JAMES COOK UNIVERSITY

P O Box 6811 CAIRNS Qld 4870 Australia Tel: (07) 4042.1275 Fax: (07) 4042 1284

SCHOOL OF PHARMACY AND MOLECULAR SCIENCES
Chemistry Department

This paper must be handed in at the end of the Examination: Yes
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FIRST SEMESTER EXAMINATIONS 2006

Cairns Campus

STUDENT NAME:
(*block letters*)

STUDENT NUMBER:

SUBJECT CODE: CH2041:03

SUBJECT NAME: ENVIRONMENTAL CHEMISTRY

EXAMINER: Dr M. Liddell **PHONE NO:** (07) 4042 1275

DURATION OF EXAMINATION (hours): TWO (2) HOURS

PERUSAL TIME (minutes): FIFTEEN (15) MINUTES

TOTAL NUMBER OF QUESTIONS: 6

INSTRUCTIONS TO STUDENTS:
Total marks for paper = **80**
Answer **ALL** questions. All questions are **not** of equal value.
Timings are indicated to allow 15 minutes of check-over time.

MATERIALS TO BE SUPPLIED BY EXAMINATION SECTION:
Examination Booklets required: Yes

MATERIALS STUDENTS MAY USE:
Any type of calculator.
Access to an English Dictionary: Yes

Question 1

Timing: you should complete this question in 16 minutes.

(a) The **atmosphere** is arranged into regions according to the variation in atmospheric temperature with altitude.

- Provide a sketch of the vertical profile of the **atmosphere** naming each of the regions and providing **temperature** and **pressure conditions** up to 100km above the surface.
- Explain how the atmosphere functions as a **radiation shield** for the biosphere.
- In which region is the **hydroxyl radical** found and how is it formed?

(6 marks)

(b) The mechanism of **stratospheric ozone destruction** in the polar regions (springtime) is fundamentally different to the general stratospheric removal mechanism.

- Discuss how the **chemistry of the CFC's** results in rapid **ozone depletion** in the polar spring. Use chemical equations to support your answer and indicate why **chlorine monoxide** is important in ozone chemistry.
- Provide a Lewis dot structure for **chlorine monoxide**.
- What **type of compounds** have replaced CFC's and why do these not cause catalytic destruction of ozone in the stratosphere?

(6 marks)

Question 2

Timing: you should complete this question in 21 minutes.

(a) **Water quality** is generally established by carrying out a series of standard tests such as pH, alkalinity and BOD.

- Explain how you would carry out a Biological Oxygen Demand (**BOD**) measurement including details of **quality control** procedures.
- What **chemical species** found in water is the BOD test concerned with?
- A freshwater may have a **high alkalinity** and yet be only **moderately basic** (pH 8.5). Explain how this can be the case.
  In your answer include a **calculation of the OH^- concentration** and provide a clear **definition of alkalinity** (including units).

(6 marks)

(b) A variety of **acids** are found in both freshwater and marine environments.

- List the typical **major acids** present in these two environments (non-polluted), indicate the **characteristic pH's** of these waters.
- Calculate the **hardness** of water in **mg $CaCO_3$ eq / L** for a sample of water which had the following analyses:
  Ca^{2+} 300ppm Mg^{2+} 200ppm Cl^- 210ppm HCO_3^- 150ppm
  Is this a soft or a hard water sample and how would you go about measuring the hardness without access to the above analyses?

(5 marks)

(c) Three major elements of the **geosphere**, silicon (27.7% abundant in the crust), aluminium (8.1%) and iron (5%), are found in low concentration in the ocean, the final repository of weathered minerals.

- Explain this apparent anomaly, in your answer you should detail how surface chemistry is important.
- What is the **exogenic cycle** as it applies to biogeochemical cycling?

(5 marks)

Question 3

Timing: you should complete this question in 14 minutes.

(a) Weathered minerals make up a substantial component (>95%) of soils.

- Define the following terms: **rock**, **mineral**.
- Provide an example of each of the following minerals, include a chemical formulae for each and indicate how they will undergo chemical weathering.
  (i) an **sulphide** mineral
  (ii) a **carbonate** mineral
- How are **sedimentary rocks** and **igneous rocks** involved in soil formation and what are these rock types?

(6 marks)

(b) The soils in coastal North Queensland are frequently highly altered due to the high average temperature and rainfall.

- What **measurements** would you need to determine if a soil is highly **altered**?
- Sketch a typical **tropical soil profile**, indicating the different horizons and the composition (minerals, organic matter etc) of each horizon.
  (N.B. you do not need to specify an exact soil profile).
- List **3 soil parameters** that are typically used to **define a soil** and provide indicative values for the soil you have described above.

