89/06(a)

The University of Sydney

CHEM1611 - CHEMISTRY 1A (PHARMACY)

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 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 14 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 table.
- 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.
- A Periodic Table and numerical values required for any question may be found on a separate data sheet.
- Pages 13, 15, 17, 19 & 20 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Page	Max	Gained
2-6	28	

Short answer section

Page	Marks Max	Gained		Marker
7	11			
8	7			
9	4			
10	5			
11	9			
12	7			
14	8			
16	10			
18	11			
Total	72			
Check Total				

Marks

- Complete the following table. Give, as required, the formula, the systematic name, the oxidation number of the underlined atom and, where indicated, the principal ions present in a solution prepared by adding the substance to water. **4**

FORMULA	SYSTEMATIC NAME	OXIDATION NUMBER	PRINCIPAL IONS IN WATER SOLUTION
$\underline{N}O_2$			N/A
$\underline{Pb}(CH_3CO_2)_2$			
			$Mg^{2+}(aq)$; $\underline{Cl}O_4^-(aq)$

Write the full electron configuration of the As^{3+} ion.

- Draw the Lewis structures, showing all valence electrons for the following species. Indicate which of the species have contributing resonance structures. **5**

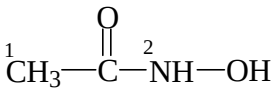
HCO_3^-	COS	CN^-
Resonance: YES / NO	Resonance: YES / NO	Resonance: YES / NO

- Name the two intermolecular forces, which best explain the difference in boiling points of 1-propanol ($CH_3CH_2CH_2OH$; bp = 97.2 °C) and 1-propanethiol ($CH_3CH_2CH_2SH$; bp = 67.8 °C). **2**

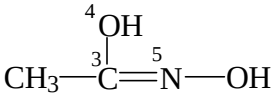
Marks 7

- Siderophores (from the Greek meaning 'iron carriers') are organic molecules produced by microorganisms to provide essential Fe^{3+} required for growth. The functional group (the group which binds Fe^{3+}) of siderophores is shown below as tautomers **I** and **II**. Complete the table below, relating to the molecular geometry about the specified atoms in **I** and **II**.

I



II



Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of atom	Geometry of bonding electron pairs around atom
^{1}C			
^{2}N			
^{3}C			
^{4}O			
^{5}N			

Desferal is a siderophore-based drug that is used in humans to treat iron-overload. One molecule of Desferal (molecular formula: $C_{25}H_{48}O_8N_6$) can bind one Fe^{3+} ion. A patient with iron-overload had an excess of 0.637 mM Fe^{3+} in his bloodstream. Assuming the patient has a total blood volume of 5.04 L, what mass of Desferal would be required to complex all of the excess Fe^{3+}?

ANSWER:

THIS QUESTION CONTINUES ON THE NEXT PAGE

	Marks
Given that haemoglobin contains 4 Fe atoms per molecule and its concentration in blood is 15.0 g per 100 mL, calculate the total mass of Fe in the patient's blood *before* being treated with Desferal. (The molar mass of haemoglobin is 6.45×10^4 g mol^{-1}.)	**4**

ANSWER:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks 5

- Some micro-organisms thrive under warm, acidic conditions where sulfuric acid is produced as a metabolic by-product from the reaction between sulfur (S), water and oxygen (O_2). Write a balanced equation for this reaction.

Calculate the volume of oxygen that is required to react to completion with 0.0655 g of sulfur at 1.00 atm and 55 °C.

ANSWER:

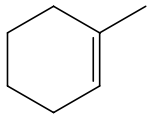
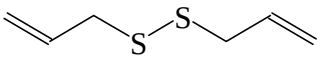
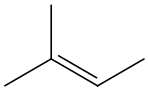
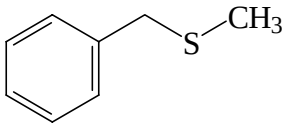
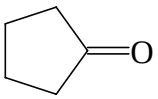
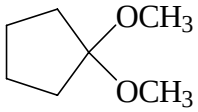
Calculate the pH of the final solution if the reaction is carried out in 20.0 L of water. Assume that the sulfuric acid fully dissociates.

