Topics in the June 2013 Exam Paper for CHEM1903

Click on the links for resources on each topic.

2013-J-2:

• Nuclear and Radiation Chemistry

2013-J-3:

- Filling Energy Levels in Atoms Larger than Hydrogen
- Periodic Table and the Periodic Trends

2013-J-4:

• Band Theory - MO in Solids

2013-J-5:

• Bonding in O₂, N₂, C₂H₂, C₂H₄ and CH₂O

2013-J-6:

• Gas Laws

2013-J-7:

- Lewis Structures
- VSEPR

2013-J-8:

- Thermochemistry
- First and Second Law of Thermodynamics

2013-J-9:

- Thermochemistry
- Nitrogen Chemistry and Compounds
- Types of Intermolecular Forces

2013-J-10:

• Chemical Equilibrium

2013-J-11:

• Equilibrium and Thermochemistry in Industrial Processes

2013-J-12:

• First and Second Law of Thermodynamics

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THE UNIVERSITY OF SYDNEY <u>CHEMISTRY 1A (ADVANCED) - CHEM1901</u> <u>CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903</u>

CONFIDENTIAL

FIRST SEMESTER EXAMINATION

JUNE 2013

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 <u>INK</u>.
- 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, Universityapproved 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 19 and 24 are for rough working only.

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Multiple choice section

	Marks			
Pages	Max	Gained		
2-10	30			

Short answer section

		Marks		
Page	Max	Gaine	d	Marker
11	8			
12	6			
13	7			
14	4			
15	4			
16	9			
17	5			
18	5			
20	2			
21	4			
22	8			
23	8			
Total	70			
Check	Total			

• Calculate the activity (in Bq) of a 1.00 g sample of ¹³⁷ Cs ¹³¹ I, if the half lives of the caesium and iodine are 30.17 years and 8.02 days respectively.	Marks 8
	_
Both nuclides in ¹³⁷ Cs ¹³¹ I are beta emitters, and the daughter nuclides are stable. Describe the sample after it has been melted and allowed to resolidify after (a) 3 months and (b) 300 years.	

Marks • Write down the ground state electron configurations for the following species. 4 Na is given as an example. [Ne] $3s^1$ Na K As Sr C^+ Name the elements described by the following configurations. [Kr] $5s^2 4d^6$ [Xe] $6s^2 5d^1 4f^{11}$ • The Periodic Table as arranged by Mendeleev allows us to make predictions about the 2 behaviours of elements based on those around them. Briefly describe why the Periodic Table works?

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Carbon, silicon, germanium and tin all adopt the diamond structure. Diamond has a band gap of 5.5 eV, while silicon absorbs wavelengths shorter than 1100 nm. Predict the band gaps of germanium and tin.				
Predict the band ga bonded to 4 C ator	ap of SiC, which also h ns, and C bonded to 4 S	as a diamond like struc Si atoms.	cture, but with Si	
	,			
Use the informatio	n in the following tabl	e to predict the density	oftin	
Element	Atomic Mass	Density (g cm ⁻³)	Bond length (pm)	
Ge	72.64	5.323	244	
Sn	118.7		280.	
		Answer:		

Marks • Oxygen exists in the troposphere as a diatomic molecule. 4 σ^* π* σ Energy π σ^* σ (a) Using arrows to indicate relative electron spin, fill the left-most valence orbital energy diagram for O₂, obeying Hund's Rule. (b) Indicate on the right-most valence orbital energy diagram the lowest energy electronic configuration for O₂ which has no unpaired electrons. Suggest a heteronuclear diatomic species, isoelectronic with O₂, that might be expected to have similar spectroscopic behaviour. The blue colour of liquid O₂ arises from an electronic transition whereby one 635 nm photon excites two molecules to the state indicated by the configuration in (b) at the same time. What wavelength photon would be emitted by one molecule returning from this state to the ground state? Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

The density of liquid oxygen is 1.141 g cm^{-3} . Calculate its molarity and compare to the molarity of oxygen in air. Air consists of 21% oxygen.				
[O ₂ (l)]:	[O ₂ (g)]:	_		
A 50.0 mL sample of liquid oxygen is tran and allowed to warm to room temperature the container?	nsferred to an evacuated 1.25 L container e (25 °C). What is the final pressure inside			
	Γ	_		
	Answer:			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Compleall atom	ete the following table on the given oxiden ns with non-zero formal charge.	s of nitrogen. Indicate the charge on	Marks 9
Molecule	Lewis Structure	Shape of molecule	
NO ₂			
N ₂ O			
NO3			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

• The atmosphere of Venus contains 96.5 % CO ₂ at 95 atm of pressure, leading to a average global surface temperature of 462 °C. The energy density of solar radiation striking Venus is 2625 J m ⁻² s ⁻¹ . The radius of Venus is 6052 km, and the average albedo (the fraction of solar radiation reflected back into space) of its surface is 0.9 Calculate the magnitude of the greenhouse effect on Venus.	Marks 5 3e 0.
Angwor	
The main absorption bands of CO_2 lie in the energy range $600 - 750 \text{ cm}^{-1}$. What range of wavelengths (in nm) corresponds to this energy range?	
Sketch the emission spectrum of Venus on the axes below. Note the wavelength of maximum intensity, and point out any other important features.	
Intensity	
Wavelength (nm)	

