22/10(a)

The University of Sydney

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 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 19 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 16, 18, 22 & 24 are for rough working only.

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Multiple choice section

	Marks	
Page	Max	Gained
2-12	50	

Short answer section

	Marks			
Page	Max	Gained		Marker
13	5			
14	10			
15	2			
17	8			
19	6			
20	6			
21	7			
23	6			
Total	50			

Marks

- Explain in terms of their electronic configurations and ionisation energies why the alkali metals (Group 1) are powerful *reducing* agents. **2**

- The half-life for the first order decomposition of N_2O_5(g) is 6.00×10^4 s at 20 °C. Calculate the rate constant, *k*, at this temperature. **3**

k =

What percentage of the N_2O_5 molecules will have reacted after one hour?

ANSWER:

Marks

- The solubility product constant of $Fe(OH)_3$ is 1×10^{-39} M^4. What is the concentration of Fe^{3+}(aq) in equilibrium with $Fe(OH)_3$ at pH 7.0? **4**

ANSWER:

To what value does the pH need to be increased to decrease the concentration of Fe^{3+}(aq) to a single Fe^{3+}(aq) ion per litre of solution?

ANSWER:

- Complete the following table. **6**

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of *d*-electrons in metal in complex ion	Species formed upon dissolving in water
$K_2[Ni(CN)_4]$				
$[Cr(NH_3)_5Cl]Cl_2$				
$[Co(en)_3]Br_3$				

en = ethylenediamine = $NH_2CH_2CH_2NH_2$

Marks

- Teeth are made from hydroxyapatite, $Ca_5(PO_4)_3OH$. Why does an acidic medium promote tooth decay and how can the decay be stopped using fluoridation of drinking water? Use chemical equations where appropriate. **2**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
8

- Solution A consists of a 0.15 M aqueous solution of nitrous acid (HNO_2) at 25 °C. Calculate the pH of Solution A. The pK_a of HNO_2 is 3.15.

ANSWER:

At 25 °C, 1.00 L of Solution B consists of 13.8 g of sodium nitrite ($NaNO_2$) dissolved in water. Calculate the pH of Solution B.

ANSWER:

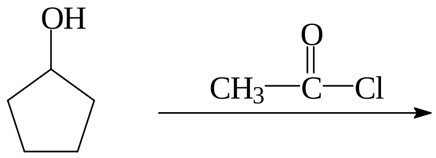
Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C. Calculate the pH of the final solution.

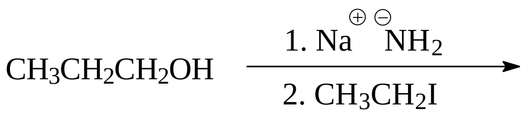
ANSWER:

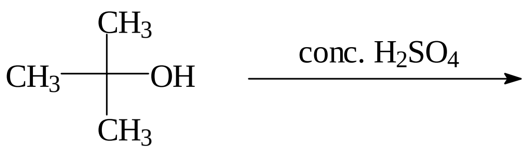
If you wanted to adjust the pH of the mixture of Solution A and Solution B to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

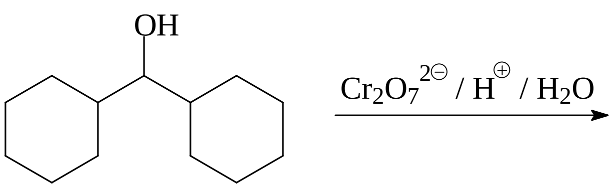
Marks
6

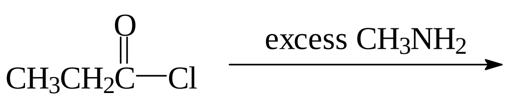
- Draw the constitutional formula(s) of the major organic product(s) formed in each of the following reactions.







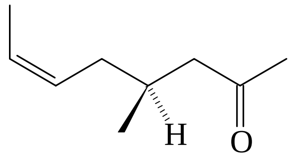




Marks
6

- Compound **X** was isolated as a derivative of a natural product.

X



Carbon 4 of **X** is a stereogenic centre. List the substituents attached to C4 in descending order of priority according to the sequence rules.

highest priority lowest priority

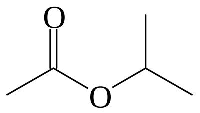
What is the systematic name for compound **X**? Make sure you include all relevant stereochemical descriptors.

Reduction of **X** with sodium borohydride ($NaBH_4$) followed by quenching the reaction with dilute acid gives **Y**. Give the constitutional formula for **Y**.

Product **Y** can be separated into two isomers. Explain.

