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

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

CONFIDENTIAL

JUNE 2005 **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 24 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 20, 24 and 28 are for rough working only.

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Multiple choice section

	Marks	
Pages	Max	Gained
2-13	40	

Short answer section

	Marks			
Page	Max	Gained		Marker
14	5			
15	8			
16	5			
17	6			
18	5			
19	4			
21	6			
22	4			
23	3			
25	6			
26	4			
27	4			
Total	60			

	Marks
• In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.	**5**
(a) antibonding orbital	
(b) paramagnetic	
(c) ionic bond	
(d) nuclear fission	
(e) electron affinity	

Marks

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

$$^{55}_{26}\text{Fe} + ^{0}_{-1}\text{e} \rightarrow \square$$

$$^{232}_{90}\text{Th} \rightarrow ^{4}_{2}\alpha + \square$$

$$^{218}_{84}\text{Po} \rightarrow ^{0}_{-1}\text{e} + \square$$

- Over 50 years, the activity of a sample of strontium-90 decreases from 1000 Bq to 303 Bq. Calculate the half-life of strontium-90 (in years) to the nearest year. **2**

Answer:

- Identify three desirable properties of an unstable isotope to be used in medical imaging. **3**

	Marks
• In the 1770's, Joseph Priestley first identified the gases we know as O_2 and CO_2 and showed that the former was converted to the latter during combustion. Briefly explain how these observations contributed to the formulation of the atomic theory.	2
• Identify one property used by Mendeleev to organise elements in his periodic table.	2
Provide a brief explanation of the origin of the periodicity of this property in terms of the quantum theory of atomic structure.	
• Arrange the following atoms and ions in order of increasing radius.	1

P, Na, Na^+, N and K

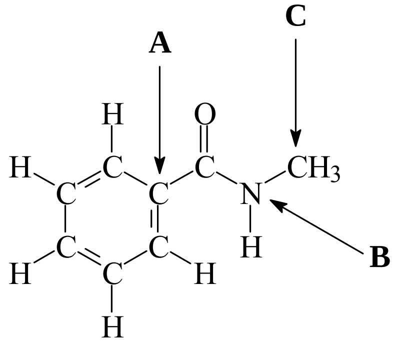
smallest radius						largest radius

	Marks
• Describe (or sketch) the shape and arrangement of the <u>nodes</u> in the following three atomic orbitals: 2*s*, 2*p* and 3*s*.	2
• Explain the different roles of neutrons and protons in stabilising nuclei.	2
• Explain, with reference to the distribution of electronic energy levels, why crystalline SiO_2 (quartz) is transparent while crystalline Fe is opaque.	2

Marks

3

- The structure of *N*-methylbenzamide is shown below. Complete the table concerning the atoms **A**, **B** and **C** indicated by the arrows.



Selected atom	Number of electron lone pairs about the selected atom	Number of σ-bonds associated with the selected atom	Geometry of bonds about the selected atom
A			
B			
C			

2

- 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 30.4 nm?

Marks
4

- The electronic configuration of molecular nitrogen in its ground state is, in order (from left to right) of orbitals of increasing energy:

$$\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\pi^4\sigma^2$$

What is the bond order of N_2?

How many of the valence electrons in N_2 are in non-bonding 'lone pairs' according to Lewis theory?

On the electron configuration of N_2 below, indicate by arrows the molecular orbitals that contain the non-bonding electrons.

$$\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\pi^4\sigma^2$$

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- Write the equation whose enthalpy change represents the standard enthalpy of formation of NO(g). **3**

Given the following data, calculate the standard enthalpy of formation of NO(g).

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ $\Delta H° = 66.6$ kJ mol^{-1}

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\Delta H° = -114.1$ kJ mol^{-1}

Answer:

Derive the relationship $K_p = K_c(RT)^{\Delta n}$ for a reaction in which gases are involved. Δn is the difference in the number of moles of gases between products and reactants. **3**

Marks
4

- In an experiment, 50.0 mL of 1.00 M HNO_3 was combined with 50.0 mL of 0.540 M NaOH in a calorimeter. Give an equation for the reaction that took place.

The temperature of the solution was found to increase by 2.98 °C. If the heat capacity of the calorimeter was 80.0 J K^{-1} and the heat capacity of the final solution was 426 J K^{-1}, determine the molar heat of reaction.

Answer:

The average bond enthalpy of the O-H bond is 463 kJ mol^{-1}. Explain briefly why the heat of neutralisation calculated in the first part of this question differs significantly from this value.

Marks
3

- At 773 K, the following reaction has an equilibrium constant, K_p, of 3.90×10^{-3} atm^{-1}.

$$^{1}/_{2}N_2(g) + ^{3}/_{2}H_2(g) \rightleftharpoons NH_3(g)$$

If sufficient ammonia were introduced into an evacuated container at 773 K to give a pressure of 1.00 atm before any decomposition occurred, what would be the partial pressures of N_2, H_2 and NH_3 at equilibrium?

$P(N_2)$ =	$P(H_2)$ =	$P(NH_3)$ =

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
6

- Use electrochemical potentials to show the following.

  Fe^{2+}(aq) is stable in oxygen-free H_2O.

  Fe^{2+}(aq) is not stable under 1 atm O_2 in a 1 M solution of HCl.

  Fe^{2+}(aq) is stable under 1 atm O_2 in the presence of iron metal.

  Cu^{+}(aq) is not stable in water.

Marks
4

- In the chlor-alkali process $OH^-(aq)$ and $Cl_2(g)$ are produced by the electrolysis of a saturated solution of sodium chloride. Explain why chlorine gas rather than oxygen gas forms at the anode.

Calculate the volume of chlorine gas produced at 0 °C and 1 atm by passing a current of 1.00 A for a period of exactly 1 hour in the chlor-alkali process.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks
4

- State the Second Law of Thermodynamics and explain how this relates to the Gibbs Free Energy.

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

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

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

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

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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}

Charge of electron, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg

Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg

Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ 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} 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
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	+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
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.28
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–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 $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = Z^2E_R(1/n^2)$	**Radioactivity** $t_{1/2} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$
Acids and Bases $pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	**Gas Laws** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$
Colligative properties $\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_fm$ $\Delta T_b = K_bm$	**Kinetics** $t_{1/2} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Electrochemistry $\Delta G° = -nFE°$ Moles of e^- = It/F $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (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** If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

June 2005

CHEM1901/1903

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]

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