22/11(a) The University of Sydney

CHEM1902 - CHEMISTRY 1B (ADVANCED)

and

CHEM1904 - CHEMISTRY 1B (SPECIAL STUDIES PROGRAM)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2005 **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 21 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 17 & 24 are for rough working only.

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Multiple choice section

	Marks	
Page	Max	Gained
2-13	50	

Short answer section

	Marks		
Page	Max	Gained	Marker
14	8		
15	7		
16	7		
18	2		
19	6		
20	6		
21	7		
22	3		
23	4		
Total	50		

Marks
4

- 2-Propanol can be oxidised to acetone using $Cr_2O_7^{2-}$ in acidic solution as indicated in the reaction below. The rate of decrease of the $Cr_2O_7^{2-}$ ion under a certain set of conditions is 3.0 mol L^{-1} s^{-1}.

$$3CH_3CH(OH)CH_3 + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3COCH_3 + 2Cr^{3+} + 7H_2O$$

What is the rate of increase in the concentration of Cr^{3+}?	
What is the rate of decrease in the concentration of 2-propanol?	

The rate law for this reaction is: $Rate = k\,[Cr_2O_7^{2-}][CH_3CH(OH)CH_3][H^+]^2$

Complete the following table by writing *increase*, *decrease* or *no change* in the box to indicate how the rate of the reaction is affected by each of the following changes.

Increase in $[CH_3CH(OH)CH_3]$	
Increase in $[CH_3COCH_3]$	
Increase in pH	
Increase in temperature	

4

- Complete the following table.

Formula	Systematic name	Oxidation state of transition metal	Number of *d*-electrons
$K_2[Pt(CN)_4]$			
$[Co(H_2O)_6]Cl_2$			

Marks 7

- Calculate the pH of a solution that is prepared by mixing 500 mL of 1.0 M NH_3 with 500 mL of 2.0 M NH_4Cl. The pK_b of NH_3 is 4.76.

ANSWER:

In the presence of excess hydroxide ion, Mg^{2+} can be precipitated as $Mg(OH)_2$(s). What amount (in mol) of solid sodium hydroxide must be added to a 0.10 M solution of $Mg(NO_3)_2$ to just cause precipitation of $Mg(OH)_2$(s). The solubility product constant of $Mg(OH)_2$ is 7.1×10^{-12} M^3.

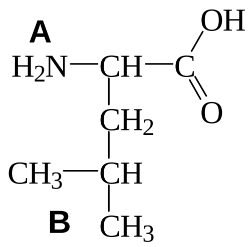
ANSWER:

In a separate experiment, the $Mg(OH)_2$ is precipitated by adding 0.10 mol of $Mg(NO_3)_2$ to 1.0 L of a 0.10 M NH_3 solution. What amount (in mol) of NH_4Cl must be added to this solution to just dissolve the precipitate?

ANSWER:

Marks
4

- Shown here is the classical form of the amino acid leucine.



List the types of intermolecular interactions in which the sites **A** and **B** could be involved.

A	
B	

Leucine has an unusually high melting point for a small molecule. Suggest a reason for this.

3

- Metal atoms participate in many biological processes. The following table shows a number of metals, one property of each metal and the biological function for which the metal is important. Complete the table.

Metal	**Property which is important for biological activity**	**Biological function to which this property is relevant**
Cu	Can exist in two oxidation states, +I and +II	
	Forms square-planar co-ordination compounds	Cancer chemotherapy
Fe		Oxygen transport in blood

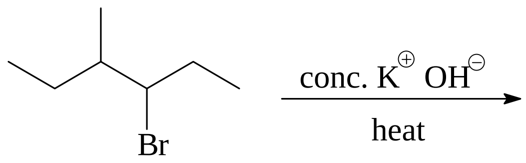
Marks
2

- Ice is less dense than liquid water. The triple point of water is 0.001 °C, 0.006 atm and its critical point is 374 °C, 218 atm. Sketch the phase diagram for water showing all the main features.

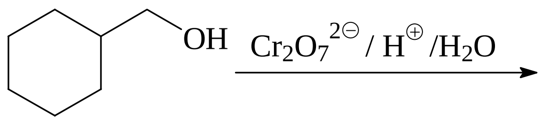
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

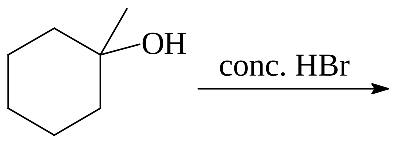
Marks
6

- Draw the structure(s) of the major organic product(s) formed in each of the following reactions. Give the names of the products where requested.



