

2012 AUSTRALIAN SCIENCE OLYMPIAD EXAMINATION

CHEMISTRY

SOLUTIONS

Question	Solution	Question	Solution
1	E	9	A
2	A	10	B
3	A	11	A
4	C	12	B
5	D	13	C
6	D	14*	A
7	E	15	D
8	C		

*Please note that Cr^{2+} should be Cr^{3+} in the given equation.

The Chemistry Guru

SECTION B: 3 SHORT ANSWER QUESTIONS
ANSWER IN THE SPACES PROVIDED

Question 16

The final step in the industrial production of copper is electrolytic refinement. This process involves submerging two electrodes in a solution of copper(II) sulfate. One electrode is composed of unrefined (crude) copper and the second electrode is composed of refined copper. The electrodes are connected and a current is induced such that copper atoms of the crude electrode lose electrons to form Cu^{2+} ions that pass into solution. Simultaneously at the other electrode, copper ions in solution gain electrons and form solid (refined) copper.

(a) (i) Write the half-equation for the process occurring at the crude copper electrode.



(ii) Is the process occurring at the crude copper electrode oxidation or reduction?

oxidation

The purpose of electrolytic refinement is to remove impurities present in the crude copper electrode. These impurities include Fe, Pb, Ni, Co, Ag, Au, Pt, Pd, Ru and Ir.

During electrolytic refinement some of these metals also form ions and pass into solution. Such metals include Fe, Ni and Co. Other metals do not react at all and form a solid mixture below the anode called the 'anode mud'. Such metals include Ag, Au, Pt, Pd, Ru and Ir.

(b) Based on the information above, which **one** of the following would lead to a chemical reaction? Place your answer of A, B, C or D in the box.

- A. Ag(s) is added to a copper(II) sulfate solution.
- B. Ir(s) is added to a dilute sulfuric acid solution.
- C. Co(s) is added to a ruthenium(III) chloride solution.
- D. None of the above

C

Lead forms Pb^{2+} ions during electrolysis. Most lead impurity, however, is found in the anode mud and not in solution.

(c) Why is lead found in the anode mud?

Pb^{2+} forms insoluble $\text{PbSO}_4(\text{s})$ which then forms part of the anode mud.

Anode mud provides a raw material from which highly valuable metals may be extracted. After the removal of lead from the anode mud, the first step in the purification of such metals is treatment of the anode mud with *aqua regia* – a mixture of concentrated nitric and hydrochloric acids. In this first step Au(s) , Pt(s) and Pd(s) pass into solution as HAuCl_4 , H_2PtCl_6 , and H_2PdCl_4 respectively, whereas Ru and Ir remain as solids and silver precipitates as AgCl(s) .

(d) What is the oxidation state of the indicated metal in each of the following compounds?

(i) Au in HAuCl_4	$+\text{III}$
(ii) Pt in $(\text{NH}_4)_2\text{PtCl}_6$	$+\text{IV}$
(iii) Pd in H_2PdCl_4	$+\text{II}$
(iv) Ru in Sr_2RuO_4	$+\text{IV}$

Next, iron(II) sulfate solution is added to the solution containing HAuCl_4 , H_2PtCl_6 , and H_2PdCl_4 in order to precipitate gold metal, Au. In this process the AuCl_4^- ion is converted into $\text{Au}_{(s)}$ and Cl^- ions. Fe^{3+} ions are also formed.

(e) Write two balanced half-equations and the overall redox equation for the reaction that occurs when iron(II) sulfate solution is added.

Oxidation Half-Equation:



Reduction Half-Equation:



Redox Equation:



Anode mud is at most 2.50% gold by mass.

(f) (i) Calculate the maximum mass of gold that can be attained from 75.0 kg of anode mud.

$$m(\text{mud}) = 75.0 \text{ kg}$$

$$\% \text{ Au} = 2.50 \%$$

$$\therefore m(\text{Au}) = 1.875 = 1.88 \text{ kg}$$

(ii) Calculate the minimum volume of a saturated (1.70 mol L^{-1}) FeSO_4 solution that is required to ensure complete precipitation of gold from 75.0 kg of anode mud.

