22/04(a)

The University of Sydney

CHEMISTRY 1A - CHEM1101

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 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 22 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 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.
- Numerical values required for any question, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheets.
- Pages 18, 21, 24, 27 and 28 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-11	36	

Short answer section

Page	Marks			Marker
	Max	Gained		
12	7			
13	7			
14	5			
15	8			
16	4			
17	5			
19	5			
20	6			
22	5			
23	4			
25	3			
26	6			
Total	64			

Marks

- Balance the following nuclear reactions by identifying the missing nuclear particle or nuclide. **4**

$${}^{1}_{1}\text{H} + {}^{1}_{1}\text{H} \rightarrow {}^{2}_{1}\text{H} + \square$$

$${}^{2}_{1}\text{H} + \square \rightarrow {}^{3}_{2}\text{He}$$

$${}^{3}_{2}\text{He} + {}^{3}_{2}\text{He} \rightarrow \square + {}^{1}_{1}\text{H} + {}^{1}_{1}\text{H}$$

Where might these reactions occur naturally?

- The half life of ^{131}I is 8.06 days. Calculate the activity, in Bq, of 12.0 g of pure ^{131}I. Calculate the specific activity of ^{131}I in Ci mol^{-1}. **3**

Answer: Bq	Answer: Ci mol^{-1}

Marks

- Describe how one of the following pieces of experimental evidence contributed to the development of quantum mechanics. **3**

  photoelectric effect OR *visible spectrum of hydrogen*

- K-shell x-ray emission ($2p \rightarrow 1s$) from an unknown element is of the same wavelength as the shortest x-rays observed as *Bremsstrahlung* when electrons are accelerated by 52.9 keV into a copper target. What is the name of the unknown element? **4**

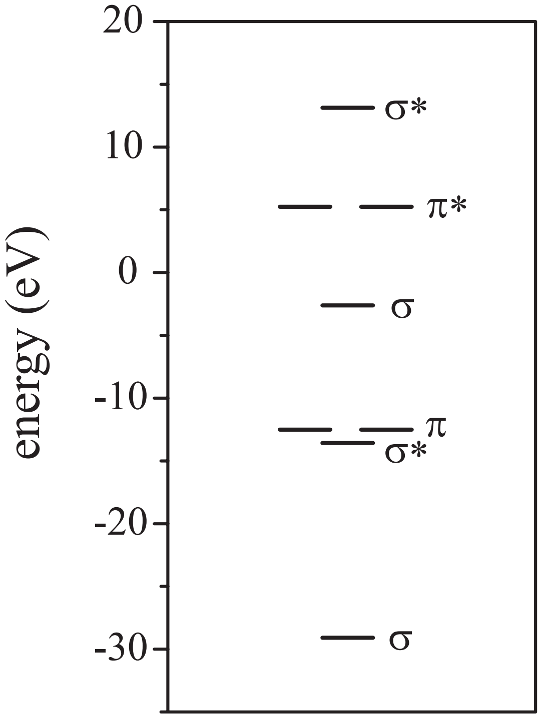
ANSWER:

Marks 5

- C_2 is a reaction intermediate observed in flames, comets and circumstellar shells.

How many valence electrons are there in C_2?

Complete the calculated MO diagram for the ground state of C_2 by inserting the appropriate number of valence electrons into the appropriate orbitals.



What is the bond order of C_2?

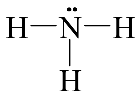
What is the longest wavelength of light that the ground state C_2^+ ion will absorb? Show working.

Answer:

Marks

4

- Complete the table below showing the total number of σ-bonding and non-bonding electron pairs, the Lewis structure and the predicted shape of each of the following species.

Formula	Total number of σ-bonding and non-bonding electron pairs on central atom	Lewis structure	Name of molecular shape
e.g. NH_3	4		trigonal pyramidal
ClF_3			
PO_4^{3-}			

2

- Explain why the first ionisation energy of an atom of oxygen is slightly lower than that of an atom of nitrogen, despite being further across the period.

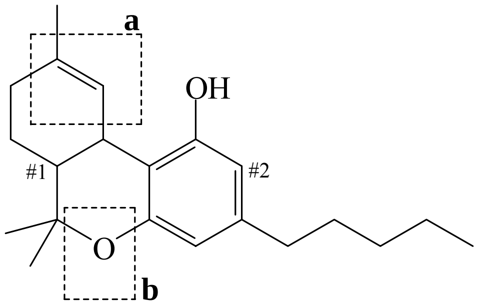
2

- Write down the ground state electron configurations of the following elements. Phosphorus is given as an example.

P	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
Se	
B	

Marks
4

- The structure of tetrahydrocannabinol may be drawn thus:



Name the functional groups in the boxes **a** and **b**.

a	
b	

What are the approximate bond angles at the atoms labelled #1 and #2?

