# UNIVERSITY OF SWAZILAND

# FINAL EXAMINATION 2014

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|---|---|---|
| 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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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 0,5$mlm^{-3}$ 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, 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]

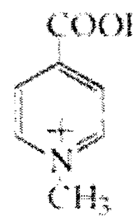
**Question 2 (25 Marks)**

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]

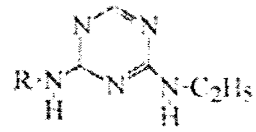
(ii). Surface complexation [5]

(iii). Protonation and Ion exchange [5]

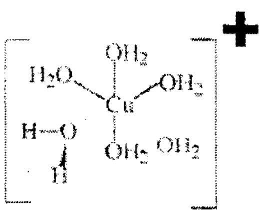


PARAQUAT

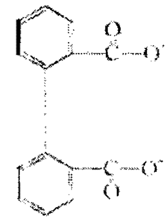
$H_3AsO_4$



ATRAZINE



$Fe(OH)_3$



DISSOLVED ORGANIC HUMIC ACID

b) Using thermodynamic assumptions derive the Langmuir adsorption equation. [3]

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

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

| Equilibrium Concentration mg/l | Toluene Sorbed (μg/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:**

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

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

**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.

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

**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:

| **Metal** | **RFr dos µg/kg/day** | **Intake dose µg/kg/day** | **Intake dose µg/g** |
|---|---|---|---|
| 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

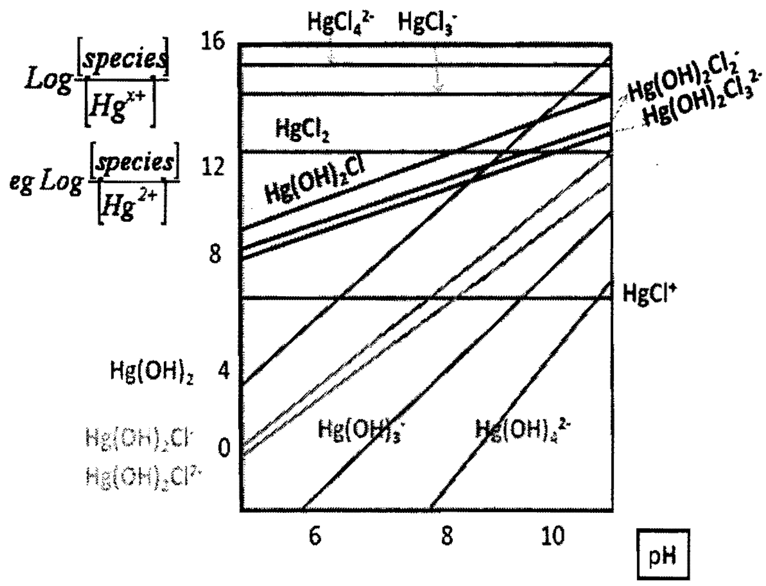
b) Given the following equilibrium equations for carbon dioxide in water,using charge balance calculate the fraction dissociated at pH 6.8 for the following species:

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

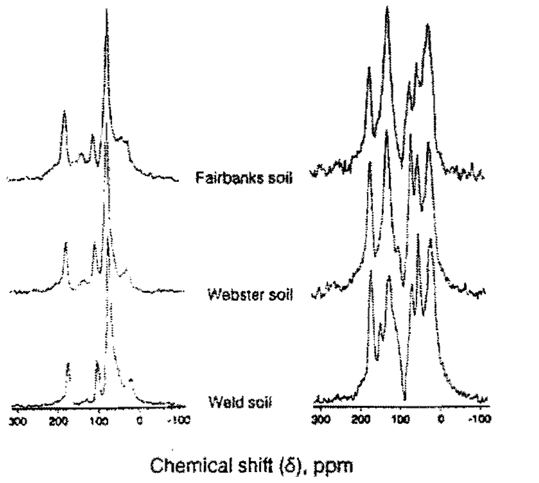
i) $Log \frac{[Hg(OH)_2]}{[Hg^+]}$ [2]

iii) $Log \frac{[HgCl_4^{2-}]}{[Hg^{2+}]}$ [2]

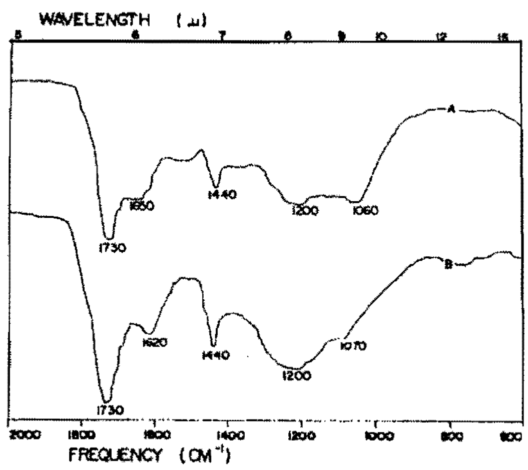
iv) Using the speciation diagram for mercury discuss the aqueous chemistry of mercury in surface water systems. [5]

## 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.

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## 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**<br>**=1 bar** | | =96.485 kJ/mol<br>= 8065.5 cm$^{-1}$ | =1.9864x10$^{-23}$J |

**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 | $\mu_o$ | 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 | | | | | | | | | | | | | | | | | 2 He 4.003 |
| 2 | 3 Li 6.94 | 4 Be 9.01 | | | | | | | | | | | 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 | | | | | | | | | | | 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 | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 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.*