← from f(i) in grams

$$n(\text{Au}) = \frac{1875 \text{ g}}{197 \text{ g mol}^{-1}} = 9.518 \text{ mol}$$

$$n(\text{Fe}^{2+}) = 9.518 \times 3 = 28.55 \text{ mol}$$

$$V(\text{FeSO}_4) = \frac{28.55 \text{ mol}}{1.70 \text{ mol L}^{-1}} = 16.80$$

16.8 L

During electrolytic refinement the concentrations of the soluble impurities – Fe, Ni and Co – build up in the copper(II) sulfate solution and must be removed before they reach levels that interfere with the refinement process.

In order to determine the amount of these impurities, the copper(II) sulfate solution obtained after the refinement of 100.0 kg of crude copper was analysed. The concentration of the copper(II) sulfate solution remained constant at 1.000 mol L^{-1} throughout electrolysis.

A 25.00 mL sample of the solution was diluted to 250.0 mL. 20.00 mL aliquots were titrated with a $0.1000 \text{ mol L}^{-1}$ solution of EDTA with an average titre at endpoint of 21.37 mL. EDTA binds strongly to Cu^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} in the following way:



(g) Calculate the total concentration of M^{2+} ions in solution following refinement.

$$n(\text{EDTA}) = 0.02137 \text{ L} \times 0.1000 \text{ M}$$

$$= 2.137 \times 10^{-3} \text{ mol}$$

$$n(\text{M}^{2+}) = 2.137 \times 10^{-3} \text{ mol}$$

$$c(\text{M}^{2+})_{\text{dilute}} = \frac{2.137 \times 10^{-3} \text{ mol}}{20.00 \times 10^{-3} \text{ L}}$$

$$= 0.10685 \text{ M}$$

$$c(\text{M}^{2+})_{\text{original}} = 1.069 \text{ M}$$

Triethanolamine was added to 50.00 mL samples of the **undiluted** solution. Triethanolamine binds to Fe^{2+} , Co^{2+} and Cu^{2+} **but not to Ni^{2+}** . Triethanolamine-bound metal ions are unable to react with EDTA. Titration of these aliquots with the $0.1000 \text{ mol L}^{-1}$ EDTA solution gave an average titre of 8.79 mL.

(h) Calculate the concentration of Ni^{2+} ions in solution following refinement.

$$\begin{aligned}
 n(\text{EDTA}) &= 0.00879 \text{ L} \times 0.1000 \text{ M} \\
 &= 8.79 \times 10^{-4} \text{ mol} \\
 n(\text{Ni}^{2+}) &= 8.79 \times 10^{-4} \text{ mol} \\
 [\text{Ni}^{2+}] &= \frac{8.79 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = \boxed{0.01758 \text{ M}}
 \end{aligned}$$

Excess ammonium sulfide solution – $(\text{NH}_4)_2\text{S}$ – is added to a 100.0 mL sample of the **undiluted** solution. Cu^{2+} , Fe^{2+} , Co^{2+} and Ni^{2+} ions all form insoluble sulfide salts of the formula $\text{MS}_{(s)}$. Filtration, drying and weighing of the resulting precipitate yielded 10.180 g.

