Topics in the November 2007 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2007-N-2:

- Strong Acids and Bases
- Weak Acids and Bases

2007-N-3:

- Weak Acids and Bases
- Calculations Involving pKa
- Periodic Trends in Aqueous Oxide

2007-N-4:

• Solubility Equilibrium

2007-N-5:

- Hydrolysis of Metal Ions
- Coordination Chemistry

2007-N-6:

- Physical States and Phase Diagrams
- Intermolecular Forces and Phase Behaviour

2007-N-7:

Kinetics

2007-N-8:

• Coordination Chemistry

2007-N-9:

- Structural Determination
- Carboxylic Acids and Derivatives

2007-N-10:

- Alkenes
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2007-N-11:

- Aromatic Compounds
- Carboxylic Acids and Derivatives

2007-N-12:

• Carboxylic Acids and Derivatives

2007-N-13:

• Structural Determination

November 2007

2007-N-14:

Synthetic Strategies

22/08(a)

NOVEMBER 2007

The University of Sydney

CHEMISTRY 1B - CHEM1102

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

TIME ALLOWED: THREE HOURS

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

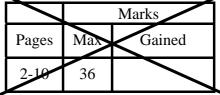
FAMILY	SID	
NAME	NUMB	SER
OTHER	TABI	LE
NAMES	NUMB	SER

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 22 pages of examinable material.
- Complete the written section of the examination paper in <u>INK</u>.
- 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.
- Page 24 is for rough working only.

OFFICIAL USE ONLY

Multiple choice section



Short answer section

		Marks						
Page	Max	Gaine	d	Marker				
11	5							
12	6							
13	4							
14	6							
15	4							
16	3							
17	3							
18	5							
19	5							
20	7							
21	5							
22	5							
23	6							
Total	64							

• Often pH is used to characterise acidic solutions. Give a brief definition of pH.	Mark 5
	_
Describe the difference between a strong acid and a weak acid.	_
In general, can pH be used to define the strength of an acid? Explain your answer.	

•	Rank H ₂ O(l), H ₂ S(aq) and HF(aq) in order your reasoning.	er of their Brønsted acid strengths. Explain	Marks 2
•	Buffer systems are frequently used in che how it functions? Use equations where a	emistry. Briefly describe a buffer system and ppropriate.	4
	What ratio of concentrations of acetic a prepare a buffer with $pH = 4.00$? The K_a	cid to sodium acetate would you require to of acetic acid is 1.8×10^{-5} M.	
		Answer:	

4

Marks • Barium sulfate is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp} , for BaSO₄, given that a maximum of 1.167×10^{-8} g will dissolve in 500 mL of water? Answer: What advantage would there be in administering BaSO₄ as a slurry that also contains 0.5 M Na₂SO₄?

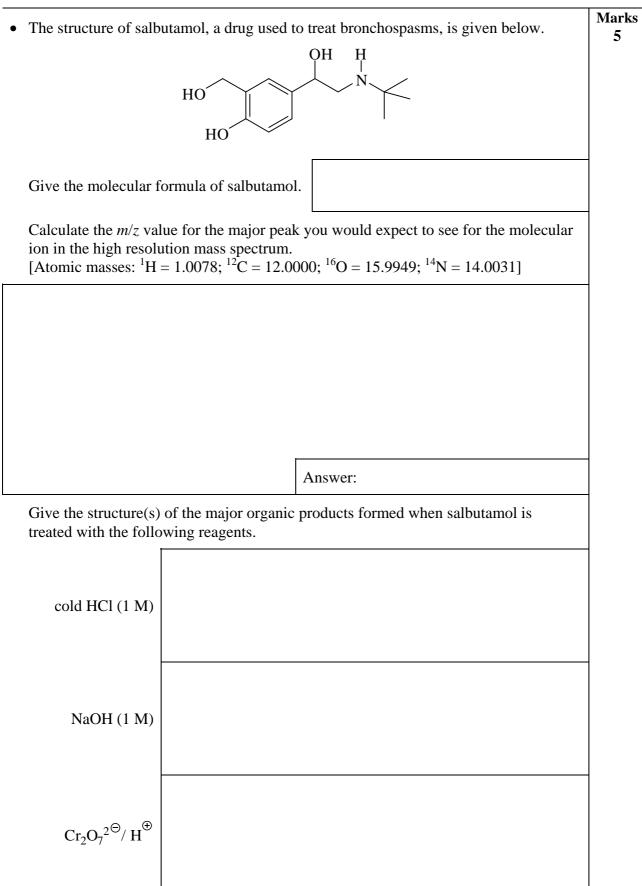
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks • What is a chelate ligand? 4 Draw all possible isomers of $[CoCl_2(en)_2]$. en = ethylenediamine = $NH_2CH_2CH_2NH_2$ • Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3} M, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9} M. 2

