Topics in the June 2014 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2014-J-2:

- Nuclear and Radiation Chemistry

2014-J-3:

- Nuclear and Radiation Chemistry

2014-J-5:

- Wave Theory of Electrons and Resulting Atomic Energy Levels
- Atomic Electronic Spectroscopy
- Ionic Bonding

2014-J-6:

- Lewis Structures
- VSEPR

2014-J-7:

- Lewis Structures
- VSEPR
- Types of Intermolecular Forces

2014-J-8:

- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

2014-J-9:

- Chemical Equilibrium
- Equilibrium and Thermochemistry in Industrial Processes

2014-J-10:

- First and Second Law of Thermodynamics
- Electrochemistry

2014-J-11:

- First and Second Law of Thermodynamics
- Equilibrium and Thermochemistry in Industrial Processes

2014-J-12:

- Electrochemistry

2014-J-13:

- Batteries and Corrosion

2014-J-14:

- Batteries and Corrosion

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THE UNIVERSITY OF SYDNEY

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

JUNE 2014 **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 •.
- Only non-programmable, University-approved calculators may be used.
- Students are warned 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 and 24 are for rough working only.

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Multiple choice section

	Marks	
Pages	Max	Gained
2-9	30	

Short answer section

Page	Marks Max	Gained		Marker
10	6			
11	6			
12	9			
13	7			
14	8			
15	5			
16	5			
17	3			
19	5			
20	4			
21	4			
22	3			
23	5			
Total	70			
Check Total				

Marks
6

- In March 2011 after a tsunami flooded the Fukushima Daiichi nuclear power plant, three of the six reactors went into meltdown, and by 31 March had released large quantities of the nuclides detailed in the table below.

Radioisotope	Initial activity of quantity released (10^{15} Bq)	Half-life
^{131}I	511	8.02 days
^{137}Cs	13.6	30.17 years

Given that the only stable nuclide of iodine is ^{127}I, would you expect the primary decay mechanism for ^{131}I to be α, β^-, or β^+ decay? Briefly explain your reasoning.

Calculate the decay constant for ^{131}I.

Answer:

Calculate the initial mass of ^{131}I released.

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Page Total:

Marks
6

One method of determining whether further radionuclide leaks are occurring is to monitor the relative activities of the different nuclides as a function of time. Calculate the expected activity due to each of these nuclides exactly 3 years after the release. Assume no more has subsequently escaped from the reactors.

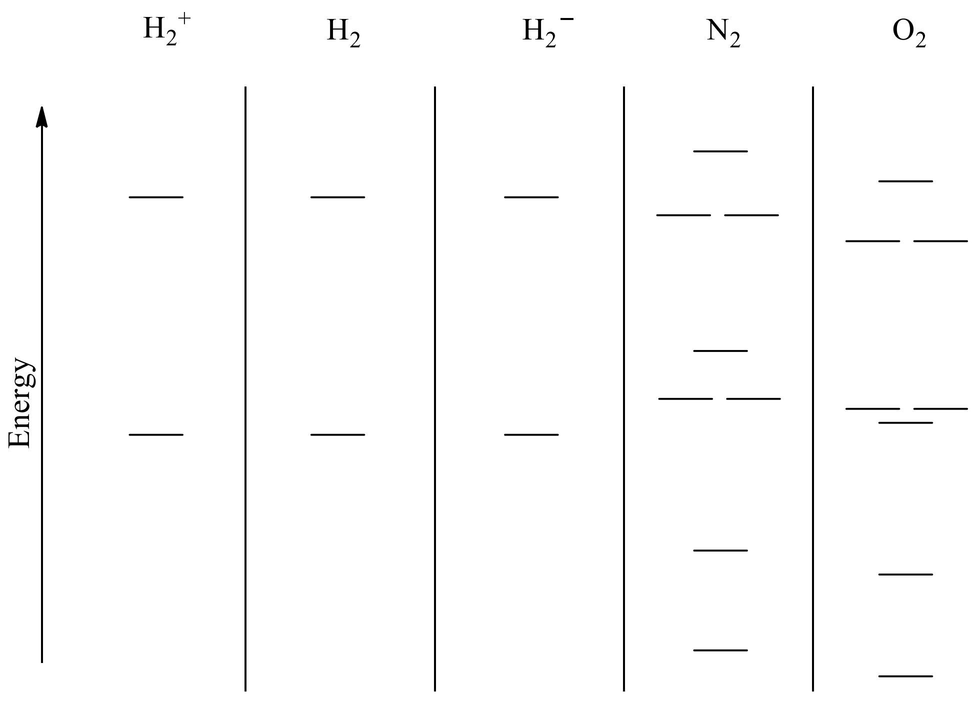
Activities	^{131}I:	^{137}Cs:

Caesium has no biological role in the human body, and is usually only present in trace amounts. On ingestion, even non-radioactive Cs isotopes are considered toxic as they are capable of partially substituting for chemically similar elements. Name a chemically similar element. State one chemically-significant difference between ions of this element and Cs^+ ions.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
9

- The molecular orbital energy level diagrams for H_2^+, H_2, H_2^-, N_2 and O_2 are shown below. Fill in the valence electrons for each species in its ground state and label the types of orbitals (σ, σ*, π, π*).



Which of the five species are paramagnetic?

Give the bond order of all species.

H_2^+:	H_2:	H_2^-:	N_2:	O_2:

Giving reasons, arrange H_2^+, H_2 and H_2^- in order of increasing bond length.

Marks

- Determine an electronic transition involving the $n = 5$ level of the He^{+} ion that emits light in the visible region (400–700 nm) of the electromagnetic spectrum. **3**

- Describe one piece of experimental evidence supporting the conclusion that electrons have wave-like character. **1**

- Consider the melting points of the following solids, which all have the halite crystal structure type. **3**

solid	AgCl	KBr	KCl	NaCl
m.p. (°C)	455	734	770	801

Rationalise the order of the melting points of KBr, KCl and NaCl in terms of the size of the constituents and the strength of the interactions holding them together.

The Ag^{+} ion is intermediate in size between Na^{+} and K^{+}. Why does AgCl have a melting point considerably lower than both KCl and NaCl?

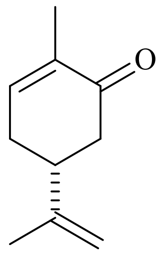
Marks
8

- Complete the table below showing the Lewis structures and the predicted shapes of the following species.

Species	Lewis Structure	Approximate F-X-F bond angle(s)	Name of molecular shape
SiF_4			
SF_4			
XeF_3^+			
XeF_3^-			

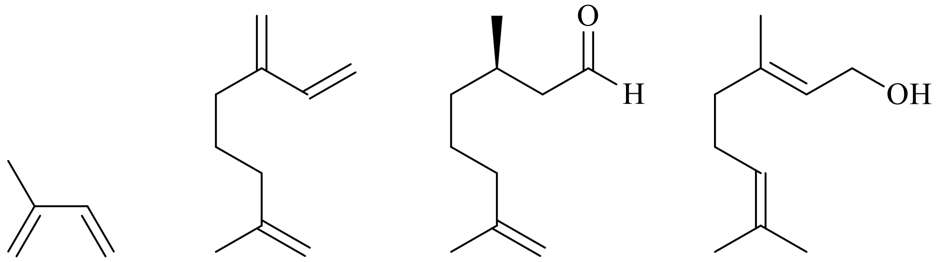
Marks
5

- (R)-Carvone is a typical terpene, a class of compounds widely distributed in nature. Circle all of the trigonal planar carbon atoms on the structure of (R)-carvone, below.



(R)-carvone

All terpenes are derived from the hydrocarbon, isoprene and many, such as myrcene, (R)-citronellal and geraniol, are used in the perfume industry.



isoprene	myrcene	(R)-citronellal	geraniol
b.p. 34 °C	b.p. 167 °C	b.p. 201 °C	b.p. 230 °C

Explain the differences in boiling points of these four compounds in terms of the type and size of the intermolecular forces present.