(i) Given that Cu, Fe, Co and Ni are only present in the M^{2+} form, calculate the concentration of Fe^{2+} and Co^{2+} . [Remember the copper(II) sulfate concentration is constant at 1.000 mol L^{-1} .]

$$\begin{aligned}
 [\text{Ni}^{2+}] &= 0.01758 \text{ M} ; [\text{Cu}^{2+}] = 1.00 \text{ M} \\
 \text{Total } m(\text{MS}) &= \sum m(\text{MS}) \\
 10.180 &= 0.1000 \times [\text{Ni}^{2+}] (58.69 + 32.06) + \\
 & 0.1000 \times [\text{Cu}^{2+}] (63.55 + 32.06) + \\
 & 0.1000 \times [\text{Fe}^{2+}] (55.85 + 32.06) + \\
 & 0.1000 \times [\text{Co}^{2+}] (58.93 + 32.06) \\
 10.180 &= 0.1595 + 9.561 + 8.791[\text{Fe}^{2+}] + 9.099[\text{Co}^{2+}] \\
 0.4595 &= 8.791[\text{Fe}^{2+}] + 9.099[\text{Co}^{2+}] \quad \text{--- (1)} \\
 [\text{M}^{2+}]_{\text{total}} &= \sum [\text{M}^{2+}] \\
 1.069 &= [\text{Cu}^{2+}] + [\text{Ni}^{2+}] + [\text{Fe}^{2+}] + [\text{Co}^{2+}] \\
 1.069 &= 1.000 + 0.01758 + [\text{Fe}^{2+}] + [\text{Co}^{2+}]
 \end{aligned}$$

More working space can be found on the next page.

$$0.05742 = [\text{Fe}^{2+}] + [\text{Co}^{2+}] \quad \text{--- [2]}$$

combining [1] and [2]

$$\rightarrow 0.4595 = 8.791(0.05142 - [\text{Co}^{2+}]) + 9.099[\text{Co}^{2+}]$$

$$7.47 \times 10^{-3} = 0.308 [\text{Co}^{2+}]$$

[Fe ²⁺]:	[Co ²⁺]:
0.0272 M	0.0242 M

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Q17

a) i) 30.0105

a) ii) 57.0577

a) iii) 102.0678

b) $C_5H_9^{35}Cl$ = 104.0391, intensity 75.8 (or 100) and $C_5H_9^{37}Cl$ = 106.0361, intensity 24.2 (or 33.2)

c) i) A) 170 or 172

c) i) B) 126 or 128

c) i) C) 176 or 178

c) i) D) 220 or 222

C) ii) Compounds A and B have related functionality. Compounds C and D have related functionality.

A and B both have the highest intensity peak at 91 with similar smaller peaks at 89-92. They also have similar peaks around 60-65.

C and D both have the highest intensity peak at 141 with similar smaller peaks at 139-142. They also have a similar peak at 115.

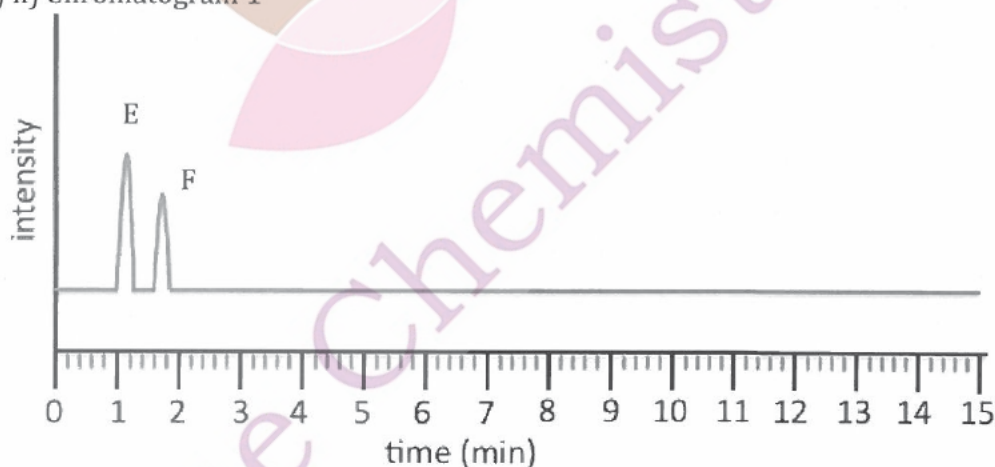
d) i) In the range of 4.20-4.45 and 9.00-9.2

