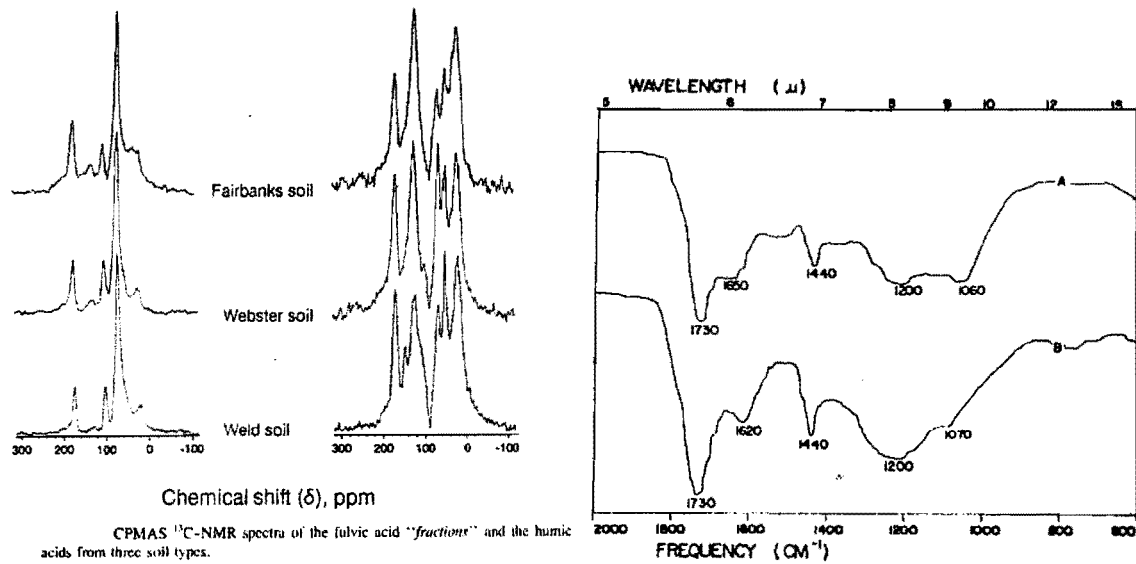
In your discussion include genesis reactions, chemical and physical properties, separation (extraction) techniques and any other important similarities/differences.

b) Using examples explain the role of humic/fulvic acids in pollutants transport. [10]

In your analysis include the role of functional groups, complexation, binding capacity and its role in oxidation reduction reactions in the aquatic environment.

Useful Relations				General Data		
$(RT)_{298.15K}$=2.4789 kJ/mol				speed of light	c	$2.997\,925\times10^{8}$ ms^{-1}
$(RT/F)_{298.15K}$=0.025 693 V				charge of proton	e	$1.602\,19\times10^{-19}$ C
T/K: 100.15 298.15 500.15 1000.15				Faraday constant	F=Le	$9.648\,46\times10^{4}$ C mol^{-1}
T/Cm^{-1}: 69.61 207.22 347.62 695.13				Boltzmann constant	k	$1.380\,66\times10^{-23}$ J K^{-1}
1mmHg=133.222 N m^{-2}				Gas constant	R=Lk	$8.314\,41$ J K^{-1} mol^{-1}
hc/k=$1.438\,78\times10^{-2}$ m K						$8.205\,75\times10^{-2}$ dm^{3} atm K^{-1} mol^{-1}
1atm	1 cal	1 eV	1cm^{-1}			
=1.01325×10^{5} Nm^{-2}	=4.184 J	=1.602 189$\times10^{-19}$ J	=0.124$\times10^{-3}$ eV	Planck constant	h	$6.626\,18\times10^{-34}$ Js
=760torr		=96.485 kJ/mol	=1.9864$\times10^{-23}$J		$\hbar = \dfrac{h}{2\pi}$	
=1 bar		= 8065.5 cm^{-1}				$1.054\,59\times10^{-34}$ Js
				Avogadro constant	L or N$_{av}$	$6.022\,14\times10^{23}$ mol^{-1}
SI-units:				Atomis mass unit	u	$1.660\,54\times10^{-27}$ kg
1 L = 1000 ml = 1000cm^3 = 1 dm^3				Electron mass	m$_e$	$9.109\,39\times10^{-31}$ kg
1 dm = 0.1 m				Proton mass	m$_p$	$1.672\,62\times10^{-27}$ kg
1 cal (thermochemical) = 4.184 J				Neutron mass	m$_n$	$1.674\,93\times10^{-27}$ kg
dipole moment: 1 Debye = 3.335 64$\times10^{-30}$ C m				Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	$8.854\,188\times10^{-12}$ J^{-1} C^2 m^{-1}
force: $1N=1J\,m^{-1}= 1kgms^{-2}$=$10^5$ dyne pressure: $1Pa=1Nm^{-2}$=1Jm^{-3}				Vacuum permeability	μ_o	$4\pi\times10^{-7}$ Js^{2}C^{-2} m^{-1}
$1J = 1\,Nm$				Bohr magneton	$\mu_B = {e\hbar}/{2m_e}$	$9.274\,02\times10^{-24}$ JT^{-1}
power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}						
magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}				Nuclear magneton	$\mu_N = {e\hbar}/{2m_p}$	5.05079×10^{-27} JT^{-1}
Prefixes:				Gravitational constant	G	6.67259×10^{-11} Nm^{2}kg^{-2}
p h m m c d k M G				Gravitational	g	9.80665 ms^{-2}
pico nano micro milli centi deci kilo mega giga				acceleration		
10^{-12} 10^{-9} 10^{-6} 10^{-3} 10^{-2} 10^{-1} 10^{3} 10^{6} 10^{9}				Bohr radius	a$_o$	$5.291\,77\times10^{-11}$ m

THE PERIODIC TABLE OF ELEMENTS

Group	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
Period 1	1 H 1.008						NON-METALS											2 He 4.003
2	3 Li 6.94	4 Be 9.01				METALLOIDS							5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31			METALS								13 Al 26.9	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.01	25 Mn 54.9	26 Fe 55.85	27 Co 58.71	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.7	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 91.22	42 Mo 95.94	43 Tc 98.9	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	71 Lu 174.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 196.9	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.9	84 Po 210	85 At 210	86 Rn 222
7	87 Fr 223	88 Ra 226.0	103 Lr 257	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

		57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.9	63 Eu 151.3	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
Lanthanides															
Actinides		89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.1	94 Pu 239.1	95 Am 241.1	96 Cm 247.1	97 Bk 249.1	98 Cf 251.1	99 Es 254.1	100 Fm 257.1	101 Md 258.1	102 No 255

Numbers below the symbol indicates the atomic masses; and the numbers above the symbol indicates the atomic numbers.