22/08(a) **The University of Sydney**

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

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 21 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 14 and 24 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-11	34	

Short answer section

Page	Marks Max	Gained		Marker
12	10			
13	8			
15	9			
16	6			
17	4			
18	6			
19	5			
20	4			
21	6			
22	4			
23	4			
Total	66			

Marks
10

- In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.

(a) anti-bonding orbital

(b) electron affinity

(c) nuclear fission

(d) electronegativity

(e) VSEPR model

Marks

- Balance the following nuclear reactions by identifying the missing nuclear particle or nuclide. **3**

$$^{36}_{17}\text{Cl} + {}^{0}_{-1}\text{e} \rightarrow \square$$

$$^{236}_{92}\text{U} \rightarrow {}^{92}_{36}\text{Kr} + {}^{141}_{56}\text{Ba} + 3\,\square$$

$$^{99}_{42}\text{Mo} \rightarrow {}^{0}_{-1}\text{e} + \square$$

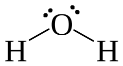
- The half-life of plutonium-239 is 24110 years. How many years (to the nearest year) must pass after $^{239}_{94}\text{Pu}$ is produced for the number of $^{239}_{94}\text{Pu}$ atoms to decay to 0.01000 of the original number? **3**

Answer:

- Provide a brief explanation of the process by which nuclear radiation causes biological damage. **2**

Marks
6

- Complete the following table.

Formula	Lewis structure	Molecular shape	Is the molecule *polar* or *non-polar*?
e.g. H_2O		bent (angular)	polar
CH_2O			
CH_2Cl_2			
C_2Cl_2			

3

- The lowest four energy levels of the He^+ ion are given.

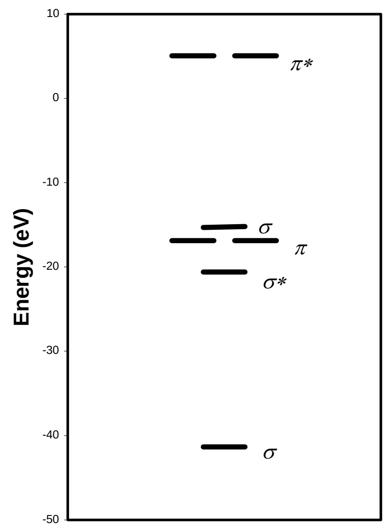
Principal quantum number (*n*)	Energy (J)
1	-8.720×10^{-18}
2	-2.180×10^{-18}
3	-0.969×10^{-18}
4	-0.545×10^{-18}

An electronic transition is identified by specifying the value of *n* of the initial state and the value of *n* of the final state. Identify the electronic transition responsible for the emission of radiation from He^+ with a wavelength of 121.5 nm?

Marks

• Nitrogen gas constitutes about 78% of the Earth's atmosphere. **4**

Complete the MO diagram for the valence electrons for the ground state electronic configuration of the nitrogen molecule by inserting the appropriate number of electrons into the appropriate orbitals.



Is N_2 paramagnetic or diamagnetic? Explain your answer.

The N_2^- anion can be generated as a transient species in an electrical discharge. What is the bond order of this molecular ion?

• Why is the H_2 molecule lower in energy than two isolated H atoms? **2**

Marks
4

- When 156 g of aluminium metal at 50.0 °C is added to 100 g of water at 20.0 °C, the final temperature becomes 30.0 °C. The heat capacity of water is 4.18 J K^{-1} g^{-1}. Calculate the specific heat capacity of aluminium.

Answer:

What would the final temperature have been if the 156 g of aluminium metal at 50 °C had been added to iced water containing 10 g ice and 90 g water at 0 °C?
ΔH for the freezing of water is –6.02 kJ mol^{-1}.

Answer:

Marks

- Explain the following features of the lead acid storage battery. **3**

  It has a relatively constant voltage.

  It needs no salt bridge.

  It can be recharged.