d) ii) In the range of 1.80-1.95 and 7.00-7.20

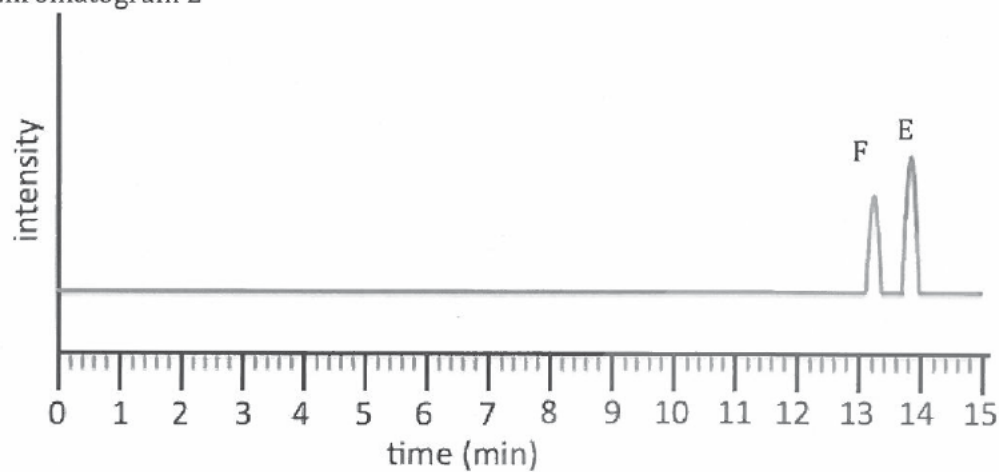
e) B, C, D, A

f) i) Normal is chromatogram 2, Reverse is chromatogram 1

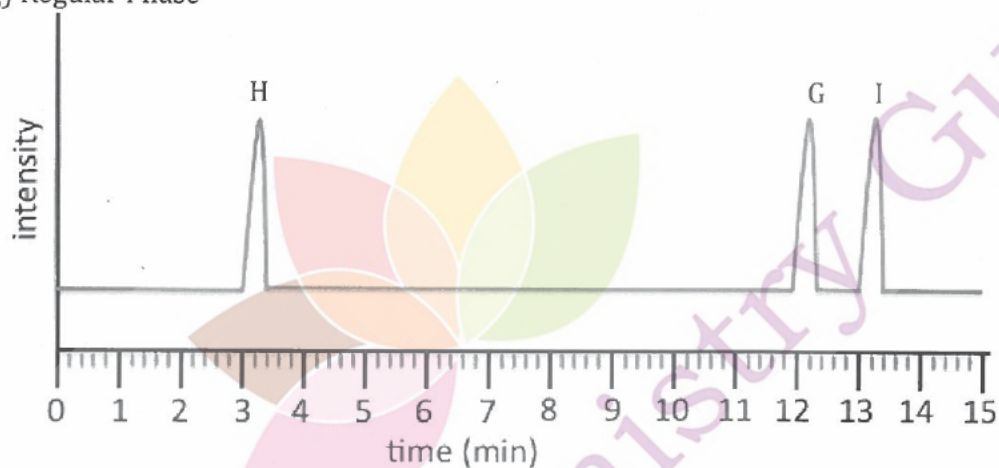
f) ii) Chromatogram 1



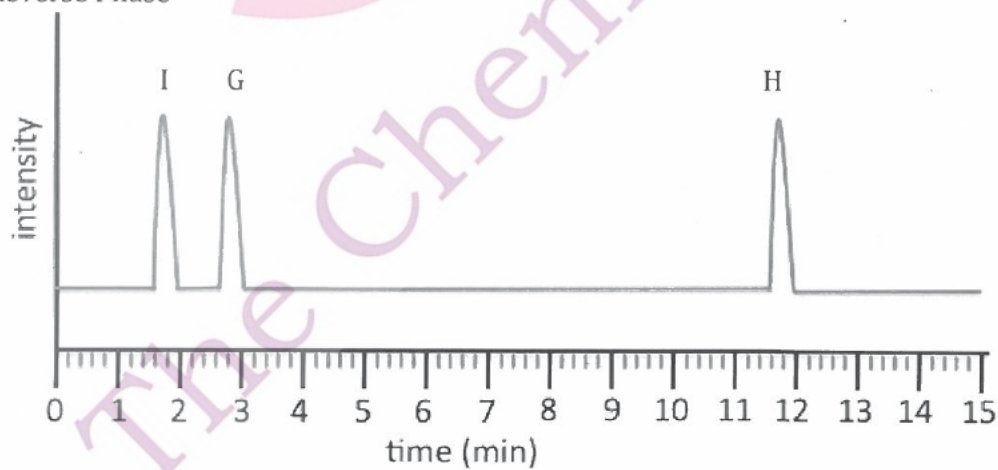
Chromatogram 2



g) Regular Phase

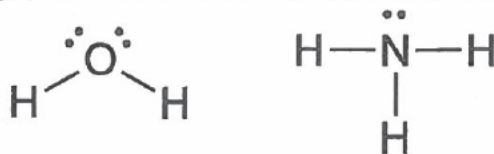


Reverse Phase



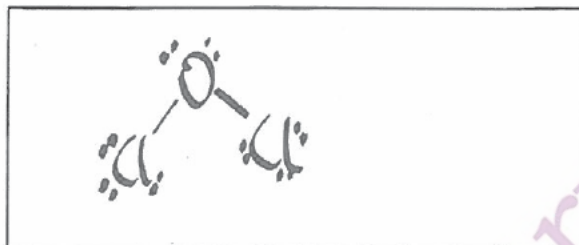
Question 18

Lewis structures provide a simple model of bonding and lone pairs of electrons and, to some extent, molecular shape. For example, Lewis structures for water and ammonia are shown below.

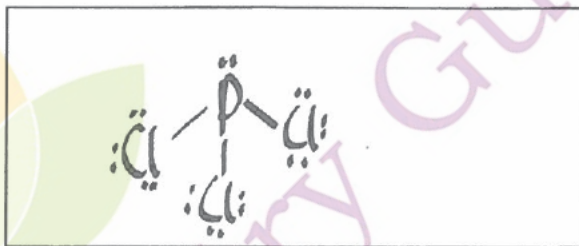


(a) Draw a Lewis structure for each of the following species:

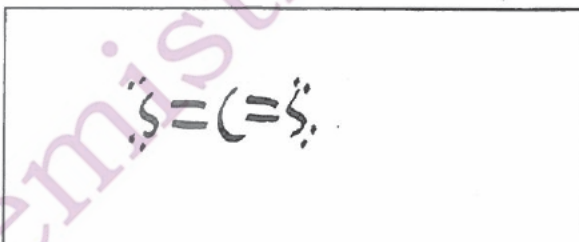
(i) Cl_2O



(ii) PCl_3



(iii) CS_2

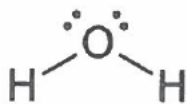


The molecular geometry of simple molecules can be predicted by identifying the number of regions of electron density around the central atom. The AXE method involves counting the number of bonding regions, denoted 'X', (single and multiple bonds are treated identically) and the number of non-bonding regions, denoted 'E', around a central atom, 'A'.

Bonding (X)	Non-bonding (E)	AXE designation	Molecular geometry
2	0	AX_2	linear
2	1	AX_2E	bent
2	2	AX_2E_2	bent
3	0	AX_3	trigonal planar
3	1	AX_3E	trigonal pyramidal
3	2	AX_3E_2	T-shaped

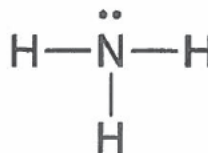
(b) What molecular geometry does each of the following molecules have?