Marks
5

- When 10.0 g of solid ammonium carbamate $NH_2CO_2NH_4$ is placed in an evacuated 1.0 L flask at 25 °C, the pressure in the flask rises to 88 mmHg. Write a balanced equation for the decomposition of ammonium carbamate into ammonia gas and carbon dioxide.

Calculate the equilibrium constant in terms of partial pressures, K_p, for the decomposition of ammonium carbamate.

Answer:

This flask is connected by a hose (of negligible volume) to another 1.0 L flask at 25 °C containing 1.00 atm of $H_2S(g)$. A tap between the flasks is opened and the gaseous contents allowed to mix. Given the following reaction data:

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad K_p = 9.40 \times 10^{-2} \text{ at } 25\ °C,$$

calculate K_p for the new equilibrium that is established, *viz.*

$$NH_2CO_2NH_4(s) + H_2S(g) \rightleftharpoons NH_3(g) + CO_2(g) + NH_4SH(s)$$

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
3

Hence calculate the total pressure in the flasks at equilibrium.

Answer:

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	Marks
• At a temperature of absolute zero, the entropy of deuterated methane CH_3D is 12 J K^{-1} mol^{-1}. Explain the significance of this value and suggest an explanation for it.	2
• A concentration cell is constructed from two beakers containing 1 M $NiCl_2$ and 0.002 M $NiCl_2$. Describe the overall change that occurs as the concentration cell runs.	3
What would be the major driving force for the overall reaction, enthalpy or entropy? Explain your answer.	

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Marks
4

- Consider the following standard free energies of formation at 1000 K.

Compound	$CO(g)$	$CO_2(g)$	$Fe_2O_3(s)$	$Li_2O(s)$
$\Delta_f G°$ / kJ mol^{-1}	–200	–396	–562	–466

Predict whether the following oxides can be reduced to metals by carbon at that temperature, and state whether the products could be CO, CO_2 or both.

$Fe_2O_3(s)$

$Li_2O(s)$

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Marks
4

A voltaic cell consists of Cd^{2+}/Cd and Ag^{+}/Ag half cells with initial concentrations of $[Cd^{2+}]$ = 1.00 M and $[Ag^{+}]$ = 0.60 M. Each half cell contains 1.00 L of solution.

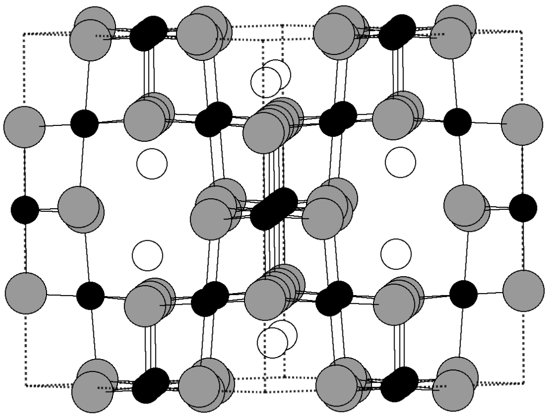
What is the voltage of the cell at 20 °C after equilibrium has been reached?

What are the concentrations of the Cd^{2+}(aq) and the Ag^{+}(aq) ions at 20 °C after equilibrium has been reached?

$[Cd^{2+}]_{eq}$ =	$[Ag^{+}]_{eq}$ =

Marks
3

- $LiMn_2O_4$ (s) is an infinite network solid with the spinel-type structure, shown below. White circles are Li atoms, black circles are Mn atoms and grey circles are oxygen atoms. Dashed lines represent the unit cell.



What are the most important types of chemical bonds responsible for making $LiMn_2O_4$ a stable solid?

$LiMn_2O_4$ is commonly used as a cathode in rechargeable lithium-ion batteries. The battery is charged by moving Li^+ ions out of this cathode to give $Li_{1-x}Mn_2O_4$. Explain how this is possible.

The anode is C (graphite), which gives Li_xC_6 on charging. Describe how the lithium is incorporated into the graphite anode.

THIS QUESTION IS CONTINUED ON THE NEXT PAGE

Marks
5

Write out the anode and cathode half-cell reactions, and the overall cell reaction, for this battery as it discharges.

