Topics in the June 2009 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2009-J-2:

- Periodic Trends in Aqueous Oxide
- Coordination Chemistry

2009-J-3:

- Strong Acids and Bases
- Kinetics - Catalysis
- Physical States and Phase Diagrams
- Crystal Structures

2009-J-4:

- Coordination Chemistry

2009-J-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2009-J-6:

- Kinetics

2009-J-7:

- Stereochemistry

2009-J-8:

- Alkenes
- Alcohols
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2009-J-9:

- Carboxylic Acids and Derivatives

2009-J-10:

- Stereochemistry

2009-J-12:

- Alkenes

2009-J-13:

- Synthetic Strategies

22/06(a)

The University of Sydney

CHEMISTRY 1B - CHEM1102

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2009 **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 14, 16 & 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-9	29	

Short answer section

Page	Marks Max	Gained		Marker
10	4			
11	8			
12	9			
13	8			
15	3			
17	8			
18	6			
19	7			
20	5			
21	4			
22	3			
23	6			
Total	71			
Check Total				

	Marks
• Explain in terms of their electronic configurations **and** ionisation energies why the halogens (Group 17) are powerful *oxidising* 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 Co^{2+}.	**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) oxygen and (ii) a pair not involving oxygen.	**2**

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

Marks 9

Formula	$K_2[CoCl_4]$	$Na_3[FeBr(CN)_5]$	$[Zn(en)_2(NO_3)_2]$
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.

Marks 8

- Solution A consists of a 0.020 M aqueous solution of propionic acid, $C_3H_6O_2$, at 25 °C. Calculate the pH of Solution A. The pK_a of propionic acid is 4.87.

Answer:

At 25 °C, 1.00 L of Solution B consists of 2.24 g of potassium propionate ($KC_3H_5O_2$) 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 to give Solution C. Calculate the pH of Solution C.

Answer:

If you wanted to adjust the pH of Solution C to be exactly equal to 5.00, which component in the mixture would you need to increase in concentration?

Marks 3

- Peroxydisulfate and iodide ions react according to the following equation.

$$S_2O_8^{2-}(aq) + 3I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$

The following rate data were collected at room temperature.

Experiment	$[S_2O_8^{2-}(aq)]_0$ (M)	$[I^-(aq)]_0$ (M)	Initial rate (mol L^{-1} s^{-1})
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.160	0.017	2.2×10^{-4}

Determine the rate law for the reaction.

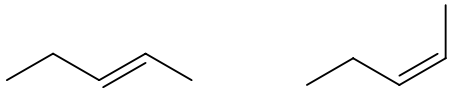
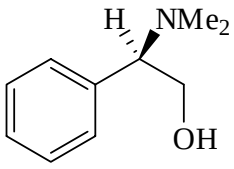
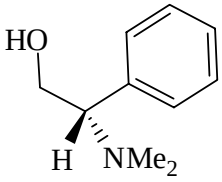
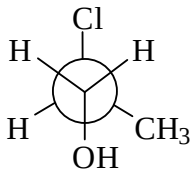
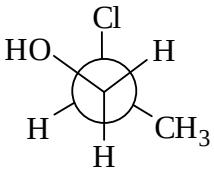
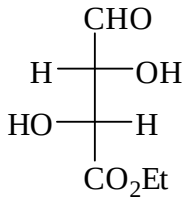
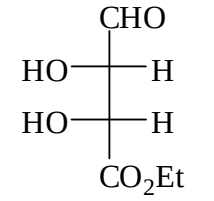
Calculate the value of the rate constant at room temperature.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks 8

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

	
 (**A**)	
 (**B**) 	
 	
  (**C**)	

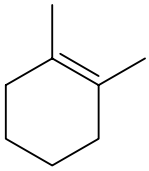
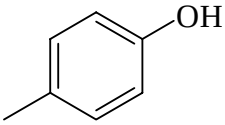
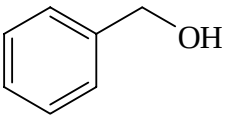
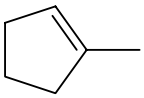
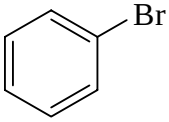
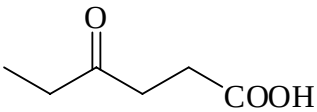
Give the full name of compound (**A**) that unambiguously describes its stereochemistry.

What is the configuration of the stereogenic centre in compound (**B**)?

