22/02(a)

The University of Sydney

FUNDAMENTALS OF CHEMISTRY 1B - CHEM1002

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 18 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 and a Periodic Table may be found on a separate data sheet.
- Page 20 is for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-12	50	

Short answer section

Page	Marks Max	Gained		Marker
13	10			
14	7			
15	8			
16	8			
17	6			
18	5			
19	6			
Total	50			

Marks

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

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu^{2+}. **2**

- 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 = $NH_2CH_2CH_2NH_2$

- What are allotropes? Give an example of a pair of allotropes involving carbon and a second example of a pair not involving carbon.

Marks 3

- The following data were obtained for the reaction between gaseous nitric oxide and chlorine at 1400 K.

4

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

EXPERIMENT NUMBER	INITIAL [NO] (mol L^{-1})	INITIAL [Cl_2] (mol L^{-1})	INITIAL REACTION RATE (mol L^{-1} s^{-1})
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.10	0.72

Deduce the rate law for this reaction and calculate the value of the rate constant.

RATE LAW	RATE CONSTANT
Answer:	Answer:

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.

pH =

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.

pH =

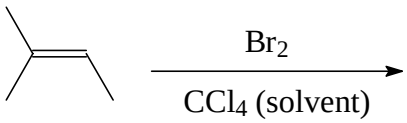
Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C. Calculate the pH of the final solution.

pH =

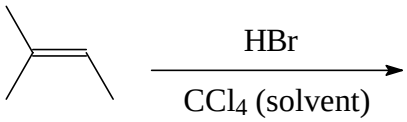
If you wanted to adjust the pH of the mixture of Solution A and Solution B to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

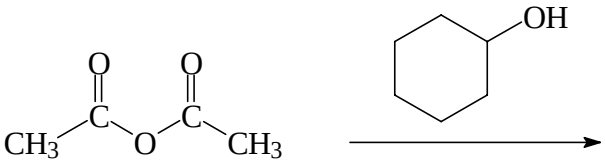
Marks 8

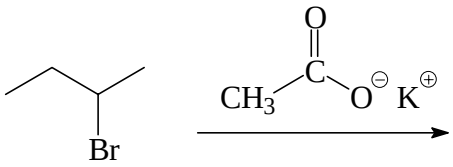
- Give the name of the starting material where indicated and the constitutional formula(s) of the major organic product(s) formed in each of the following reactions.



Name:







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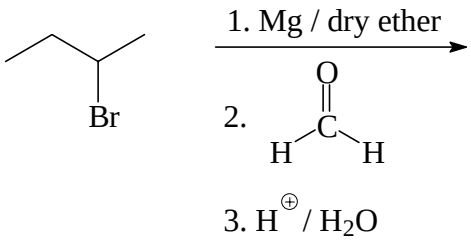
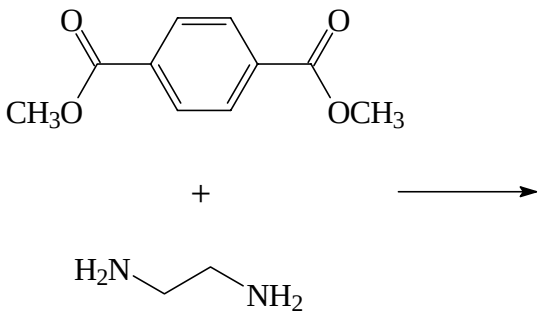
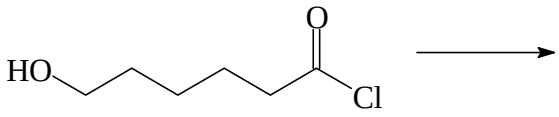


- Draw the repeating unit of the polymer formed in the following reactions.