(6 marks)

Question 4

Timing: you should complete this question in 24 minutes.

(a) Describe the apparatus you would use for sampling and the methods that you would use for analysing the following samples :

- **Formaldehyde** vapour in workplace air.
- **Heavy metals** (Pb, Cd) in leachate from a tailings damn.
- A soil contaminated with polychlorinated biphenyl (**PCB**) residues.

(6 marks)

(b) **Chemiluminescence** is a technique frequently used for the real time analysis of NO_x and O_3 pollution in urban air-sheds.

- Indicate the typical features of a **chemiluminescence spectrometer** used for analyzing NO_x.
- How does the phenomenon of **chemiluminescence** differ from that of **fluorescence**?

(5 marks)

(c) **High Performance Chromatography** (**HPLC**) is the major technique used for the analysis of

water soluble organic compounds, especially those with low volatility.

- Sketch the features of a typical HPLC instrument and include details of the **stationary phase** and the type of **mobile phase** that would be used.
- Explain the basic principle of operation of (i) **MS detection** and (ii) **photodiode array** (PDA) detection.
- Provide an example of an **environmental pollutant** that is routinely analysed by HPLC.

(6 marks)

Question 5

Timing: you should complete this question in 16 minutes.

(a) In South East Queensland **photochemical smog** ensures that the air above the city of Brisbane is rarely perfectly clean.

- What are the **physical conditions required** for the formation of a typical photochemical smog.
- What are the **primary** and **secondary pollutants** in a photochemical smog.
- How does **vegetation** in and around the city of Brisbane influence air quality?
- What **measurements** are made in South East Queensland to determine the extent of smog formation?

(6 marks)

(b) The **radiation balance** at the Earth's surface is sensitive to the concentration of **greenhouse gases** in the troposphere and the planetary **albedo**.

- Draw a simple diagram indicating the **radiation balance** at the Earth's surface.
- List three major natural **greenhouse gases**.
- Define the planetary **albedo**.
- Explain the terms **global warming potential** and **relative warming potential** as they apply to the greenhouse gases.

(6 marks)

Question 6

Timing: you should complete this question in 14 minutes.

(a) Provide an example (molecular structure) of each of the following classes of common **organic pollutants** and describe the **use** or **origin** of the pollutatant

- **Organophosphate** (OP).
- **Polycyclic aromatic hydrocarbon** (PAH)

Indicate if the molecules that you have chosen biomagnify in the environment, explaining what
the term **biomagnify** means.
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(6 marks)

(b) Despite the fact that both mercury and lead have long been known as **toxic metals** they are still
in widespread use.

- Compare and contrast the **uses**, **chemistry** and **toxicity** of **mercury** and **lead**.

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(5 marks)

TABLE OF FORMULAE

$p_{Total} = \Sigma p_i$

$[i_{(aq)}] = p_i K_H$

$p_i = (\%_i / 100)\ p_{atm}$

$\%_i = ppmv_i \times 10^{-4}$

$p_z = p_o e^{(\frac{-z}{H})}$ where H = 8.4 km

$\rho = p\,M / RT$

$R.H. = \frac{p(H_2O)}{p(H_2O)sat.} \times 100\,\%$

Flux = A / τ

$a_i = [i_{(aq)}] \times \gamma_i$

$pH = -\log_{10}\{a_{H^+}\}$

$[BNC] = [HA] + [H^+] - [OH^-]$

$[ANC] = [A^-] + [OH^-] - [H^+]$

$[alk]_{tot} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

$I = ½\, \Sigma\, c_i z_i^{\,2}$

$pE^o = E^o_{1/2} / 0.0591$ at 25°C

$pE = pE^o - 1/n \log ([Red] / [Ox])$

For the cell reaction aA + bB $\rightarrow$ cC + dD

$E^o_{cell} = E^o_{Red} - E^o_{Ox}$

$K_{sp} = [cation]^c[anion]^d$

$Q = [cation]_o^c[anion]_o^d$

Lifetime(i) = Inventory(i) / Input(i)