- Explain why aluminium metal cannot be produced by the electrolysis of aqueous solutions of aluminium salts. Explain why aluminium is produced by the electrolysis of a molten mixture of Al_2O_3 and Na_3AlF_6 rather than by the electrolysis of molten Al_2O_3 alone. **3**

Marks
5

- RDX ($C_3H_6N_6O_6$) is a powerful explosive. Write the balanced chemical equation to describe the complete combustion of RDX to give water, carbon dioxide and nitrogen.

How does the equation for the explosive decomposition of RDX differ from the above equation?

What properties of RDX make it a good explosive?

How much heat is liberated from the complete combustion of 100 g of RDX?

Compound	$\Delta H_f°$ (kJ mol^{-1})
$H_2O(l)$	–286
$CO_2(g)$	–394
RDX(s)	+65

Answer:

Is the explosive decomposition of RDX likely to be entropically favourable?
(*i.e.* Is $\Delta S > 0$?) Give reasons for your answer.

Marks
4

- Aluminium metal is a very effective agent for reducing oxides to their elements. For example, it is used as a component of the solid fuel in the space shuttle, and in the thermite reaction shown in lectures:

$$Fe_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Fe(s)$$

Write a balanced equation for the reduction of SiO_2(s) to silicon by Al(s).

Given the following thermochemical data, evaluate the enthalpy change per gram of reactants for the SiO_2 and Fe_2O_3 reactions above.

Compound	ΔH_f° (kJ mol^{-1})
Fe_2O_3	-821
Al_2O_3	-1668
SiO_2	-877

Answer (SiO_2):	Answer (Fe_2O_3):

Which set of reactants would make the better rocket fuel on the basis of most energy provided per mass of fuel (*i.e.* biggest “bounce per ounce”)?

Marks
6

- Consider a solution that is 1 M in both H^+ and Fe^{2+} ions under 1 atm of oxygen gas. Use the standard reduction potentials on the data sheet to show that Fe^{2+} ions are unstable under these conditions.

Why can such solutions be preserved by the addition of iron metal?

Will the change in the Gibbs Free Energy, ΔG, for the following reaction be positive or negative?

$$Fe(s) + 2Fe^{3+}(aq) \rightleftharpoons 3Fe^{2+}(aq)$$

Calculate the reduction potential of a half-cell consisting of a platinum electrode immersed in a 2.0 M Fe^{2+} and 0.20 M Fe^{3+} solution at 25 °C.

Answer:

Marks
4

- A saturated solution of iodine in water contains 0.330 g I_2 per litre, but more than this amount can dissolve in a potassium iodide solution because of the following equilibrium.

$$I^-(aq) + I_2(aq) \rightleftharpoons I_3^-(aq)$$

A 0.100 M KI solution dissolves 12.5 g of I_2 per litre, most of which is converted to $I_3^-(aq)$. Assuming that the concentration of $I_2(aq)$ in all saturated solutions is the same, calculate the equilibrium constant for the above reaction.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
4

- State the Second Law of Thermodynamics and give an equation to express this Law mathematically. Use this equation to derive the relationship between spontaneity and the Gibbs Free Energy of a reaction, *i.e.* show that $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} < 0$ for a spontaneous reaction.

Give an example of a chemical reaction or a chemical process that corresponds to each of the following.

$\Delta S > 0$, $\Delta H > 0$, $\Delta G < 0$

$\Delta S > 0$, $\Delta H < 0$, $\Delta G < 0$

$\Delta S < 0$, $\Delta H < 0$, $\Delta G < 0$

CHEM1901 - CHEMISTRY 1A (ADVANCED)
CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

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

CHEM1901 - CHEMISTRY 1A (ADVANCED)
CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

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

CHEM1901 - CHEMISTRY 1A (ADVANCED)
CHEM1903 - CHEMISTRY 1A (SPECIAL STUDIES PROGRAM)

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]