UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2013

TITLE OF PAPER	:	ENVIRONMENTAL CHEMISTRY
COURSE NUMBER	:	ERM640
TIME ALLOWED	:	3 HRS
INSTRUCTIONS	:	THIS EXAMINATION HAS SEVEN (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

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Question 1 (25 Marks)

a) Using diagrams, examples and or equations write short notes on any two of the following terms.

i) Octanol / water partition coefficient, K_{ow}

ii) Water Solubility, S_w

iii) Henry's, H

In each highlight the environmental relevance, methods of determination and where applicable give methods of estimation using Quality Structure Activity Relationships (QSAR's) [10]

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 10 m. Water has a 3-cm layer of sediment, contains 5 ml of suspended solids per cubic meter, and 0,5 mlm^{-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, respectively. [10]

ii) Establish the overall distribution of the pollutant in this environment using the fugacity concept. [5]

Question 2 (25 Marks)

a) Write short notes on Soil Sorption as an environmental fate property. [15]

b) i) Using thermodynamic assumptions derive the Langmuir adsorption equation. [4]

$$\Gamma = \frac{\Gamma_{\infty} K C_{equil.}}{1 + K C_{equil.}}$$

ii) The sorption of Cr^{+6} on a slit loam yielded the following results:

Equilibrium Concentration mg/1	Cr^{+6} Sorbed (μg/g)
0.08	13
0.20	31
0.32	51
0.40	67
0.53	86

Verify whether or not this sorption follows a one site Langmuir or the Freundlich Sorption Isotherm. [2]

Useful relations:

$$\Gamma = KC_{eq.}^{N} \qquad \Gamma = \frac{\Gamma_{\infty} KC_{equil.}}{1 + KC_{equil.}}$$

Determine the appropriate constants and comment on their magnitude. [4]

Question 3 [25 Marks]

a) Write short notes on the following pollutant transport processes in aquatic environments.

i) Diffusion [8]

ii) Advection [6]

iii) Dispersion [6]

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 ? [5]

Useful relation.

$$C = \frac{C_0 A}{2(\sqrt{\pi})^2 \{(2D_x t)(2D_y t)\}^{1/2}} \exp\left[-\frac{1}{2}\left\{\frac{(x - x_0 - u_x t)^2}{2D_x t} + \frac{(y - y_0 - u_y t)^2}{2D_y t}\right\}\right]$$

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:

[illegible]	[illegible]	[illegible]	[illegible]
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:

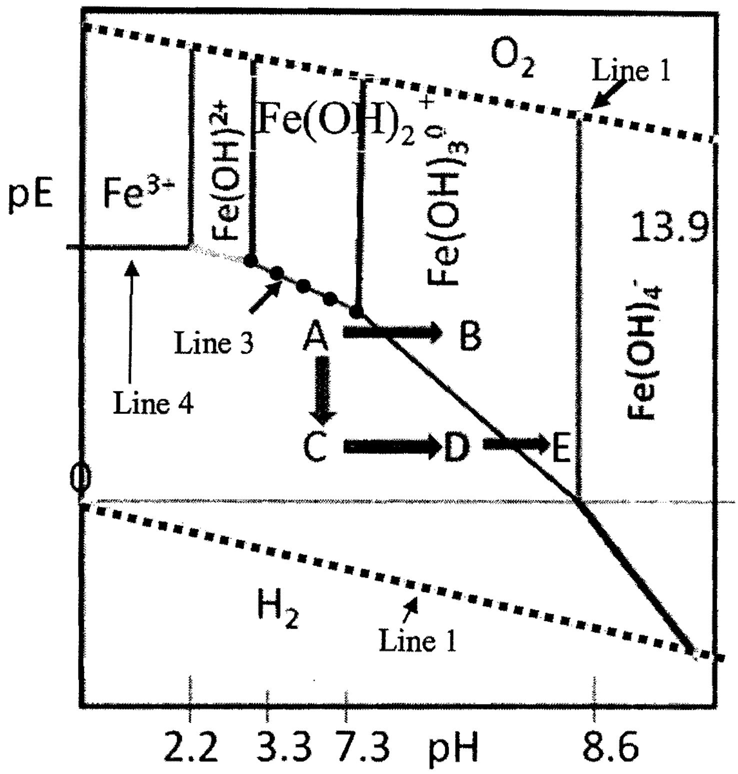
$$HQ = \frac{EFr \times ED_{tot} \times SFI \times MCS}{RFDo \times BWa \times ATn}$$