Marks

- Compound **Z** can readily be identified by [1]H NMR spectroscopy. **3**

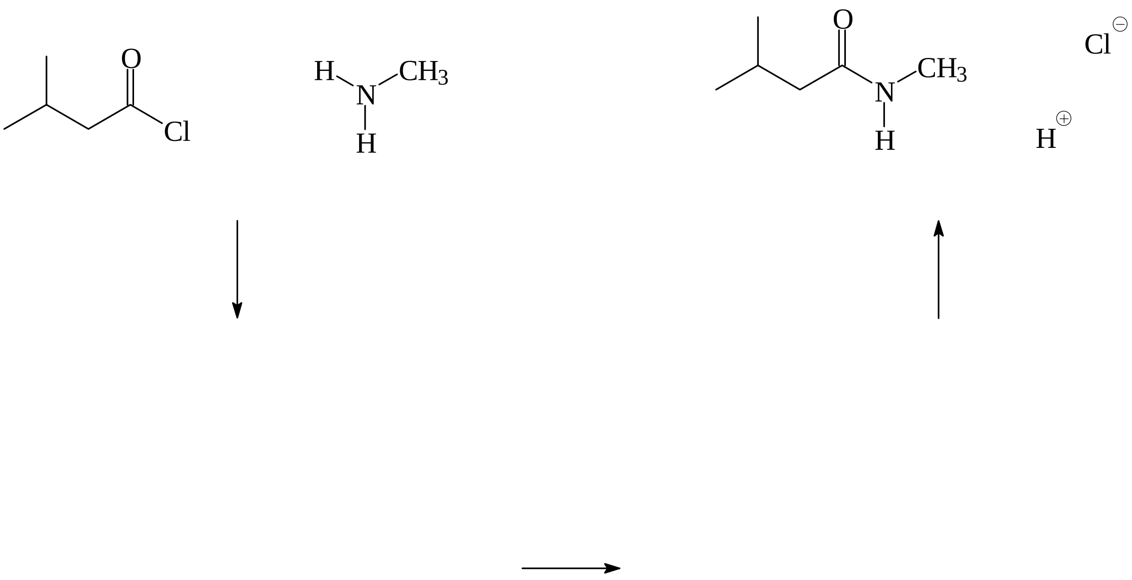
Z 

How many signals would you expect to see in the [1]H NMR spectrum of compound **Z**?

Write the letters **a**, **b**, **c**, *etc* on the diagram of compound **Z** to identify each unique hydrogen environment giving rise to a signal in the [1]H NMR spectrum.

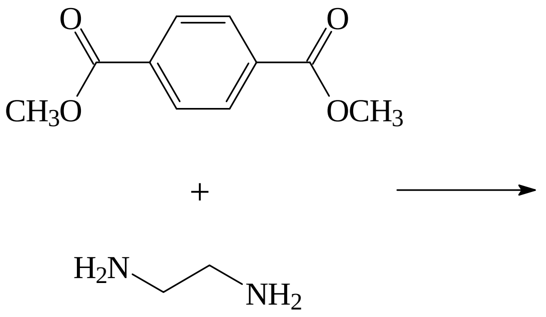
Sketch the [1]H NMR spectrum for compound **Z**. Label each signal in the spectrum with **a**, **b**, **c**, *etc* to correspond with your assignments on the diagram of **Z** above. Make sure you show the relative number of hydrogens and the splitting pattern (number of fine lines) you would expect to see for each signal.

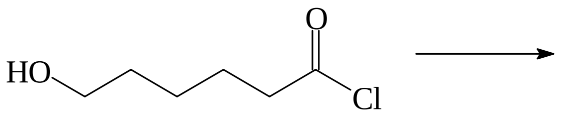
- Complete the three step mechanism for the reaction given below. Draw intermediate structures, curly arrows and partial charges as appropriate to illustrate the bonding changes that take place. **4**



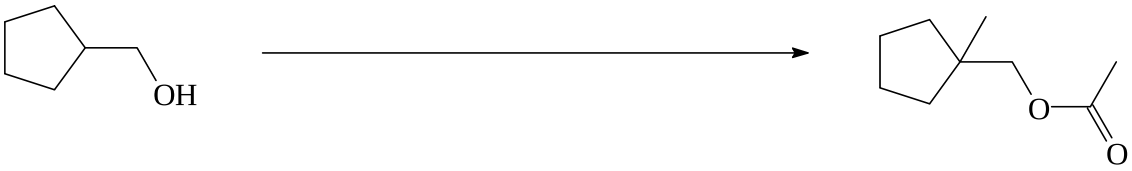
Marks

- Draw the repeating unit of the polymer formed in the following reactions. **2**





- Show clearly the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds. **4**
  NOTE: More than one step is necessary.



CHEM1902 - CHEMISTRY 1B (ADVANCED)
CHEM1904 - CHEMISTRY 1B (SSP)

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}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

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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CHEM1904 - CHEMISTRY 1B (SSP)

Standard Reduction Potentials, $E°$

Reaction	$E°$ / V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+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
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+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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CHEM1904 - CHEMISTRY 1B (SSP)

Useful Formulas

Quantum Chemistry

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

$\lambda = h/mu$

$4.5k_BT = hc/\lambda$

$E = Z^2E_R(1/n^2)$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT\ \ln Q$

$\Delta G° = -RT\ \ln K$

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

Kinetics

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

$t_{½} = \ln 2/k$

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

Radioactivity

$A = \lambda N$

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

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

Gas Laws

$PV = nRT$

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

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

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

Colligative Properties

$\pi = cRT$

$p = kc$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$\Delta T_f = K_fm$

$\Delta T_b = K_bm$

Electrochemistry

$\Delta G° = -nFE°$

$Moles\ of\ e^- = It/F$

$E = E° - (RT/nF)\ \ln Q$

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

$E° = (RT/nF)\ \ln K$

$\quad = (RT/nF) \times 2.303\ \log K$

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

Polymers

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

Mathematics

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

$\ln x = 2.303 \log x$

November 2004

CHEM1902/1904

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]

22/10(b)