22/09(a) **The University of Sydney**

CHEM1907 - CHEMISTRY 1 LIFE SCIENCES A MOLECULAR (ADVANCED)

CHEM1908 - CHEMISTRY 1 LIFE SCIENCES A (ADVANCED)

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 16 pages of examinable material.
- Complete 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 short answer question 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. Logarithms may also be used.
- Numerical values required for any question as well as a Periodic Table are printed on a separate data sheet.
- Pages 9, 13 and 20 are for rough work only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-7	35	

Short answer section

Page	Marks: Max	Marks: Gained		Marker
8	11			
10	7			
11	4			
12	5			
14	13			
15	3			
16	6			
17	4			
18	4			
19	8			
Total	65			

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
<u>N</u>O_2			N/A
<u>Pb</u>$(CH_3CO_2)_2$			
			Mg^{2+}(aq); <u>Cl</u>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**

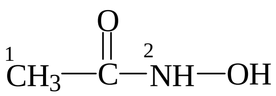
HCO_3^-	COS	CN^-
Resonance: YES / NO	Resonance: YES / NO	Resonance: YES / NO

- 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**

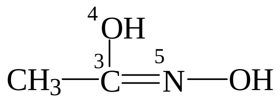
Marks 7

- 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
4

Given that haemoglobin contains 4 Fe atoms per molecule and its concentration in blood is 15 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}.)

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:

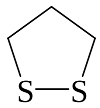
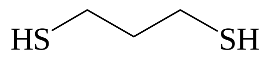
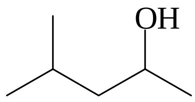
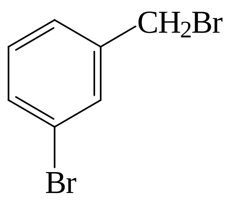
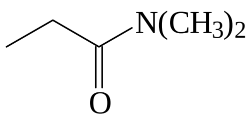
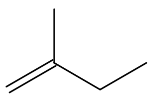
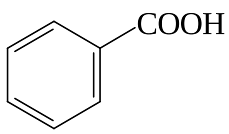
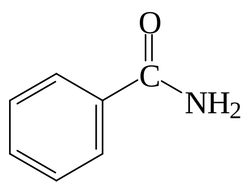
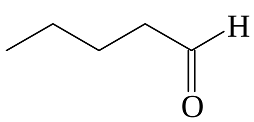
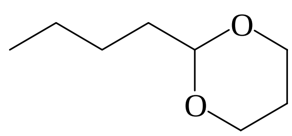
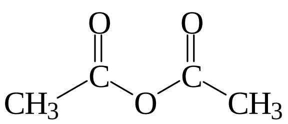
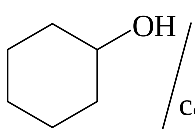
Calculate the pH of the final solution if the reaction is carried out in 20.0 L of water. Assume that the sulfuric acid fully dissociates.

ANSWER:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
13

- Complete the following table. Make sure you complete the name of the starting material where indicated.

STARTING MATERIAL NAME (where required)	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
		
 **Name:**	$H^{\oplus}$ / $Cr_2O_7^{2\ominus}$	
	$K^{\oplus}$ $^{\ominus}CN$	
	conc. HCl / heat	
 **Name:**	Cl_2 / CCl_4(solvent)	
		
 **Name:**		
	 / $H^{\oplus}$ catalyst	

Marks
3

- 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 may be necessary.

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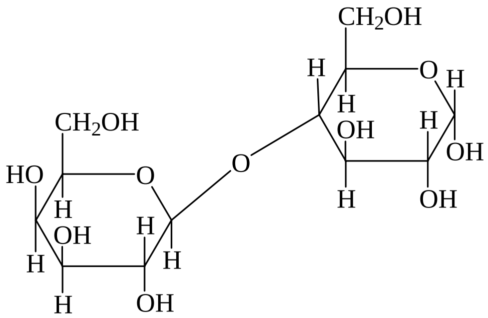
Marks
6

- Lactose, 4-*O*-(β-D-galactopyranosyl)-α-D-glucopyranose is the major sugar in human and cow's milk.



Lactose

Does lactose display mutarotation? Justify you answer.

Draw the Fischer projection of the open chain form of D-galactose.

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

methanol / $H^{\oplus}$ / heat	$[Ag(NH_3)_2]^{\oplus}$ / $OH^{\ominus}$ solution

THIS QUESTION IS CONTINUED ON THE NEXT PAGE.

	Marks
Acid hydrolysis of a non-reducing disaccharide yields D-galactose as the only product. Draw the Haworth structure of one such disaccharide.	**4**
How many different disaccharides are possible in the preceding question? What is the relationship between these compounds?	

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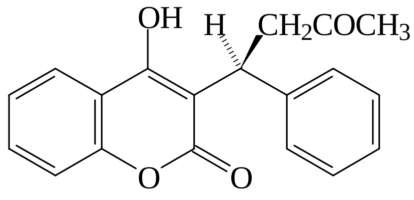
Marks
4

- Warfarin, whose structure is shown below, is a synthetic anticoagulant.



Give the molecular formula of warfarin.

What is the configuration at the stereogenic (chiral) carbon centre of warfarin?

Draw the structures of two tautomers of warfarin.

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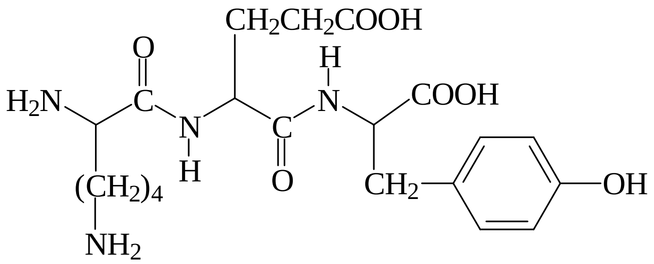
Marks
8

- Consider the tripeptide L-lysyl-L-glutamyl-L-tyrosine (Lys-Glu-Tyr), (**F**), whose constitutional formula is shown below.

(**F**)



Draw the Fischer projections with L-configurations for the amino acids (in their correct ionisation states) obtained from the hydrolysis of (**F**) using hot concentrated HCl solution.

The pK_a values of lysine are pK_{a1} = 2.18 (α-COOH), pK_{a2} = 8.95 (α-$NH_3^{\oplus}$) and pK_{a3} = 10.53 (-$(CH_2)_4NH_3^{\oplus}$). Draw the structure of the zwitterionic form of lysine.

At what pH will this be the predominant species in aqueous solution?

Give the constitutional formulas for the following dipeptides present in water solution at the indicated pH values.

Glu-Tyr, pH 12.0	Glu-Lys, pH 1.0

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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}

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
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+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

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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 $e^- = It/F$

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

$E° = (RT/nF) \times 2.303 \log K$

$E = E° - \frac{0.0592}{n} \log Q$ (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

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

Mathematics

$\ln x = 2.303 \log x$

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

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]