Name(s):





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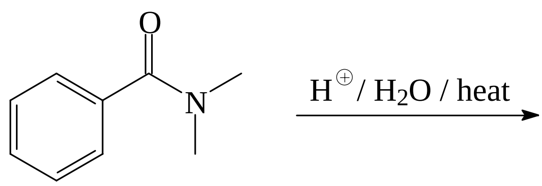

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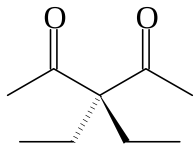
Marks
6

- Compound **X** can be reduced by treatment with sodium borohydride followed by dilute hydrochloric acid to form a mixture of diol compounds.

X 

Clearly draw all possible product stereoisomers that can form from this reduction, taking care to represent clearly the stereochemistry of the products.

Clearly label each isomer drawn above as either chiral or achiral (not chiral).

Circle one of the product isomers you have drawn above and provide a full systematic name for this compound below. Make sure you include all relevant stereochemical descriptors.

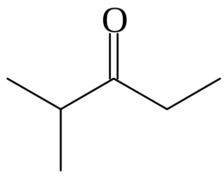
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
7

- Compound **Y** can readily be identified by ^{1}H NMR spectroscopy.

  On the diagram of **Y**, write the letters **a**, **b**, **c**, *etc*. as necessary to identify each unique hydrogen environment giving rise to a signal in the ^{1}H NMR spectrum.

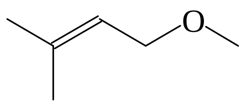
Y



Sketch the ^{1}H NMR spectrum of compound **Y**. Label each signal in the spectrum with **a**, **b**, **c**, *etc.* to correspond with your assignments on the diagram of **Y**. Make sure you show the splitting pattern (number of fine lines) you expect to see for each signal. Also write the relative number of hydrogens you expect above each signal.

Compound **Z** is an isomer of **Y**.

Z

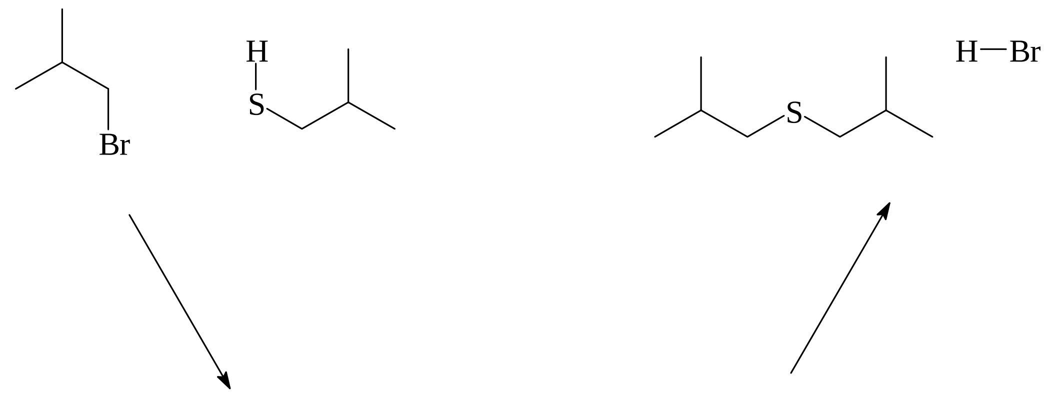


What kind of isomers are they?

Compounds **Y** and **Z** can be readily distinguished by instrumental techniques. Suggest how three different techniques can be used to distinguish between the two structures.

- Complete the two 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.

Marks
3



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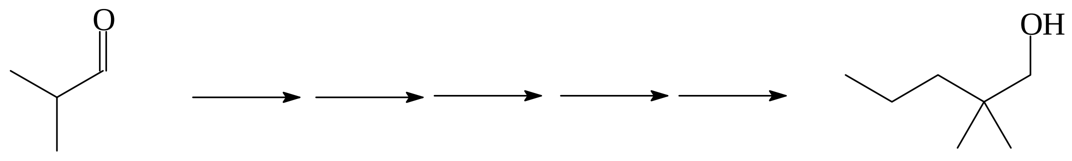
- Show clearly the reagents you would use to carry out the following chemical conversion. Draw constitutional formulas for any intermediate compounds.
  NOTE: More than one step is necessary.

Marks
4



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}
Charge of electron, $e = 1.602 \times 10^{-19}$ C
Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg
Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg
Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ kg

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
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+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
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

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

Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$	**Radioactivity** $t_{½} = \ln2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = $8033 \ln(A_0/A_t)$
Acids and Bases $pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	**Gas Laws** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$
Colligative properties $\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_fm$ $\Delta T_b = K_bm$	**Kinetics** $t_{½} = \ln2/k$ $k = Ae^{-E_a/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Electrochemistry $\Delta G° = -nFE°$ *Moles of e*$^-$ $= It/F$ $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (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 $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

November 2005

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]