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) Write short notes on the following terms [12]
   i) Chemical speciation
   ii) Water stratification in lakes

The diagram below illustrates some oxidation/reduction chemistry of Iron.



b) Using the diagram above and any other pertinent information:
   i) What are denoted by the two dashed lines indictaes a line 1 and line 2 [2]
   ii) Locate the pH and redox conditions in the following types of water [5]
      1) Oceans
      2) Acid mine drainage
      3) Anoxic sediments
      4) Ground water
      5) Peat bogs

c) Using the appropriate equilibrium reactions of iron species below derive the equation for the equilibrium lines denotes line 3 and line 4. [6]

Oxidation $Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad \text{Log K} = +13.2$

Hydrolysis reactions for Fe^{3+}

$$Fe^{+3} + H_2O \rightleftharpoons Fe(OH)^{2+} + H^+ \quad \log K_1 = -2.2$$

$$Fe(OH)^{2+} + H_2O \rightleftharpoons Fe(OH)_2^+ + H^+ \quad \log K_2 = -3.3$$

$$Fe(OH)_2^{2+} + H_2O \rightleftharpoons Fe(OH)_3^o + H^+ \quad \log K_3 = -7.3$$

$$Fe(OH)_3^o + H_2O \rightleftharpoons Fe(OH)_4^- + H^+ \quad \log K_4 = -8.3$$

$$Fe(OH)_3 + 3H^+ \rightleftharpoons Fe^{+3} + 3H_2O \quad \log K_s = -2.0$$

hydrolysis reactions of Fe^{2+}

$$Fe(OH)_2^+ + 2H^+ + 2e^- \rightleftharpoons Fe^{+2} + 2H_2O \quad \log K_s = +18.7$$

$$Fe(OH)_3^0 + 3H^+ + e^- \rightleftharpoons Fe^{+2} + 3H_2O \quad \log K_s = +26$$

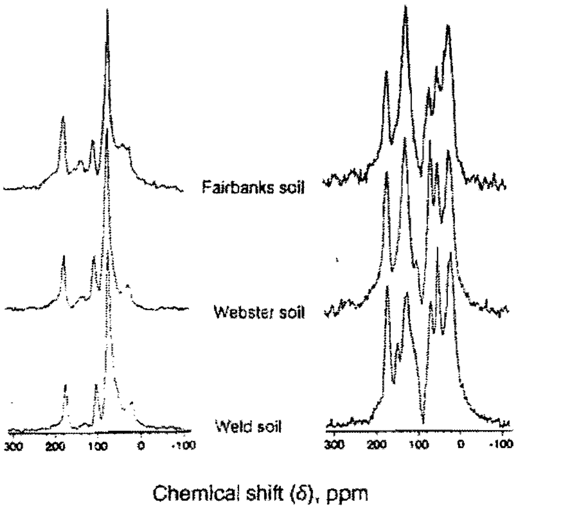
$$Fe(OH)_4^- + 4H^+ + e^- \rightleftharpoons Fe^{+2} + 4H_2O \quad \log K_s = +34.6$$

Interconversion

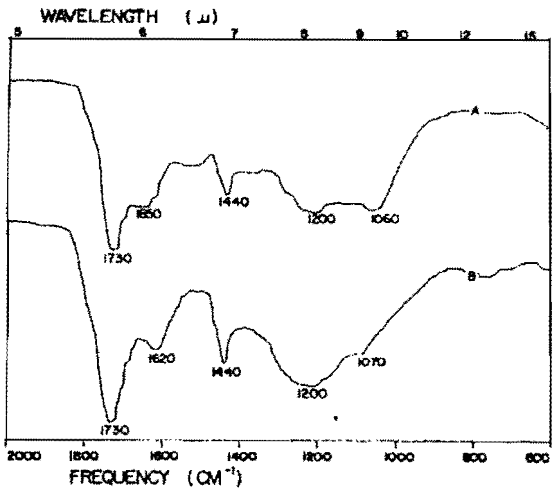
$$Fe^{+3} + 3H_2O \rightleftharpoons Fe(OH)_3 \quad \log K = -4.0$$

