22/03(a) # The University of Sydney

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2001 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-11	42	

Short answer section

Page	Marks			Marker
	Max	Gained		
12	6			
13	6			
15	7			
16	5			
17	8			
18	6			
19	4			
20	4			
21	6			
22	3			
23	3			
Total	58			

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 21 pages of examinable material.
- Complete the examination paper in **INK.**
- Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.
- The total score for this paper is 100. The possible score per page is shown in the adjacent tables.
- Each new question begins with a •.
- Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.
- Some useful formulas, a Periodic Table and numerical values required for any question may be found on a separate data sheet.
- Pages 14 and 24 are for rough working only.

Marks 6

- At the high temperatures reached in a cylinder of a car engine, some N_2 reacts with O_2 to form nitric oxide, NO, which further reacts to form NO_2, a toxic pollutant that contributes to smog. The equations for the reactions are:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_{p1} = 4.3 \times 10^{-25}$ at 298 K

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $K_{p2} = 2.5 \times 10^{8}$ atm^{-1} at 298 K

Calculate K_c for the reaction: $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ at 298 K

K_c =

Calculate $\Delta G°$ for the reaction: $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ at 298 K.

$\Delta G°$ =

At what temperature will the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ become spontaneous? Use the following data.

	$\Delta H°_f$ / kJ mol^{-1}	$S°$ / J K^{-1} mol^{-1}
$O_2(g)$	0	205
$N_2(g)$	0	192
NO(g)	90	211

	$T =$

Marks
6

- Complete the table by drawing the Lewis structure and indicating the molecular geometry and hybridisation of the underlined atom.

Species	Lewis structure	Shape of molecule or ion	Hybridisation of underlined atom
$\underline{Cl}F_3$			
$\underline{N}O_2^+$			
$\underline{S}F_6$			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

5

- In a laboratory experiment similar to the one you undertook on calorimetry, 5.0 g of NaOH pellets was dissolved in 200 mL of water in a calorimeter that had an overall heat capacity (including the solution) of 910 J K^{-1}. A temperature increase of 4.75 °C was noted. In another experiment, 100 mL of 0.50 M HCl was mixed with 100 mL of 0.50 M NaOH in the calorimeter and a temperature increase of 3.26 °C was noted.

  Write the equations of the two processes that are occurring and calculate the enthalpy change (in kJ mol^{-1}) of each.

In a third experiment, the enthalpy change of the reaction

$NaOH(s) + H^+(aq) \rightarrow Na^+(aq) + H_2O$ was measured to be –95 kJ mol^{-1}.

Comment on this value in the light of the first two experiments.

2

- The Haber Process, used in the production of ammonia, is catalysed by iron.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ_f(NH_3) = -46 \text{ kJ mol}^{-1}$$

How might temperature affect the formation of NH_3 from N_2 and H_2?

Marks

- The following data were obtained for the osmotic pressure of solutions of a particular protein at four different concentrations at 37 °C. **3**

Conc. (mg L^{-1})	Osmotic Pressure (mPa)
10	0.26
50	1.26
800	17.1
10000	163.7

From these data, what is the best estimate for the molecular weight of this protein?

Answer:

What is a reasonable explanation for the curvature seen in the data?

- The freezing point depression constant for water is 1.86 K kg mol^{-1}. Calculate the freezing point of sea water given that it contains the following ions: **2**

0.460 mol kg^{-1} Na^{+}
0.054 mol kg^{-1} Mg^{2+}
0.011 mol kg^{-1} Ca^{2+}
0.010 mol kg^{-1} K^{+}
0.540 mol kg^{-1} Cl^{-}
0.028 mol kg^{-1} SO_4^{2-}
0.004 mol kg^{-1} HCO_3^{-}

Answer:

Marks

- The $H_2PO_4^-$ and HPO_4^{2-} ions play a role in maintaining the pH of intracellular fluid. Write equations to show how a solution containing these ions functions as a buffer. **6**

At what pH is the $H_2PO_4^-$ / HPO_4^{2-} buffer system most effective? Why?