CHEM1901/3 2013-J-9 June 2013 Marks • The structural formula of nitroglycerine, C₃H₅N₃O₉, is shown below. 5 The boiling point of nitroglycerine is 50 °C. What is the most important type of intermolecular force contributing to keeping nitroglycerine in the liquid state at room temperature, and which atoms in particular are involved? Write a balanced equation for the explosive decomposition of liquid nitroglycerine. The products are water, carbon dioxide, nitrogen and oxygen. The standard enthalpy change associated with this explosive decomposition is -1414 kJ mol⁻¹. What other factor(s) would contribute to the free energy released in the decomposition of nitroglycerine? Briefly describe a calorimetry experiment that could reliably measure the enthalpy of decomposition of nitroglycerine.

• The vapour pressure of mercury above its liquid at 25 °C is 0.265 Pa. Calculate the free energy of formation (in kJ mol ⁻¹) of gaseous mercury at 25 °C.	he Marks 2
Answer:	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

• The principal chemical reaction in the Hall process, used to refine aluminium from its oxide, is: $Al_2O_3 \text{ (in molten cryolite) + 3C(s) \rightarrow 2Al(l) + 3CO(g)}$ The free energy change for this reaction is $\Delta G^\circ = 594 \text{ kJ mol}^{-1} \text{ at 1000 °C}$. Recycling aluminium essentially only requires enough energy to melt it. The melting point of aluminium is 660 °C, its heat of fusion is 10.7 kJ mol⁻¹ and its heat capacity is 0.900 J K⁻¹ g⁻¹. Calculate the percentage of energy saved by recycling aluminium vs. refining it from Al_2O_3. (Assume that the ambient temperature is 25 °C.) Answer: THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks • Differential scanning calorimetry (DSC) is an experimental technique that measures 8 the temperature of a sample as a function of the heat supplied to it. Negative or positive peaks on a DSC curve therefore indicate endothermic or exothermic processes respectively. The figure below shows a series of DSC curves collected for methane at different pressures. The scales of all the heat flow curves are the same, but they have been offset from zero for clarity. Clearly identify the type of phase change associated with every peak in the DSC curve. 100 bar ····· 10 bar Heat flow ••••• 1 bar 0.1 bar 0.01 bar 0 100 300 200 $T(\mathbf{K})$ Use the DSC data shown to sketch a pressure-temperature phase diagram on the graph below (note that pressure is on a log scale). Label all the important regions of the phase diagram. 100 10 P (bar) 1 0.1 0.01 0 100 200 300 $T(\mathbf{K})$

Marks • Consider the following aqueous voltaic cell at 25 °C: 8 $Pb(s) | Pb^{2+} (0.0010 \text{ M}) || Sn^{2+} (2.0 \text{ M}) | Sn(s)$ Write balanced equations for the reactions occurring at the anode, cathode and overall. anode: cathode: overall: Calculate the potential of the cell under the stated conditions. Answer: What will be the concentrations of $Pb^{2+}(aq)$ and $Sn^{2+}(aq)$ in the cell when it comes to equilibrium? $[Pb^{2+}(aq)] =$ $[Sn^{2+}(aq)] =$

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DATA SHEET

Physical constants Avogadro constant, $N_{\rm A} = 6.022 \times 10^{23} \text{ mol}^{-1}$ Faraday constant, $F = 96485 \text{ C mol}^{-1}$ Planck constant, $h = 6.626 \times 10^{-34} \text{ J s}$ Speed of light in vacuum, $c = 2.998 \times 10^8 \text{ m s}^{-1}$ Rydberg constant, $E_{\rm R} = 2.18 \times 10^{-18} \text{ J}$ Boltzmann constant, $k_{\rm B} = 1.381 \times 10^{-23} \text{ J K}^{-1}$ Permittivity of a vacuum, $\varepsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ Gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$ Charge of electron, $e = 1.602 \times 10^{-19} \text{ C}$ Mass of electron, $m_{\rm p} = 1.6726 \times 10^{-27} \text{ kg}$ Mass of neutron, $m_{\rm n} = 1.6749 \times 10^{-27} \text{ kg}$

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	$1 \text{ Ci} = 3.70 \times 10^{10} \text{ Bq}$
0 °C = 273 K	$1 \text{ Hz} = 1 \text{ s}^{-1}$
$1 L = 10^{-3} m^3$	1 tonne = 10^3 kg
$1 \text{ Å} = 10^{-10} \text{ m}$	$1 \text{ W} = 1 \text{ J s}^{-1}$
$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$	