<u>Question 6 [25 Marks]</u>

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

$(RT)_{298.15K}$=2.4789 kJ/mol

$(RT/F)_{298.15K}$=0.025 693 V

T/K:	100.15	298.15	500.15	1000.15
T/Cm^{-1}:	69.61	207.22	347.62	695.13

1mmHg=133.222 N m^{-2}

hc/k=1.438 78x10^{-2} m K

1atm	1 cal	1 eV	1cm^{-1}
1.01325x10^{5} Nm^{-2}	4.184 J	1.602 189x10^{-19} J	0.124x10^{-3} eV
760torr		96.485 kJ/mol	1.9864x10^{-23}J
1 bar		8065.5 cm^{-1}	

SI-units:

1 L = 1000 ml = 1000cm^{3} = 1 dm^{3}

1 dm = 0.1 m

1 cal (thermochemical) = 4.184 J

dipole moment: 1 Debye = 3.335 64x10^{-30} C m

force: ***1N=1J m^{-1}= 1kgms^{-2}***=10^{5} dyne pressure: ***1Pa=1Nm^{-2}***=1Jm^{-3}

1J = 1 Nm

power: 1W = 1J s^{-1} potential: 1V =1 J C^{-1}

magnetic flux: 1T=1Vsm^{-2}=1JCsm^{-2} current: 1A=1Cs^{-1}

Prefixes:

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

General Data

speed of light	c	**2.997 925x10^{8} ms^{-1}**
charge of proton	*e*	1.602 19x10^{-19} C
Faraday constant	F=L*e*	9.648 46x10^{4} C mol^{-1}
Boltzmann constant	k	**1.380 66x10^{-23} J K^{-1}**
Gas constant	R=Lk	**8.314 41 J K^{-1} mol^{-1}**
		8.205 75x10^{-2} dm^{3} atm K^{-1} mol^{-1}
Planck constant	h	**6.626 18x10^{-34} Js**
	$\hbar = \frac{h}{2\pi}$	1.054 59x10^{-34} Js
Avogadro constant	**L or N$_{av}$**	**6.022 14x10^{23} mol^{-1}**
Atomis mass unit	u	1.660 54x10^{-27} kg
Electron mass	**m_e**	**9.109 39x10^{-31} kg**
Proton mass	m_p	1.672 62x10^{-27} kg
Neutron mass	m_n	1.674 93x10^{-27} kg
Vacuum permittivity	$\varepsilon_o = \mu_o^{-1}c^{-2}$	8.854 188x10^{-12} J^{-1} C^{2} m^{-1}
Vacuum permeability	μ_o	4πx10^{-7} Js^{2}C^{-2} m^{-1}
Bohr magneton	$\mu_B = e\hbar/2m_e$	9.274 02x10^{-24} JT^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	5.05079x10^{-27} JT^{-1}
Gravitational constant	G	6.67259x10^{-11} Nm^{2}kg^{-2}
Gravitational acceleration	g	**9.80665 ms^{-2}**
Bohr radius	a_o	5.291 77x10^{-11} m

THE PERIODIC TABLE OF ELEMENTS

NON-METALS

METALLOIDS

METALS

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																	[illegible]
2	3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3	11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.9	14 **Si** 28.09	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]
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	[illegible]
7	87 **Fr** 223	88 **Ra** 226.0	103 **Lr** 257	104 **Unq**	105 **Unp**	106 **Unh**	107 **Uns**	108 **Uno**	109 **Une**									

Lanthanides	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
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.*
SOURCE: International Union of Pure and Applied Chemistry, I mills, ed., Quantities, Units, and symbols in Physical Chemistry, Blackwell Scientific publications, Boston, 1988, pp 86-98.