22/07(a)

The University of Sydney

CHEMISTRY 1B - CHEM1102

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2004

TIME ALLOWED: THREE HOURS

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

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

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 20 pages of examinable material.
- Complete the written section of 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 of the short answer section 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.
- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheet.
- Pages 18, 21 & 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-12	47	

Short answer section

Page	Marks Max	Gained		Marker
13	5			
14	6			
15	7			
16	4			
17	6			
19	6			
20	4			
22	6			
23	9			
Total	53			
Check Total				

Marks 5

- Briefly describe two factors that determine whether a collision between two molecules will lead to a chemical reaction.

Briefly describe the relationship between the rate of a reaction and the activation energy for the reaction.

The rate constant for the decomposition of N_2O_5 increases from 1.52×10^{-5} s^{-1} at 25 °C to 3.83×10^{-3} s^{-1} at 45 °C. Calculate the activation energy for the reaction.

E_a =

Marks 6

- Using equations, explain how a buffer functions.

Why is the buffer most effective when pH = pK_a?

Why is it not possible to make a buffer using a strong acid and its conjugate base?

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 5.00? The pK_a of acetic acid is 4.76.

ANSWER:

Marks

- Consider the compound with formula $[CoCl_2(NH_3)_4]Br \cdot 2H_2O$ **3**

  Write the formula of the complex ion.

  Write the symbols of the ligand donor atoms.

  What is the *d* electron configuration of the metal ion in this complex?

- Stalactites and stalagmites can be found in limestone caves near Sydney. Using chemical equations as part of your answer, explain how stalactites, stalagmites and the caves have been formed. **4**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
4

- A phase diagram of a pure compound has a triple point at 20 °C and 0.25 atm, a normal melting point at 25 °C, and a normal boiling point at 87 °C.

  Describe what happens when the pressure is reduced from 2 atm to 0.05 atm at a constant temperature of 15 °C?

Describe what happens when the temperature is raised from 13 °C to 87 °C at a constant pressure of 1.25 atm?

Which is more dense, the solid or the liquid? Explain your reasoning.

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Marks 6

- Magnesium hydroxide, $Mg(OH)_2$, is used as treatment for excess acidity in the stomach. Calculate the pH of a solution that is in equilibrium with $Mg(OH)_2$. The solubility product constant, K_{sp} of $Mg(OH)_2$ is 7.1×10^{-12} M^2.

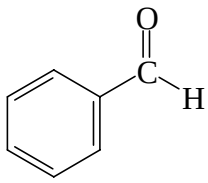
ANSWER:

Determine whether 2.0 g of $Mg(OH)_2$ will dissolve in 1.0 L of a solution buffered to a pH of 7.00.

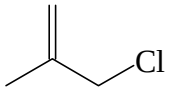
ANSWER: YES / NO

- Draw the constitutional structure of the major organic product formed in the following reactions.

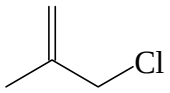
Marks 6



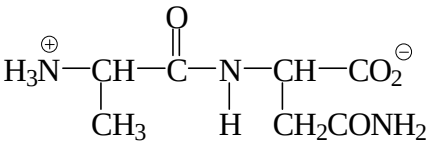
$\xrightarrow[2.\ H^{\oplus} / H_2O]{1.\ CH_3CH_2MgBr}$