Cathode	
Anode	
Overall	

Many researchers are exploring the possibility of replacing Li^+ with Na^+ in these batteries, because sodium is much cheaper and less toxic than lithium. Explain two potential *disadvantages* of switching to sodium, in terms of battery performance.

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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}
Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-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 = 1.013 bar	1 Ci = 3.70×10^{10} Bq
0 °C = 273 K	1 Hz = 1 s^{-1}
1 L = 10^{-3} m^3	1 tonne = 10^3 kg
1 Å = 10^{-10} m	1 W = 1 J s^{-1}
1 eV = 1.602×10^{-19} J	1 J = 1 kg m^2 s^{-2}

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
10^{12}	tera	T

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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
$MnO_4^{–}(aq) + 8H^{+}(aq) + 5e^{–} \rightarrow Mn^{2+}(aq) + 4H_2O$	+1.51
$Au^{3+}(aq) + 3e^{–} \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^{–} \rightarrow 2Cl^{–}(aq)$	+1.36
$O_2 + 4H^{+}(aq) + 4e^{–} \rightarrow 2H_2O$	+1.23
$Pt^{2+}(aq) + 2e^{–} \rightarrow Pt(s)$	+1.18
$MnO_2(s) + 4H^{+}(aq) + e^{–} \rightarrow Mn^{3+} + 2H_2O$	+0.96
$NO_3^{–}(aq) + 4H^{+}(aq) + 3e^{–} \rightarrow NO(g) + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^{–} \rightarrow Pd(s)$	+0.92
$NO_3^{–}(aq) + 10H^{+}(aq) + 8e^{–} \rightarrow NH_4^{+}(aq) + 3H_2O$	+0.88
$Ag^{+}(aq) + e^{–} \rightarrow Ag(s)$	+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
$BiO^{+}(aq) + 2H^{+}(aq) + 3e^{–} \rightarrow Bi(s) + H_2O$	+0.32
$Sn^{4+}(aq) + 2e^{–} \rightarrow Sn^{2+}(aq)$	+0.15
$2H^{+}(aq) + 2e^{–} \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^{–} \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^{–} \rightarrow Pb(s)$	–0.126
$Sn^{2+}(aq) + 2e^{–} \rightarrow Sn(s)$	–0.136
$Ni^{2+}(aq) + 2e^{–} \rightarrow Ni(s)$	–0.24
$Co^{2+}(aq) + 2e^{–} \rightarrow Co(s)$	–0.28
$Cd^{2+}(aq) + 2e^{–} \rightarrow Cd(s)$	–0.40
$Fe^{2+}(aq) + 2e^{–} \rightarrow Fe(s)$	–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
$Sc^{3+}(aq) + 3e^{–} \rightarrow Sc(s)$	–2.09
$Mg^{2+}(aq) + 2e^{–} \rightarrow Mg(s)$	–2.36
$Na^{+}(aq) + e^{–} \rightarrow Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^{–} \rightarrow Ca(s)$	–2.87
$Li^{+}(aq) + e^{–} \rightarrow Li(s)$	–3.04

CHEM1901 - CHEMISTRY 1A (ADVANCED)

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Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $E = -Z^2 E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$ $T\lambda = 2.898 \times 10^6$ K nm	**Electrochemistry** $\Delta G° = -nFE°$ Moles of $e^- = It/F$ $E = E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)
Acids and Bases $pH = -\log[H^+]$ $pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	**Gas Laws** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$ $E_k = ½mv^2$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = 8033 $\ln(A_0/A_t)$ years	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-Ea/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Colligative Properties & Solutions $\Pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $c = kp$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	**Thermodynamics & Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $\Delta_{univ} S° = R \ln K$ $K_p = K_c\left(\frac{RT}{100}\right)^{\Delta n}$
Miscellaneous $A = -\log\frac{I}{I_0}$ $A = \varepsilon cl$ $E = -A\frac{e^2}{4\pi\varepsilon_0 r}N_A$	**Mathematics** If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$ Area of circle = πr^2 Surface area of sphere = $4\pi r^2$