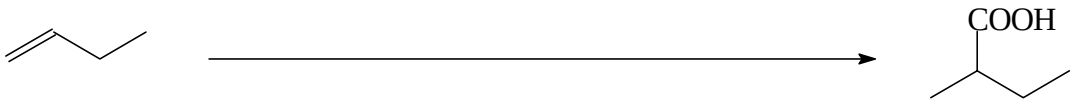
Marks 2





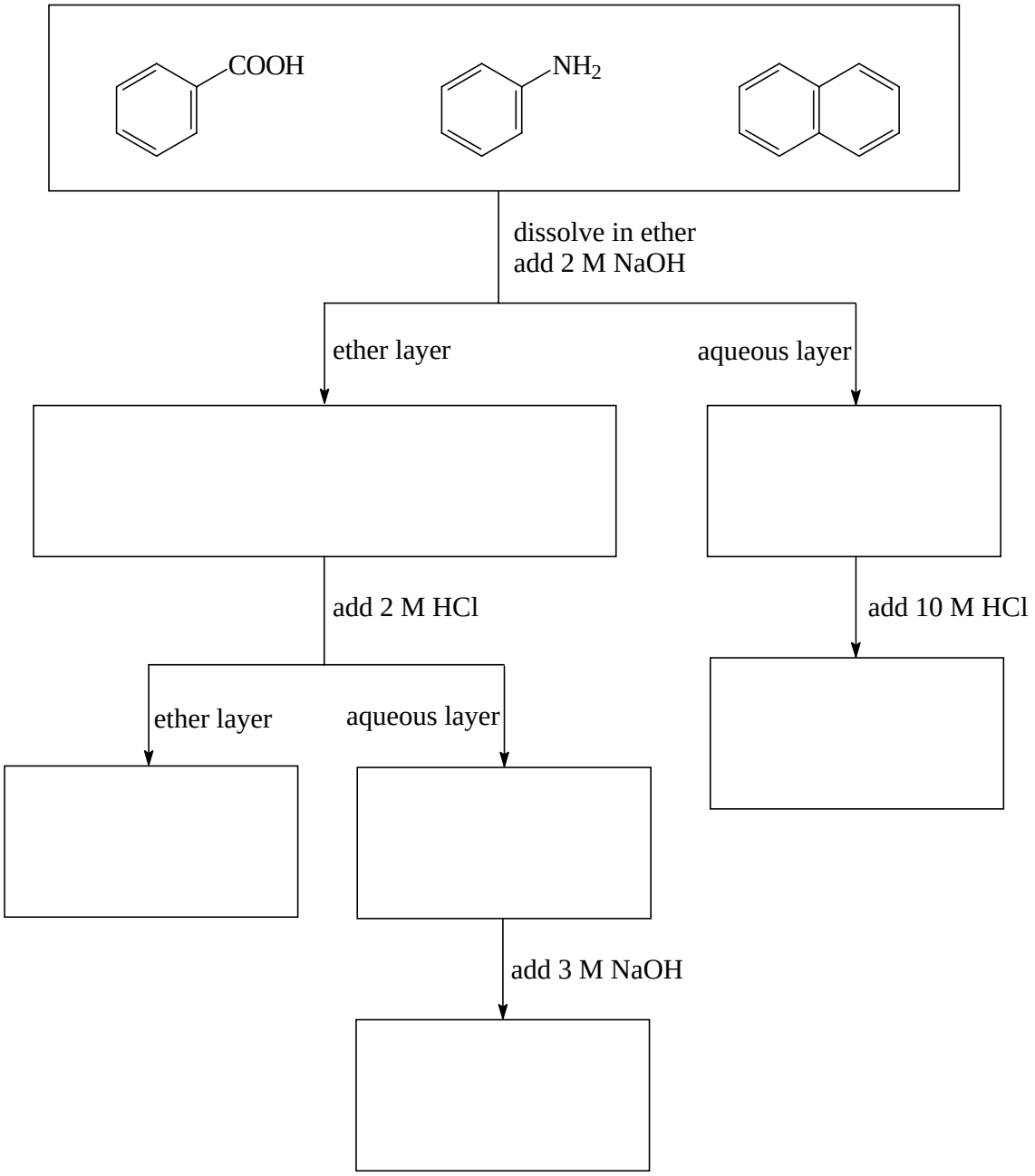
4

- 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.



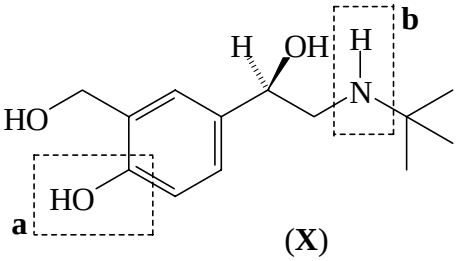
Marks
5

- Organic compounds may be readily separated in the laboratory by extraction methods using acid-base chemistry. Complete the following flow chart by showing the constitutional formulas of all species that will be present in the aqueous and organic phases and hence show how this mixture can be separated into its individual components.



Marks 6

- Salbutamol (**X**) is the active ingredient in the asthma treatment Ventolin™. Although the drug is marketed as a racemic mixture, the enantiomer of (**X**) shown is solely responsible for the beneficial pharmacological action (smooth muscle relaxation).



(**X**)

What is the molecular formula of (**X**)?

List the substituents attached to the stereogenic centre in descending order of priority according to the sequence rules.

highest priority			lowest priority

What is the absolute stereochemistry of (**X**)? Write (*R*) or (*S*).

Name the functional groups, highlighted by the boxes **a** and **b** present in (**X**).

a =	**b** =

Give the constitutional formula of the product formed when (**X**) is treated with cold dilute sodium hydroxide solution.

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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}

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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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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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

$A = \lambda N$

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

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

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

$\pi = cRT$

$p = kc$

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

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Electrochemistry

$\Delta G° = -nFE°$

$\text{Moles of } e^- = It/F$

$E = E° - (RT/nF) \ln Q$

$= E° - (RT/nF) \times 2.303 \log Q$

$E° = (RT/nF) \ln K$

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

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

Polymers

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

Mathematics

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

$\ln x = 2.303 \log x$

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]