• You may recall from a lecture demonstration or your laboratory work that solid CO ₂ sublimes under ambient conditions while ice melts. Define the terms sublimation and melting.	Marks 3
What is a triple point (<i>e.g.</i> in the phase diagram of CO ₂ or H ₂ O)?	
What does the different behaviour of ice and solid CO ₂ indicate about the relative positions of their respective triple points?	
• Carbon has a number of allotropes, the two major ones being graphite and diamond. The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?	1

Marks • Hydrogenation of nitric oxide to nitrogen and water is a potential means of reducing 3 smog-forming NO_x gases: $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0) . Rate / kPa s^{-1} Run $P_0(H_2) / kPa$ P_0 (NO) / kPa 1 53.3 40.0 0.137 2 53.3 0.033 20.3 3 38.5 53.3 0.213 4 19.6 53.3 0.105 Derive an expression for the rate law for this reaction. Answer: Calculate the value of the rate constant. Answer: What is the order of the reaction?

Marks • Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess 3 iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (Desferal), a natural substance isolated from fungi. HN NH 0 Desferal HO 0 \cap OH HO \oplus H₃N Desferal is taken over 8-12 hour periods up to six times per week. A value of $\log K = 30.6$ is associated with the following equilibrium: $\operatorname{Fe}^{3+} + \operatorname{LH}_3^+ = \operatorname{FeL}^+ + 3\operatorname{H}^+$ where $\operatorname{LH}_3^+ = Desferal$ Briefly describe the chemical basis for the use of *Desferal* in iron overload therapy.

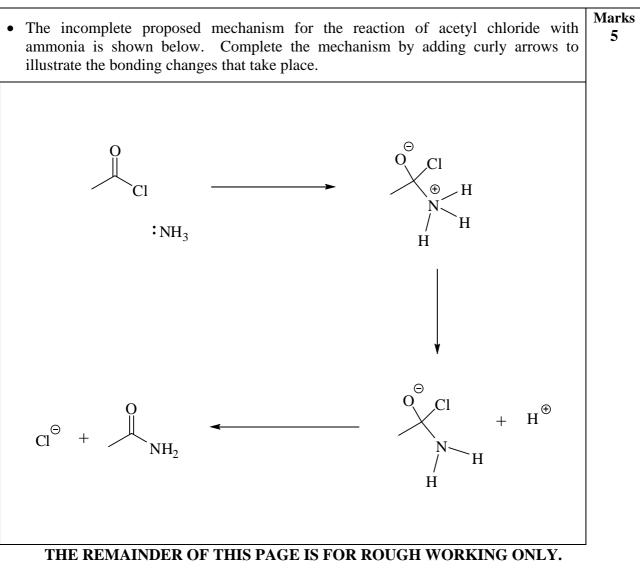


• Complete the following table.										
Starting material	Reagents / Conditions	Major organic product(s)								
ОН										
	HCl									
H	1. NaBH₄ 2. H [⊕] / H ₂ O									
Br	hot conc. KOH ethanol (solvent)									
	CN ^O									