For phosphoric acid: $K_{a1} = 7.1 \times 10^{-3}$ M, $K_{a2} = 6.3 \times 10^{-8}$ M, $K_{a3} = 4.2 \times 10^{-13}$ M.

pH =

Calculate the ratio of $[H_2PO_4^-]$ / $[HPO_4^{2-}]$ required to give a buffer with a pH of 7.68.

Answer:

- The solubility product constant, K_{sp}, of $Mg(OH)_2$ is 7.1×10^{-12} M^3. Calculate the solubility of $Mg(OH)_2$ (in mol L^{-1}) in a water solution buffered at pH 10.00. **2**

	Answer:

Marks

- Briefly outline three kinds of isomerism possible in coordination complexes, giving examples and simple diagrams to show how the isomerism arises. **3**

- A solution is prepared by dissolving $Zn(NO_3)_2$ (0.10 mol) and ammonia (3.0 mol) in water to give 1.00 L of solution. What is the equilibrium concentration of $Zn^{2+}(aq)$ given K_{stab} $[Zn(NH_3)_4]^{2+} = 1 \times 10^9$ M^{-4}? **3**

	Answer:

Marks 4

- The ascorbate ion ($AscH_2^-$) is readily oxidised in water solution to the dehydroascorbate ion (Asc^-).

$$AscH_2^- \rightleftharpoons Asc^- + 2H^+ + 2e^- \quad E° = –0.390\ V$$

Calculate the value of $E°'$ for this half cell at pH 7 and 298 K.

Answer:

The pyruvate ion (Pv^-) is reduced to the lactate ion (PvH_2^-) at pH 7 in the following half cell.

$$Pv^- + 2H^+ + 2e^- \rightleftharpoons PvH_2^- \quad E°' = –0.190\ V$$

Assume this half cell is combined with the ascorbate ion half cell at pH 7.

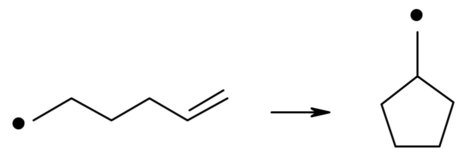
Write the overall cell reaction.

What is the $E°'$ of this cell at pH 7?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

- The rearrangement of the 5-hexenyl radical to give a cyclopentylmethyl radical proceeds with a rate constant of 1.0×10^5 s^{-1} at 25 °C. What is the half-life of the 5-hexenyl radical at 25 °C?



$t_{½}$ =

The activation energy for the 5-hexenyl radical rearrangement is 25.4 kJ mol^{-1}. What is the rate constant for the rearrangement of the 5-hexenyl radical at 37 °C?

k =

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Marks

- Ozone is destroyed in the stratosphere by the reactions: 2

$$X + O_3 \rightarrow XO + O_2$$

$$XO + O \rightarrow X + O_2$$

where X is the H, OH, NO, Cl or Br radical.

The concentrations of all X species in the atmosphere are extremely low, and ozone molecules are continually being generated in the atmosphere at a much greater rate than these reactions can destroy them. These reactions, however, still have a significant impact on the amount of ozone in the atmosphere. Why?

- 'The more bubbles there are in the dishwater, the better it is for cleaning dishes.' 2

Explain what is wrong with this statement.

- Sodium oleate can be used to make an **oil-in-water** emulsion, but to make a **water-in-oil** emulsion, magnesium oleate is more effective. Draw a diagram to illustrate the physical basis for this effect. 2