C#1		C#2	

The infrared spectrum of tetrahydrocannabinol shows strong absorption at 3600 cm^{-1}. Explain this in terms of the functional groups present in the molecule.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
5

- Two students determined the specific heat capacity of steel as follows. Student 1 poured 200 mL of recently boiled water into a styrofoam cup calorimeter and measured the temperature of the water to be 90.0 °C. A steel teaspoon (25 g) at room temperature (20.0 °C) was placed into the cup, where it was completely submerged. After equilibrium was presumedly reached, the temperature was measured to be 88.7 °C. Student 2 took the same cup and filled it with 200 mL of water at room temperature (20.0 °C) and placed the same teaspoon from the freezer (– 40.0 °C) into the cup. After equilibrium was presumedly reached, the temperature recorded was 19.2 °C. Determine the specific heat capacity of steel using the experimental data of each student. The specific heat capacity of water is 4.184 J g^{-1} K^{-1}. Assume the density of water is 1.00 g mL^{-1} at all temperatures.

Student 1:	Student 2:

Which student's value is more accurate? Give reasons for your answer.

Marks

- The mechanism of copper toxicity to aquatic organisms is unknown. Most theories attribute the toxicity to the Cu^{2+} species because Cu^{+} is unstable in aqueous solution. Given the half-reactions and half-cell potentials on the data page, show that it is electrochemically favourable for $Cu^{+}(aq)$ to react with itself to form $Cu^{2+}(aq)$ and Cu(s). **3**

- The Co^{3+} ion is unstable in aqueous solution, but for a different reason to Cu^{+} above. Using the table of reduction potentials on the data page, propose the reason why this might be so. **2**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- When 1.0 mol of acetic acid and 1.0 mol of ethanol are mixed they react according to the following equation. **3**

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

At equilibrium the mixture contains 0.67 mol of the ester ($CH_3COOC_2H_5$). What is the equilibrium constant for the reaction?

ANSWER:

- Bromine-containing compounds are even more ozone depleting than the analogous chlorine-containing compounds. In the stratosphere, an equilibrium exists between bromine and the NO_x species. One of these equilibrium reactions is: **3**

$$2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$$

To study this reaction, an atmospheric chemist places a known amount of NOBr in a sealed container at 25 °C to a pressure of 0.250 atm and observes that 34% of it decomposes into NO and Br_2. What is K_p for this reaction?

ANSWER:

Marks 5

- During exercise, fat molecules react with water (hydrolyse) to form a group of compounds called fatty acids. These fatty acids are then converted to carbon dioxide and water, releasing energy to power the muscles. A typical human fatty acid is palmitic acid, $CH_3(CH_2)_{14}COOH$. Write a balanced equation for the complete oxidation of palmitic acid to produce $CO_2(g)$ and $H_2O(l)$.

The direct combustion of palmitic acid in a calorimeter yields the same products as in the body together with the production of 9980 kJ of heat per mole of palmitic acid. What is the standard enthalpy of formation of palmitic acid?

Data:

Compound	$\Delta H_f°$ (kJ mol^{-1})
$H_2O(l)$	–285.8
$CO_2(g)$	–393.5

Answer:

One gram of carbohydrate yields about 17 kJ of energy in the body. Calculate the equivalent energy value per gram of palmitic acid.

Answer:

Marks
4

- The bacterium *Azotobacter chroococcum*, growing aerobically in a medium free of nitrogen containing compounds, obtains all of its nitrogen by the "fixation" of atmospheric N_2. The solubility of N_2 in water is governed by the following equilibrium:

$$N_2(aq) \rightleftharpoons N_2(g) \qquad K = 1.6 \times 10^3 \text{ atm L mol}^{-1}$$

What is the concentration of dissolved N_2 available to the bacterium at 1.0 atm and 30 °C? (Air is 78% N_2.)

Answer:

A culture of these bacteria (1.0 L) grows to a density of 0.84 mg dry weight per mL of culture and has a nitrogen content of 7.0% of the dry weight. What volume of air at 1.0 atm and 30 °C would supply this nitrogen requirement?

Answer:

Marks
3

- Some physical properties of three hydrogen-bonded compounds are listed in the table below.

Compound (A)	Energy of A…A H-bond (kJ mol^{-1})	Boiling point (K)
HF	27	293
H_2O	22	373
NH_3	17	240

Explain the origin of the trends in the A…A H-bond energy.

Explain why the boiling point of H_2O appears anomalously high in comparison to the other two compounds.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- A concentration cell is constructed of two hydrogen electrodes; one immersed in a solution with $[H^+]$ = 1.0 M and the other in hydrochloric acid of unknown concentration. The observed cell potential was 0.25 V. What is the pH of the unknown hydrochloric acid? **3**

Answer:

- Consider the organic solvents ethanol (CH_3CH_2OH) and ether ($CH_3CH_2OCH_2CH_3$). Which liquid will have the higher vapour pressure? Give a brief reason for your answer. **3**

Consider the liquids mercury and water. Which liquid will have the higher surface tension? Give a brief reason for your answer.

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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}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

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
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+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
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+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
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–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

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

$\lambda = h/mu$

$4.5k_BT = hc/\lambda$

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

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

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

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 $\ln(A_0/A_t)$

Gas Laws

$PV = nRT$

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

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

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

Colligative Properties

$\pi = cRT$

$p = kc$

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

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Electrochemistry

$\Delta G° = -nFE°$

Moles of $e^- = It/F$

$E = E° - (RT/nF) \ln Q$

$= E° - (RT/nF) \times 2.303 \log Q$

$E° = (RT/nF) \ln K$

$= (RT/nF) \times 2.303 \log K$

$E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)

Polymers

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

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]									

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]