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

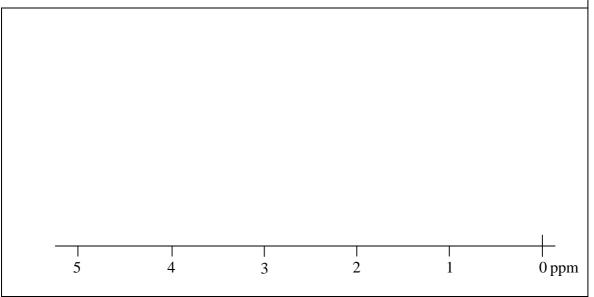
arks

Marks • A mixture of concentrated nitric and sulfuric acids generates the nitronium ion, NO₂⁺. 2 Benzene will react with such a mixture to give nitrobenzene. NO_2 conc. HNO_3 / conc. H_2SO_4 What 3-part name is given to the mechanism of this nitration reaction? 2 • Consider the reaction sequence below. ·ОН O B H⊕ Α \mathbf{C} Draw the structures of products A and B. A B • Draw the structure of the product, **C**, from the following reaction. 3 С excess H₂ Pd/C catalyst OCH₃ Product C undergoes hydrolysis when heated with 4 M NaOH. Give the structures of the products (in their correct ionic states) formed in this reaction.



5

• Sketch the ¹H NMR spectrum of bromoethane, CH₃CH₂Br. The signals appear at 1.7 and 3.3 ppm. Clearly indicate the splitting patterns of both signals and show their relative intensities.



THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks • Devise a synthesis of 3-methylheptan-3-ol using the two starting materials shown. 6 Show the structures of any intermediate products involved, as well as the reagents required for each step. More than one step is required. and Br ÓН OH Would the product be isolated as a racemic mixture or a single enantiomer or is the product achiral?

CHEM1102 - CHEMISTRY 1B

DATA SHEET

 $Physical \ constants$ Avogadro constant, $N_{\rm A} = 6.022 \times 10^{23} \ {\rm mol}^{-1}$ Faraday constant, $F = 96485 \ {\rm C} \ {\rm mol}^{-1}$ Planck constant, $h = 6.626 \times 10^{-34} \ {\rm J} \ {\rm s}$ Speed of light in vacuum, $c = 2.998 \times 10^8 \ {\rm m} \ {\rm s}^{-1}$ Rydberg constant, $E_{\rm R} = 2.18 \times 10^{-18} \ {\rm J}$ Boltzmann constant, $k_{\rm B} = 1.381 \times 10^{-23} \ {\rm J} \ {\rm K}^{-1}$ Gas constant, $R = 8.314 \ {\rm J} \ {\rm K}^{-1} \ {\rm mol}^{-1}$ $= 0.08206 \ {\rm L} \ {\rm atm} \ {\rm K}^{-1} \ {\rm mol}^{-1}$ Charge of electron, $e = 1.602 \times 10^{-19} \ {\rm C}$ Mass of electron, $m_{\rm p} = 1.6726 \times 10^{-27} \ {\rm kg}$ Mass of neutron, $m_{\rm n} = 1.6749 \times 10^{-27} \ {\rm kg}$

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} m³ 1 Å = 10^{-10} m 1 eV = 1.602×10^{-19} J 1 Ci = 3.70×10^{10} Bq 1 Hz = 1 s⁻¹

Deci	mal fract	ions	Deci	Decimal multiples					
Fraction	Prefix	Symbol	Multiple	Prefix	Symbol				
10^{-3}	milli	m	10^{3}	kilo	k				
10^{-6}	micro	μ	10^{6}	mega	Μ				
10^{-9}	nano	n	10^{9}	giga	G				
10^{-12}	pico	р							