Marks

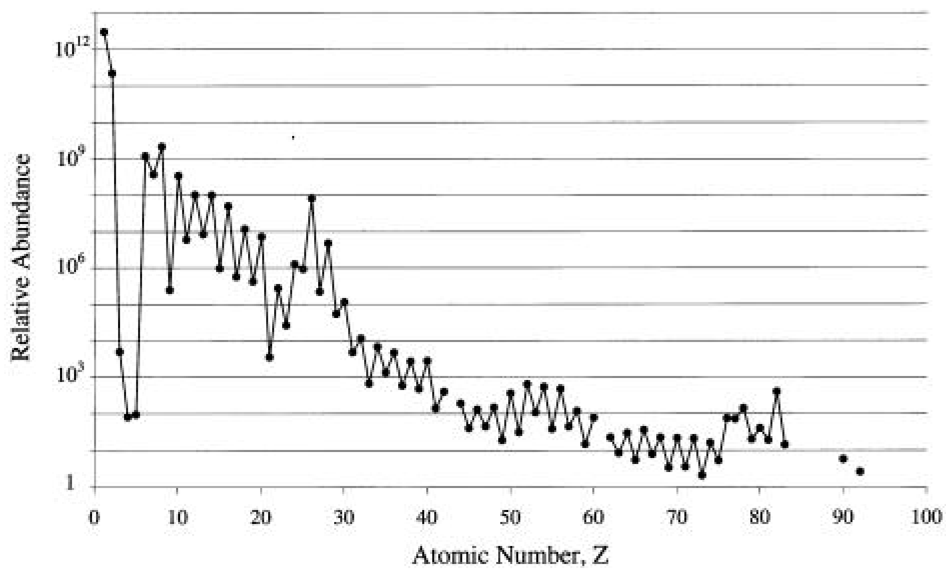
- It has recently been suggested that 'cancer clusters' are associated with high-voltage overhead power lines that produce negative ions. It is thought that the negative ions cause the aggregation of colloidal particles of airborne carcinogens, which subsequently settle out nearby. Explain, with the aid of a diagram, how this aggregation might occur. **2**

- Double beta decay is a rare nuclear process where two beta particles are released simultaneously from an unstable nucleus. Write the equation for the double beta decay of ^{100}Mo. **1**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
3

- The figure below shows the estimated abundance of each element in the universe on a log scale.



Briefly explain why the curve has the general shape it does.

Briefly explain one of the deviations from this general trend.

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Faraday constant = F = 96485 C mol^{-1}

Speed of light = c = 2.998×10^{8} m s^{-1}

Planck constant = h = 6.626×10^{-34} J s

Avogadro constant = N_A = 6.022×10^{23} mol^{-1}

Standard atmosphere = 101 325 Pa = 760 mmHg

Ideal gas constant = R = 8.314 J K^{-1} mol^{-1} = 0.08206 L atm K^{-1} mol^{-1}

Conversion factors

0 °C = 273 K	1 mL = 10^{-3} L	1 L = 10^{-3} m^3	1 mPa = 10^{-3} Pa
1 kJ = 10^3 J	1 mA = 10^{-3} A	1 nm = 10^{-9} m	1 mg = 10^{-3} g

Standard Reduction Potentials at 298 K

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E° = +0.34$

$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ $E° = -0.44$

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ $E° = 0.00$

$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O$ $E° = +1.23$

Useful Formulas

Thermodynamics and Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = -RT \ln K$

$K_p = K_c (RT)^{\Delta n}$

Colligative properties

$\pi = cRT$

$p = kc$

Acids and Bases

$pK_w = pH + pOH = 14$

$pK_w = pK_a + pK_b = 14$

$pH = pK_a + \log\{ [base] / [acid] \}$

Kinetics

$t_{½} = \ln 2/k$

$k = Ae^{-E_a/RT}$

$\ln[A] = \ln[A]_o - kt$

Electrochemistry

$\Delta G° = -nFE°$

$E = E° - RT/nF \ln Q$

$E° = RT/nF \ln K$

Moles of e^- $= It/F$

Quantum Chemistry

$E = h\nu = hc/\lambda$

A periodic table is printed on the other side of this data sheet.
Atomic weights are included in the periodic table.

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [266]	107 BOHRIUM **Bh** [262]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [266]									

LANTHANIDES	57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97
ACTINIDES	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]

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