$\xrightarrow{NaCN}$



$\xrightarrow{HCl}$

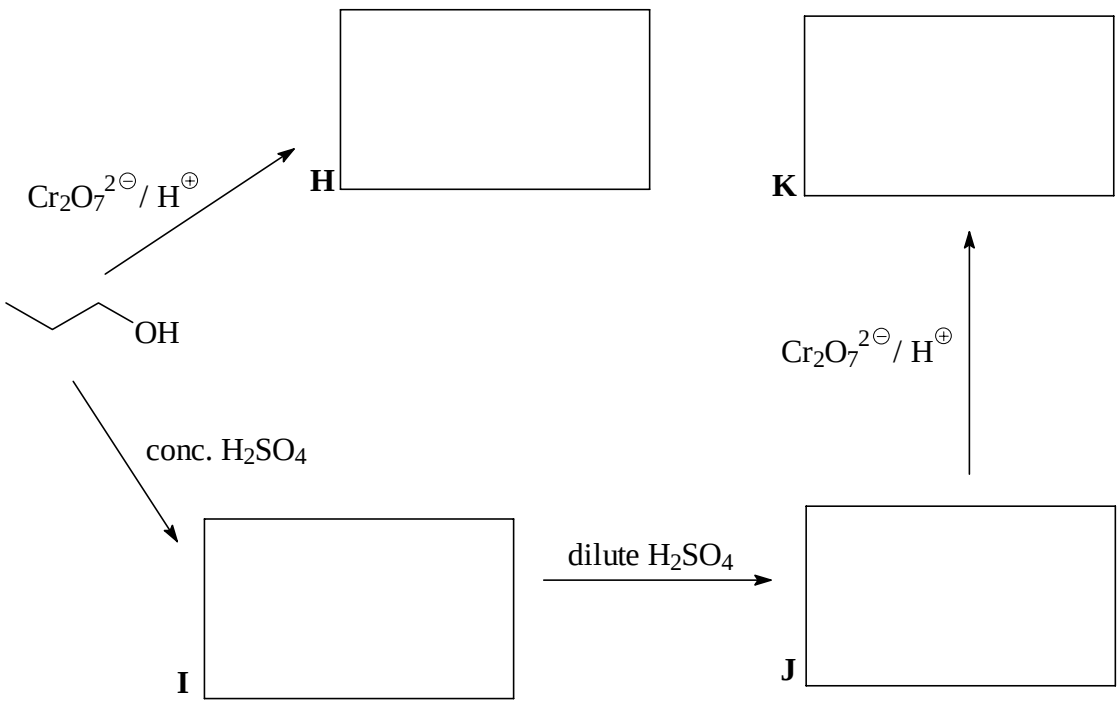


$\xrightarrow{H_2O / H^{\oplus}\ (6\ M)}$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks 4

- Give the constitutional formulas of the compounds **H – K**. Relevant spectral data are given in the table below.



	1-propanol	**H**	**I**	**J**	**K**
Molecular ion *m/z* =	60	74	42	60	58
IR ~ 3500 cm^{-1}	✓	✓	X	✓	X
~ 1700 cm^{-1}	X	✓	X	X	✓
^{13}C nmr: no. of signals	3	3	3	2	2
Relative sizes of ^{13}C nmr signals	1:1:1	1:1:1	1:1:1	2:1	2:1

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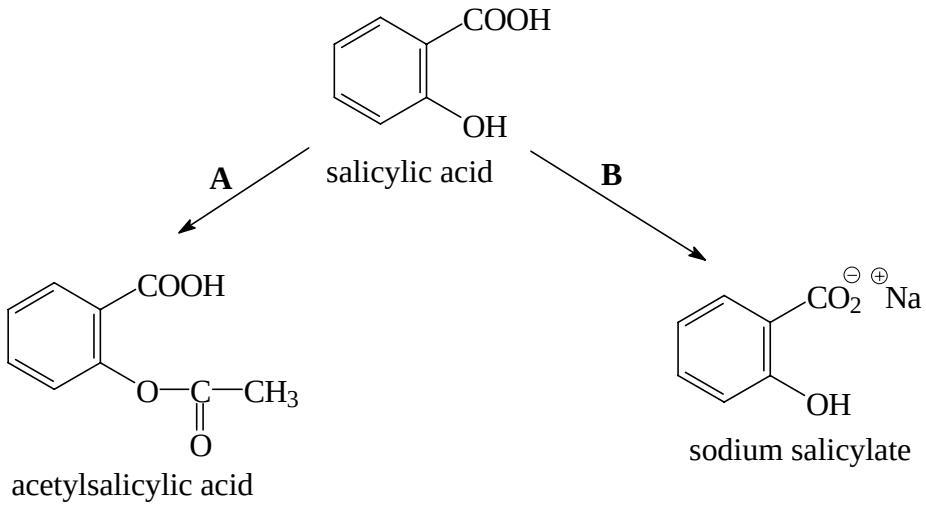
Marks
2

