22/06(a)

The University of Sydney

CHEMISTRY 1B - CHEM1102

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2008 **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 13, 15, 21 & 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-8	29	

Short answer section

Page	Marks Max	Gained		Marker
9	4			
10	8			
11	9			
12	6			
14	5			
16	8			
17	7			
18	5			
19	5			
20	6			
22	6			
23	2			
Total	71			
Check Total				

	Marks
• Explain in terms of their electronic configurations **and** ionisation energies 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, explain why most Fe^{2+} and Fe^{3+} compounds are paramagnetic.	**2**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

	Marks
• BF_3 is a Lewis acid in its reaction with diethyl ether. Explain what is meant by a Lewis acid and draw the product of this reaction.	**2**
• What is a catalyst and, in general terms, how does it work? Make reference to an energy level diagram in your answer.	**2**
• The gas methane, CH_4, has a critical point at –82 °C and 46 atm. Can methane be liquefied at 25 °C? Explain your answer.	**2**
• Define what is meant by an "allotrope". Give an example of a pair of allotropes involving (i) phosphorus and (ii) a pair not involving phosphorus.	**2**

- Complete the following table. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

Marks 9

Formula	$(NH_4)_2[CoCl_4]$	$[Cr(NH_3)_5(H_2O)]Cl_3$	*cis*-$[PtCl_2(en)_2]$
Oxidation state of transition metal ion			
Coordination number of transition metal ion			
Number of *d*-electrons in the transition metal ion			
Charge of the complex ion			
Geometry of the complex ion			
List all the ligand donor atoms			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Calculate the pH of a 0.20 M solution of potassium fluoride. The pK_a of HF is 3.17.

Marks
3

Answer:

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO_3, is 0.79, how many moles of sodium iodate, $NaIO_3$, would need to be added to this solution to raise its pH to 2.00?

3

Answer:

Marks 5

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

The following rate data were collected at 225 ^oC.

Experiment	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial rate (d[NO]/dt, M s^{-1})
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	1.3×10^{-2}	2.2×10^{-3}	1.0×10^{-4}
3	6.4×10^{-3}	4.4×10^{-3}	5.1×10^{-5}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 225 ^oC.

Answer:

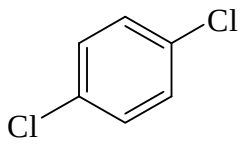
Calculate the rate of appearance of N_2O when $[NO] = [H_2] = 6.6 \times 10^{-3}$ M.

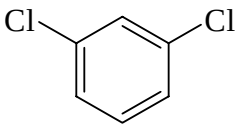
Answer:

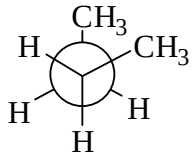
Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

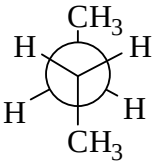
Marks 8

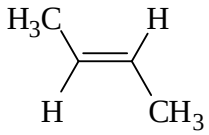
- Consider the following pairs of compounds. Indicate the isomeric relationship that exists between the compounds in each set.



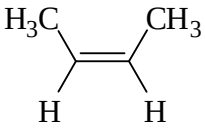


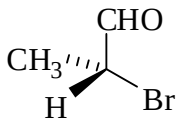


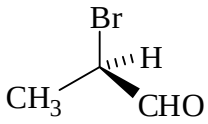




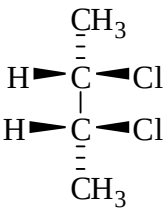
(**L**)

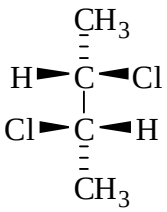






(**M**)





(**N**)

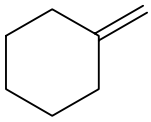
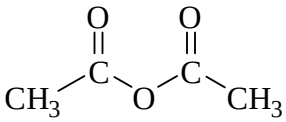
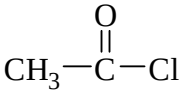
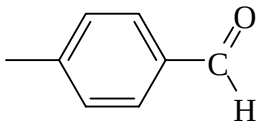
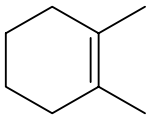
Give the name of compound (**L**) that unambiguously describes its stereochemistry.

Give the name of compound (**M**) that unambiguously describes its stereochemistry.

Is compound (**N**) optically active? Give a reason for your answer.

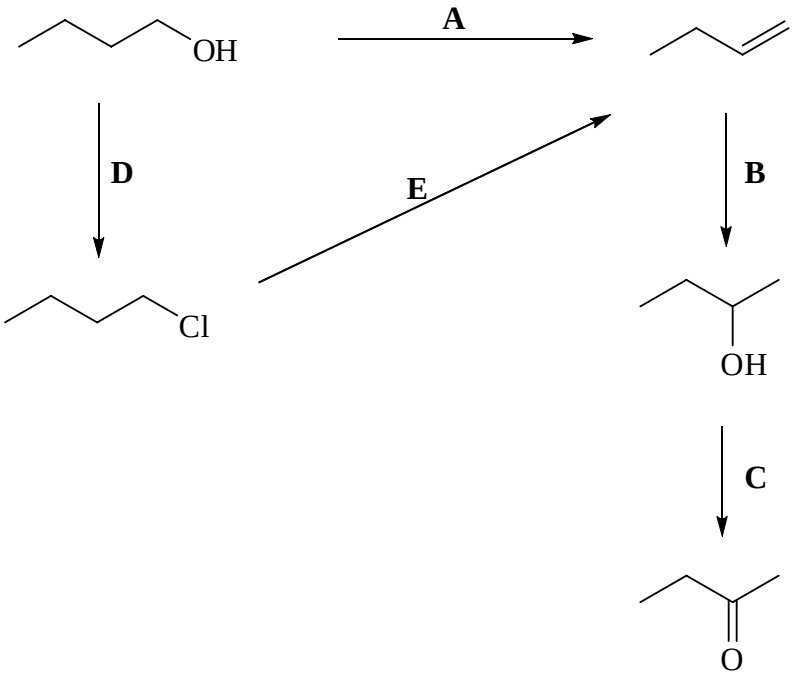
- Complete the following table. Make sure you indicate any relevant stereochemistry.