GR= P± R- ET-MR

$IAP = a_{Cation}^{n+} \times a_{Anion}^{n-}$

$\Omega = IAP / K_{sp}$

$F = v_g [i_g]$

$F = \frac{1}{r}\left([\boldsymbol{i}_g] - [\boldsymbol{i}_l]\right)$

$K_{part} = \frac{[\boldsymbol{i}_{(aer)}]}{[\boldsymbol{i}_g][aerosol]}$

$K_{dist} = \frac{[\boldsymbol{i}_s]}{[\boldsymbol{i}_w]}$

$[i_s] = K_F\,[i_w]^n$

$CIA = \left(\frac{Al_2O_3}{Al_2O_3 + CaO* + Na_2O + K_2O}\right) \times 100$

$SAR = \frac{[Na^+]}{\sqrt{([Ca^{2+}] + [Mg^{2+}])/2}}$

$\frac{ESP}{(100 - ESP)} = 0.015\,SAR$

$K_{OW} = i_{(solubility\ octanol)} / i_{(solubility\ H2O)}$

$BCF = [i_{(organism)}] / [i_{(water)}]$

$E_{photon} = hc / \lambda$

$\alpha = K_2/K_1 = k_2'/k_1' = t_{r2}'/t_{r1}'$

$A = \varepsilon\, l\, [i]$

$I = k\, P_o\, [i]$

$\frac{[u_i]}{[u_i] + [s_i]} = \frac{I_u}{I_{u+s}}$

$\frac{[u_i]/[u_j]}{[ref_i]/[ref_j]} = \frac{I_{u(i)} / I_{u(j)}}{I_{ref(i)} / I_{ref(j)}}$

$\ln N_o - \ln N = k\,t$

$t_{½} = \ln 2 / k$

$\Delta E_{BE} = \Delta mc^2$

$mrem = 1\ rad \times RBE \times 10^{-3}$

$R = 8.314\ J\ mol^{-1}\ K^{-1}$

1 atm. = 1.013×10^5 Pa = 760 torr

T(K) = T(°C) + 273.15

$c = 3.00 \times 10^8\ m\ s^{-1}$

TABLE OF EQUATIONS

$\{CH_2O\} + O_2$	$\rightarrow CO_2 + H_2O$	pE^o_w 22	ΔG^o -475 kJ/mol
$5\{CH_2O\} + 4NO_3^-$	$\rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	pE^o_w 21	ΔG^o -448 kJ/mol
$\{CH_2O\} + 3CO_2 + H_2O + 2MnO_2$	$\rightarrow 2Mn^{2+} + 4HCO_3^-$	pE^o_w 18	ΔG^o -349 kJ/mol
$\{CH_2O\} + 7CO_2 + 4Fe(OH)_3$	$\rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	pE^o_w 9.2	ΔG^o -114 kJ/mol
$2\{CH_2O\} + SO_4^{2-}$	$\rightarrow H_2S + 2HCO_3^-$	pE^o_w 4.5	ΔG^o -77 kJ/mol
$2\{CH_2O\}$	$\rightarrow CH_4 + CO_2$	pE^o_w 4.1	ΔG^o -58 kJ/mol
$3\{CH_2O\} + 2N_2 + 4H^+ + 3H_2O$	$\rightarrow 4NH_4^+ + 3CO_2$		ΔG^o -56 kJ/mol
$CO_2 + H_2O + h\nu$	$\rightarrow \{CH_2O\} + O_2$		ΔG^o +478 kJ/mol

$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O$

$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2$

$2CaCO_3 + 2SO_2 + O_2 + 4H_2O \rightarrow 2CaSO_4.2H_2O + 2CO_2$

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4$

$KAl_3Si_3O_{10}(OH)_2 + 3C_2O_4^{2-} + 10H^+ \rightarrow 3AlC_2O_4^+ + 3Si(OH)_4 + K^+$

$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow 2Na^+ + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4$

$2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4$ (Mn cat.)

$CH_4 + OH + 2O_2 + 2NO \rightarrow HCHO + 2NO_2 + H_2O + OH$

$CH_3CHO + OH + O_2 + NO_2 \rightarrow CH_3COO_2NO_2 + H_2O$

$106CO_2 + 16NH_4^+ + H_2PO_4^- + 106H_2O \leftrightarrows C_{106}H_{263}O_{110}N_{16}P_1 + 106O_2 + 15H^+$

PERIODIC TABLE
CH2041:03

Period	1	2	3	4	5	6	7	8	9	10	11	12	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
								1 H 1.008										2 He 4.003
2	3 Li 6.941	4 Be 9.012											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 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	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	La-Lu	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 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po 210.0	85 At 210.0	86 Rn 222.0
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	. . . .								

s block | *d* block | *p* block

	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 146.2	61 Pm 144.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
Actinide	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252.1	100 Fm 257.1	101 Md 258.1	102 No 259.1	103 Lr 262.1

f block