CHEM1102 - CHEMISTRY 1B

Standard Reduction Potentials, E°

Reaction	E° / V
$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.01
$\mathrm{Co}^{3+}(\mathrm{aq}) + \mathrm{e}^{-} \rightarrow \mathrm{Co}^{2+}(\mathrm{aq})$	+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
$Br_2 + 2e^- \rightarrow 2Br^-(aq)$	+1.10
$MnO_2(s) ~+~ 4H^+(aq) ~+~ e^- \rightarrow ~Mn^{3+} ~+~ 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^{-} \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$\operatorname{Fe}^{3+}(\operatorname{aq}) + \operatorname{e}^{-} \rightarrow \operatorname{Fe}^{2+}(\operatorname{aq})$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$\operatorname{Cu}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Cu}(s)$	+0.34
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.15
$2\mathrm{H}^{+}(\mathrm{aq}) + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{g})$	0 (by definition)
$\operatorname{Fe}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Fe}(s)$	-0.04
$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$	-0.13
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Sn}(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.24
$\operatorname{Co}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Co}(s)$	-0.28
$\operatorname{Fe}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Fe}(s)$	-0.44
$\operatorname{Cr}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Cr}(s)$	-0.74
$\operatorname{Zn}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Zn}(s)$	-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	Electrochemistry
$E = hv = hc/\lambda$	$\Delta G^{\circ} = -nFE^{\circ}$
$\lambda = h/mv$	Moles of $e^- = It/F$
$4.5k_{\rm B}T = hc/\lambda$	$E = E^{\circ} - (RT/nF) \times 2.303 \log Q$
$E = -Z^2 E_{\rm R}(1/n^2)$	$= E^{\circ} - (RT/nF) \times \ln Q$
$\Delta x \cdot \Delta(mv) \ge h/4\pi$	$E^{\circ} = (RT/nF) \times 2.303 \log K$
$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$	$= (RT/nF) \times \ln K$
	$E = E^{\circ} - \frac{0.0592}{n} \log Q \text{ (at 25 °C)}$
Acids and Bases	Gas Laws
$pK_{\rm w} = pH + pOH = 14.00$	PV = nRT
$\mathbf{p}K_{\mathrm{w}} = \mathbf{p}K_{\mathrm{a}} + \mathbf{p}K_{\mathrm{b}} = 14.00$	$(P + n^2 a/V^2)(V - nb) = nRT$
$pH = pK_a + \log\{[A^-] / [HA]\}$	
Colligative properties	Kinetics
$\pi = cRT$	$t_{1/2} = \ln 2/k$
$P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$	$k = A e^{-E_{a}/RT}$
$\mathbf{p} = k\mathbf{c}$	$\ln[\mathbf{A}] = \ln[\mathbf{A}]_{\rm o} - kt$
$\Delta T_{\rm f} = K_{\rm f} m$	$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
$\Delta T_{\rm b} = K_{\rm b} m$	$k_1 R T_1 T_2'$
Radioactivity	Thermodynamics & Equilibrium
$t_{1/2} = \ln 2/\lambda$	$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$
$A = \lambda N$	$\Delta G = \Delta G^{\circ} + RT \ln Q$
$\ln(N_0/N_t) = \lambda t$	$\Delta G^{\circ} = -RT \ln K$
14 C age = 8033 ln(A_0/A_t)	$K_{\rm p} = K_{\rm c} \ (RT)^{\Delta n}$
Miscellaneous	Mathematics
$A = -\log_{10} \frac{I}{I_0}$	If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$A = \varepsilon c l$	$\ln x = 2.303 \log x$
$E = -A \frac{e^2}{4\pi\varepsilon_0 r} N_{\rm A}$	