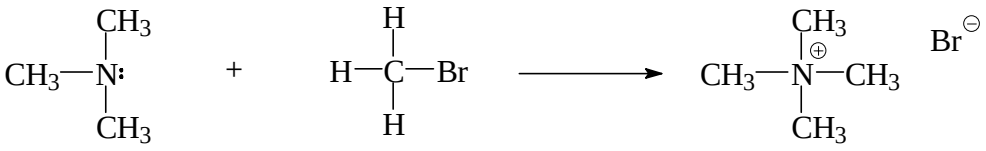
- Give the reagents **A** and **B** used for the following reactions.



A	
B	

- Draw in appropriate partial charges ($\delta\oplus$ and $\delta\ominus$) and curly arrows to show the mechanism of the following reaction. Classify the starting materials as nucleophile, electrophile or neither, indicating your choice in the appropriate box.

4



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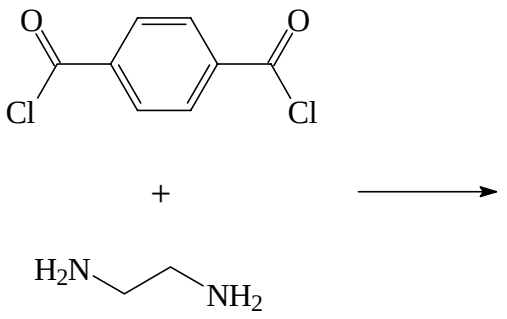
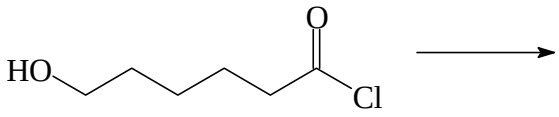
- Draw the repeating unit of the polymer formed in the following reactions.

Marks
6





Considering the polymers formed above, which:
(i) would be more stable towards acid-catalysed hydrolysis, and
(ii) would have a greater tensile strength? Give reasons for your answers.

- Briefly describe what is meant by the primary, secondary and tertiary structure of a protein.

3

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DATA SHEET

Physical constants

Avogadro constant, $N_A = 6.022 \times 10^{23}$ mol^{-1}

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

Planck constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light in vacuum, $c = 2.998 \times 10^{8}$ m s^{-1}

Boltzmann constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Gas constant, $R = 8.314$ J K^{-1} mol^{-1}

$= 0.08206$ L atm K^{-1} mol^{-1}

Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L

Density of water at 298 K = 0.997 g cm^{-3}

Conversion factors

1 atm = 760 mmHg = 101.3 kPa

0 °C = 273 K

1 L = 10^{-3} m^3

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J

1 Ci = 3.70×10^{10} Bq

1 Hz = 1 s^{-1}

Decimal fractions

Fraction	Prefix	Symbol
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Decimal multiples

Multiple	Prefix	Symbol
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

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Standard Reduction Potentials, E°

Reaction	*E°* / V
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.89
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71

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Useful formulas

Quantum Chemistry

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

$\lambda = h/mu$

$4.5k_BT = hc/\lambda$

Gas Laws

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Radioactivity

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age $= 8033 \ln(A_0/A_t)$

Colligative properties

$\pi = cRT$

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Kinetics

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

$t_{½} = \ln 2/k$

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

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

$E = E° - (RT/nF) \times 2.303 \log Q$

$E° = (RT/nF) \times 2.303 \log K$

$$E = E° - \frac{0.0592}{n}\log Q \text{ (at 25 °C)}$$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

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

Polymers

$$R_g = \sqrt{\frac{nl_0^2}{6}}$$

Mathematics

If $ax^2 + bx + c = 0$, then $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$\ln x = 2.303 \log x$

June 2004

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22/07(b)

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]