Is compound (**C**) a *meso* isomer? Give a reason for your answer.

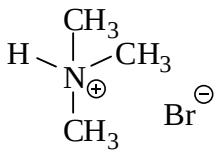
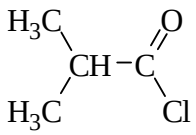
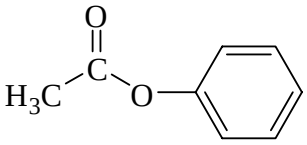
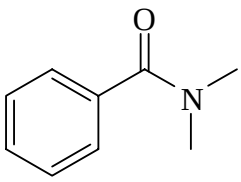
- Complete the following table. Make sure you indicate any relevant stereochemistry.

Marks 6

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	H_2/Pd/C (catalyst)	
	1. dilute NaOH 2. CH_3Br	
	$Cr_2O_7^{2\ominus}$/ $H^{\oplus}$	
	aqueous H_2SO_4	
	1. Mg / dry ether 2. H_2O	
	1. $NaBH_4$ 2. H^+ / H_2O	

Marks 7

- Give the constitutional formula(s) of the organic product(s) formed when each of the following compounds is treated with 4 M sodium hydroxide. The first three reactions proceed at room temperature; the last two require heating.

COMPOUND	ORGANIC PRODUCT(S)
CH_3CH_2COOH	
	
	
	
	

Marks 5

- 1,2-Dichloropropane can exist in two enantiomeric forms, compounds I and II. In the boxes below draw structures of the two enantiomers of 1,2-dichloropropane clearly showing the stereochemistry at the chiral carbon.

compound I	compound II

There are three other compounds, III, IV and V with molecular formula $C_3H_6Cl_2$. In the boxes below, give the constitutional formulas and names of these compounds.

Structure	Name
compound III	
compound IV	
compound V	

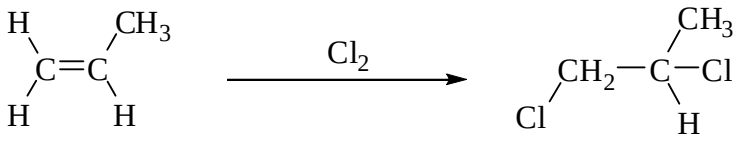
THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks 4

Compounds I, II, III, IV and V are isomers. From the list *enantiomers, diastereomers, conformers, constitutional isomers* complete the following table.

PAIR OF COMPOUNDS	ISOMERIC RELATIONSHIP BETWEEN PAIR OF COMPOUNDS
I and III	
I and IV	
II and IV	

1,2-Dichloropropane can be synthesised in the laboratory by treatment of propene with chlorine as is shown in the following equation.



Which of the following best describes the product: (*R*)-enantiomer, (*S*)-enantiomer, racemate?

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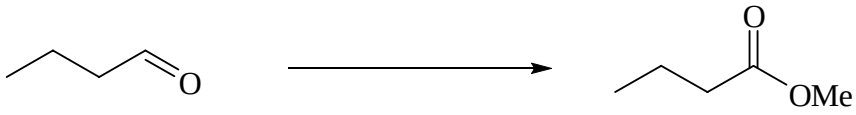
Marks 3

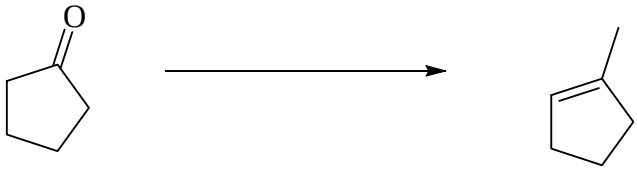
- Give the mechanism of the reaction that occurs when 1-methylcyclohexene is converted to 1-bromo-1-methylcyclohexane by the addition of HBr. Give the structure of the intermediate carbocation that is formed and indicate (with curly arrows) all the bonding changes that occur.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

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





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

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

$\lambda = h/mv$

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

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

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

$T\lambda = 2.898 \times 10^6$ K 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

$PV = nRT$

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

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

Kinetics

$t_{½} = \ln 2/k$

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

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

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

Colligative properties

$\Pi = cRT$

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

$c = kp$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta_{univ} S° = R \ln K$

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

Miscellaneous

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

$A = \varepsilon cl$

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

Mathematics

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

$\ln x = 2.303 \log x$

Area of circle = πr^2

Surface area of sphere = $4\pi r^2$

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]							

LANTHANOIDS	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
ACTINOIDS	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]