Marks 7

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
CH_3CH_2COOH	1. $SOCl_2$ 2. CH_3CH_2OH	
	dry HI	
$H-C\equiv C-CH_3$	excess Br_2 in CCl_4 solvent	
$CH_3CH_2CH_2CH_2CH_2OH$	 conc. H_2SO_4 catalyst	
	H_2O	
	1. $LiAlH_4$ / dry ether 2. $H^{\oplus}$ / H_2O	
	H_2 / Pd / C	

Marks
5

- Consider the following reaction sequence.



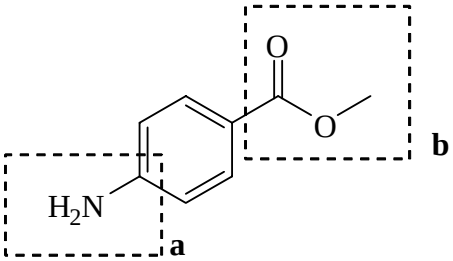
Clearly state the reagents required (including conditions and solvent where appropriate) for each of the steps.

A:
B:
C:
D:
E:

Marks
5

- The structure of methyl 4-aminobenzoate, (**E**), is given below.

(**E**)



Give the molecular formula of compound (**E**).

Name the functional groups in molecule (**E**) indicated by the boxes "**a**" and "**b**".

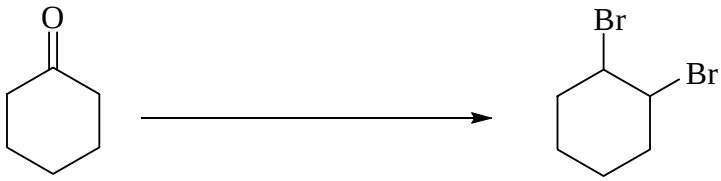
a:	**b**:

Give the structure(s) of all organic products formed when compound (**E**) is treated with the following reagents. If no reaction occurs, write "NO REACTION".

cold HCl (1 M)	
hot NaOH (4 M)	
hot HCl (4 M)	

Marks
6

- Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.



Marks 6

- Consider the isomers 1,1-dichloroethane and 1,2 dichloroethane, which can be readily identified by their ^{1}H NMR spectra.

  On the structures below, 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 spectra of these compounds.

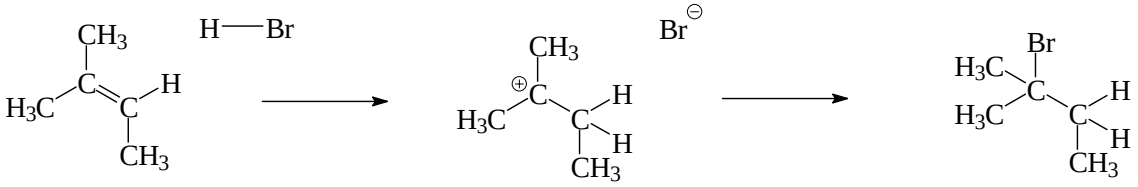
Sketch the ^{1}H NMR spectrum of each compound. Label each signal in the spectra with **a**, **b**, **c**, *etc.* to correspond with your assignments on the diagram above. Make sure you show the splitting pattern (number of fine lines) you expect to see for each signal. Also write the relative number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

Spectrum of 1,1-dichloroethane

Spectrum of 1,2-dichloroethane

Marks 2

- The incomplete proposed mechanism for the reaction of 2-methyl-2-butene with HBr is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.



Which one of the two reactants is the electrophile?

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CHEM1102 - CHEMISTRY 1B

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}

Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-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}

1 tonne = 10^3 kg

1 W = 1 J 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

CHEM1102 - CHEMISTRY 1B

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
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pt^{2+}(aq) + 2e^- \rightarrow Pt(s)$	+1.18
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O$	+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
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–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

CHEM1102 - CHEMISTRY 1B

Useful formulas

Quantum Chemistry

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

$\lambda = h/mv$

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

$\Delta x \cdot \Delta(mv) \geq h/4\pi$

$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$

$4.5 k_B T = hc/\lambda$

$T = 2.898 \times 10^6/\lambda(\text{nm})$

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)

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

$\pi = cRT$

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

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Kinetics

$t_{½} = \ln 2/k$

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

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

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

Radioactivity

$t_{½} = \ln 2/\lambda$

$A = \lambda N$

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

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

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

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

Miscellaneous

$A = -\log \frac{I}{I_0}$

$A = \varepsilon c l$

$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_A$

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]	110 DARMSTADTIUM **Ds** [271]	111 ROENTGENIUM **Rg** [272]							

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]