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 hydrogen H 1.008																	2 нешим Не 4.003
3 LITHIUM Li 6.941	4 Beryllium Be 9.012											5 вогом В 10.8	6 carbon C 12.01	7 Nitrogen N 14.01	8 0xygen 0 16.00	9 ^{FLUORINE} F 19.00	10 _{NEON} 20.18
11 sodum Na 22.99	12 MAGNESIUM Mg 24.31											13 ALUMINI Al 26.93	M 14 SILICON Si	14.01 15 рноярновиз Р 30.97	16	17. CHLORINE Cl 35.45	18 ARGON Ar 39.95
19 ротаssium К 39.10	20 салстим Са 40.08	21 scandium Sc 44.96	22 TITANIUM Ti 47.88	23 VANADIUM V	24 ^{снгомим} Сг 52.00	25 manganese Mn 54.94	26 IRON Fe	27 COBALT CO 58.02	28 NICKEL NI	29 COPPER Cu 63.55	30 ZINC Zn 65.39	31 GALLIU Ga	1 32 GERMANIUM Ge	33 ARSENIC AS 74.92	34 selenium Se	35 BROMINE Br 79.90	36 krypton Kr
37 RUBIDIUM Rb	38 strontium Sr	39 ^{yttrium} Y	40 zirconium Zr	50.94 41 NIOBIUM Nb	42 molybdenum Mo	43 тесняетим Тс	55.85 44 RUTHENIUM RU	58.93 45 кнодіим Rh	58.69 46 palladium Pd	47 silver Ag	48 CADMIUN Cd	49 NDIUM In	50 тв Sn	51 ANTIMONY Sb	78.96 52 TELLURIUM Te	53 iodine I	83.80 54 xenon Xe
85.47 55 caesium Cs	87.62 56 barium Ba	88.91 57-71	91.22 72 наfnium Hf	92.91 73 tantalum Ta	95.94 74 ^{TUNGSTEN} W	[98.91] 75 ^{RHENIUM} Re	101.07 76 озмиим Os	102.91 77 ікілічм Іг	106.4 78 PLATINUM Pt	107.87 79 _{GOLD} Au	<u>112.4</u> 80 мексик Нд	81 THALLIU TI	M 82 LEAD Pb	121.75 83 візмитн Ві	127.60 84 роlonium Ро	126.90 85 ASTATINE At	131.30 86 RADON Rn
132.91 87 francium Fr	radium Ra	89-103	178.49 104 rutherfordium Rf	180.95 105 dubnium Db	183.85 106 seaborgium Sg	186.2 107 воняним Вћ	190.2 108 назвішм Hs	192.22 109 меттлегим Mt	195.09 110 darmstadtium Ds	196.97 111 roentgenium Rg	200.5	9 204.3	7 207.2	208.98	[210.0]	[210.0]	[222.0]
[223.0]	[226.0]		[261]	[262]	[266]	[262]	[265]	[266]	[271]	[272]							
LANTHANIDE	57 LANTHA LANTHA 138.	NUM CER	IUM PRA	59 seodymium Pr 40.91	60 ^{NEODYMUM} Nd 144.24	61 promethium Pm [144.9]	62 samarium Sm 150.4	63 еигорим Еи 151.96	64 GADOLINIT Gdd 157.2		им і D	66 ysprosium Dy 162.50	67 ноіміим Но 164.93	68 еквиим Er 167.26	69 тнилим Тт 168.93	70 ytterbium Yb 173.04	71 _{цитетним} Lu 174.97
ACTINIDES	89 ACTINI			91 Mactinium	92 uranium	93 NEPTUNIUM	94 plutonium	95 AMERICIUM	96 CURIUM	97 BERKEL		98 ALIFORNIUM	99 EINSTEINIUM	100 Fermium	101 mendelevium	102 NOBELIUM	103 LAWRENCIUM

Cm

[247.1]

Am

[243.1]

Bk

[247.1]

Cf

[252.1]

Es

[252.1]

Fm

[257.1]

Md

[256.1]

No

[259.1]

Lr

[260.1]

Np [237.0]

Pu

[239.1]

U

238.03

Th

232.04

Ac

[227.0]

Pa

[231.0]

PERIODIC TABLE OF THE ELEMENTS