ANSWER:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

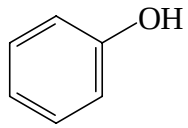
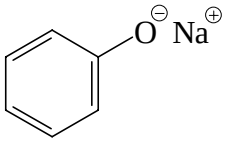
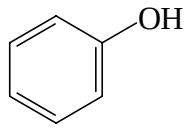
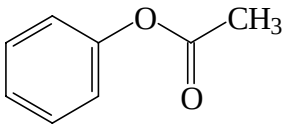
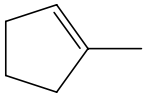
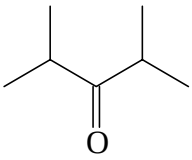
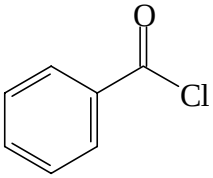
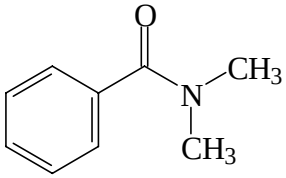
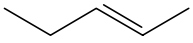
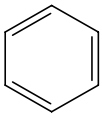
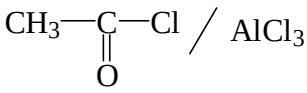
Marks 9

- Complete the following table. Make sure you give the name of the product or starting material where requested.

STARTING MATERIAL	REAGENTS/CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
 **Name:**	HBr / CCl_4 (solvent)	
	$Zn / H^{\oplus}$	
 **Name:**	Br_2 / CCl_4 (solvent)	
	$CH_3S^{\ominus}$	
$CH_3CH_2CH_2Br$	$(CH_3CH_2)_3N$	
 **Name:**		

Marks 7

- Complete the following table.

STARTING MATERIAL	REAGENTS/CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
		
		
	$H^{\oplus}$ / H_2O	
	1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	
		
	H_2 / Pd	
		

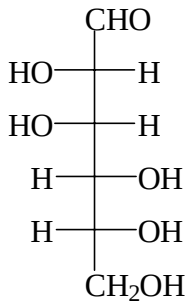
Marks 8

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

Marks 10

- The stucture of D-mannose is shown below. Draw the Fischer projection of L-mannose in the space provided.

D-mannose



L-mannose

D-Mannose is in equilibrium with two cyclic pyranose forms. Give the Haworth projection of these two cyclic forms.

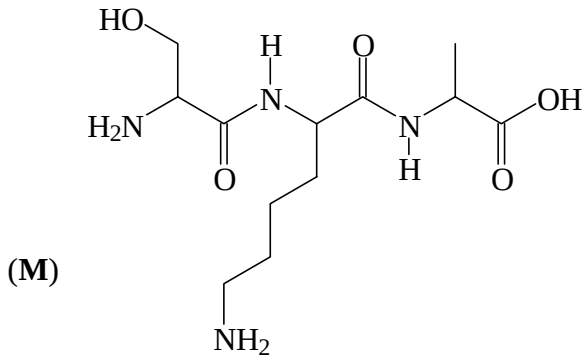
Give the products obtained when D-mannose is treated with the following reagents.

methanol / $H^{\oplus}$	$[Ag(NH_3)_2]^{\oplus}/OH^{\ominus}$ solution	1. $NaBH_4$ 2. dilute acid

Draw the Haworth structure of a reducing disaccharide, which, on acid hydrolysis, yields D-mannose as the only product.

Marks 11

- The constitutional formula of the tripeptide seryllysylalanine (Ser-Lys-Ala), **M**, is shown below.



(**M**)

Draw the Fischer projections for the L-configurations of the amino acids formed when compound **M** is hydrolysed with hot 6 M hydrochloric acid.

The pK_a values of lysine are pK_{a1} = 1.82 (α-COOH), pK_{a2} = 8.95 (α-$NH_3^{\oplus}$) and pK_{a3} = 10.53 (-$(CH_2)_4$)$NH_3^{\oplus}$). Give the structures of the predominant species present in a solution of lysine at pH 12 and at pH 5.6.

pH 12.0	pH 5.6

Give the constitutional formulas for the following dipeptides in their zwitterionic states.

Lys-Ser	Ser-Ala

CHEM1611 - CHEMISTRY 1A (PHARMACY)

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}

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

CHEM1611 - CHEMISTRY 1A (PHARMACY)

Standard Reduction Potentials, E°

Reaction	*E°* / V
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+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
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+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

CHEM1611 - CHEMISTRY 1A (PHARMACY)

Useful formulas

Quantum Chemistry

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

$\lambda = h/mu$

$4.5k_BT = hc/\lambda$

Gas Laws

$PV = nRT$

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

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 age $= 8033 \ln(A_0/A_t)$

Colligative properties

$\pi = cRT$

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

$E = E° - (RT/nF) \times 2.303 \log Q$

$E° = (RT/nF) \times 2.303 \log K$

$E = E° - \dfrac{0.0592}{n} \log Q$ (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

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

Mathematics

$\ln x = 2.303 \log x$

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

June 2004

CHEM1611 – CHEMISTRY 1A (PHARMACY)

89/06(b)

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]