Decimal fractions		Deci	Decimal multiples		
Fraction	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-3}	milli	m	10^{3}	kilo	k
10^{-6}	micro	μ	10^{6}	mega	Μ
10^{-9}	nano	n	10 ⁹	giga	G
10^{-12}	pico	р	10^{12}	tera	Т

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Standard Reduction Potentials. E	Standard	Reduction	Potentials.	Е°
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Reaction	E° / V
$\operatorname{Co}^{3+}(\operatorname{aq}) + e^{-} \rightarrow \operatorname{Co}^{2+}(\operatorname{aq})$	+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
$\operatorname{Au}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Au}(s)$	+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
$NO_{3}^{-}(aq) + 10H^{+}(aq) + 8e^{-} \rightarrow NH_{4}^{+}(aq) + 3H_{2}O$	+0.88
$\operatorname{Ag}^{+}(\operatorname{aq}) + \operatorname{e}^{-} \rightarrow \operatorname{Ag}(\operatorname{s})$	+0.80
$Fe^{3+}(aq) + e^{-} \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$\operatorname{Cu}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Cu}(s)$	+0.34
$\operatorname{BiO}^{+}(\operatorname{aq}) + 2\operatorname{H}^{+}(\operatorname{aq}) + 3\operatorname{e}^{-} \rightarrow \operatorname{Bi}(\operatorname{s}) + \operatorname{H}_{2}\operatorname{O}$	+0.32
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.15
$2\mathrm{H}^{+}(\mathrm{aq}) + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{g})$	0 (by definition)
$\operatorname{Fe}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Fe}(s)$	-0.04
$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$	-0.126
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Sn}(s)$	-0.136
$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$	-0.24
$\operatorname{Co}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Co}(s)$	-0.28
$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s)$	-0.40
$\operatorname{Fe}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Fe}(s)$	-0.44
$\operatorname{Cr}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Cr}(s)$	-0.74
$\operatorname{Zn}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Zn}(s)$	-0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$\operatorname{Cr}^{2+}(\operatorname{aq}) + 2e^{-} \rightarrow \operatorname{Cr}(s)$	-0.89
$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$	-1.68
$\operatorname{Sc}^{3+}(\operatorname{aq}) + 3e^{-} \rightarrow \operatorname{Sc}(s)$	-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
$\text{Li}^+(\text{aq}) + e^- \rightarrow \text{Li}(s)$	-3.04

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Useful formulas

Quantum Chemistry	Electrochemistry
$E = hv = hc/\lambda$	$\Delta G^{\circ} = -nFE^{\circ}$
$\lambda = h/mv$	Moles of $e^- = It/F$
$E = -Z^2 E_{\rm R}(1/n^2)$	$E = E^{\circ} - (RT/nF) \times \ln Q$
$\Delta x \cdot \Delta(mv) \ge h/4\pi$	$E^{\circ} = (RT/nF) \times \ln K$
$q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$	$E = E^{\circ} - \frac{0.0592}{1000} \log Q$ (at 25 °C)
$T\lambda = 2.898 \times 10^6 \text{ K nm}$	n n n n
Acids and Bases	Gas Laws
$pH = -log[H^+]$	PV = nRT
$pK_{\rm w} = pH + pOH = 14.00$	$(P+n^2a/V^2)(V-nb) = nRT$
$pK_w = pK_a + pK_b = 14.00$	$E_{\rm k} = \frac{1}{2}mv^2$
$pH = pK_a + \log\{[A^-] / [HA]\}$	
Radioactivity	Kinetics
$t_{\frac{1}{2}} = \ln 2/\lambda$	$t_{\frac{1}{2}} = \ln 2/k$
$A = \lambda N$	$k = A e^{-Ea/RT}$
$\ln(N_0/N_t) = \lambda t$	$\ln[\mathbf{A}] = \ln[\mathbf{A}]_0 - kt$
14 C age = 8033 ln(A_0/A_t) years	$\ln \frac{k_{2}}{k_{1}} = \frac{E_{a}}{R} \left(\frac{1}{T_{1}} - \frac{1}{T_{2}} \right)$
Colligative Properties & Solutions	Thermodynamics & Equilibrium
$\Pi = cRT$	$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$
$P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$	$\Delta G = \Delta G^{\circ} + RT \ln Q$
c = kp	$\Delta G^{\circ} = -RT \ln K$
$\Delta T_{\rm f} = K_{\rm f} m$	$\Delta_{\rm univ}S^{\rm o} = R \ln K$
$\Delta T_{\rm b} = K_{\rm b} m$	$K_{\rm p} = K_{\rm c} \left(\frac{RT}{100}\right)^{\Delta n}$
Miscellaneous	Mathematics
$A = -\log \frac{I}{I_0}$	If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
$A = \varepsilon c l$	$\ln x = 2.303 \log x$
$F = -4 - \frac{e^2}{N}$	Area of circle = πr^2
$L = \frac{1}{4\pi\varepsilon_0 r} r^{N_A}$	Surface area of sphere = $4\pi r^2$

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PERIODIC TABLE OF THE ELEMENTS

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