(i)



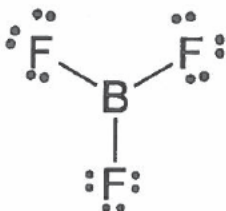
bent

(ii)



trigonal pyramidal

(iii)



trigonal planar

In any covalent bond between atoms of different electronegativity (a measure of the nucleus' attraction for electrons) there will be an asymmetric distribution of charge. Such bonds are said to have a bond dipole moment.

Similarly, if there is an asymmetric distribution of charge over a molecule, it is said to have a net dipole moment. The presence of individual bond dipole moments and the symmetry of the molecule determine whether a molecule has a net dipole moment. A molecule will **not** possess a net dipole moment if the symmetry of the molecule results in the individual bond dipole moments cancelling each other out.

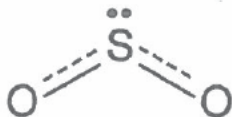
Bonds or molecules with a net dipole moment are said to be polar.

(c) Circle any polar bonds in the molecules shown below.

All bonds!

(d) Tick the appropriate box to indicate whether or not the molecule is polar.

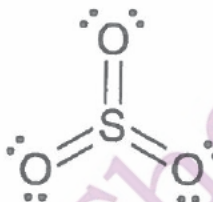
(i)



polar

non-polar

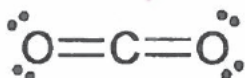
(ii)



polar

non-polar

(iii)



polar

non-polar

Vibrational modes are characteristic displacements of one or more atoms in a molecule. A linear molecule with N atoms will have $3N-5$ vibrational modes and a non-linear molecule with N atoms will have $3N-6$ vibrational modes.

(e) How many vibrational modes will POCl_3 have?

9

For a vibrational mode to absorb infrared (IR) radiation, the displacement of atoms involved must give rise to a change in the net dipole moment of the molecule. If this occurs, the vibrational mode is said to be "IR active" and will give rise to an absorption in the IR spectrum.

(f) The table below shows the 3 vibrational modes of SO_2 (arrows indicate displacement of the atoms involved). Indicate which of these will be IR active by filling out the right-hand column.

Vibration type	Equilibrium structure	Displaced structure	IR active? (Y/N)
symmetric stretch			Y
asymmetric stretch			Y
deformation			Y

(g) How many vibrational modes will water have, and how many of these will be IR-active?

Number of vibrational modes:

3

IR-active modes:

3

IR spectroscopy provides evidence for molecular shape. In the following example, we consider what the IR spectrum of SO_2 would look like if it were linear rather than bent.

(h) The table below shows the 4 vibrational modes of "linear SO_2 " (again, arrows indicate displacement of the atoms involved; + and - symbols indicate displacement out of and into the plane of the page respectively). Complete the table by adding the following features:

(i) Vibration 1: Displaced structure and IR activity.

(ii) Vibration 2: Displaced structure and IR activity.

(iii) Vibration 3: Direction arrows on equilibrium structure to show movement of atoms.

Vibration	Equilibrium structure	Displaced structure	IR active? (Y/N)
1			N
2			Y
3			Y
4			Y

We would expect "linear SO_2 " to have four vibrational modes, as shown above, however in practice two of these vibrational modes are of equal energy. Such vibrational modes are called *degenerate* and give rise to a single absorption in the IR spectrum.

(i) Which of the four "linear SO_2 " vibrational modes in the table above are degenerate (of equal energy)?

3 & 4

(j) How many absorptions in the IR spectrum would you expect for "linear SO_2 "?

2

(k) The table below shows 4 vibrational modes of SO_3 (again, arrows indicate displacement of the atoms involved; + and - symbols indicate displacement out of and into the plane of the page respectively). Indicate which of these will be IR active by filling out the right-hand column.

Vibration type	Equilibrium structure	IR active? (Y/N)
symmetric stretch		N
asymmetric stretch		Y
asymmetric deformation 1 (doubly degenerate)		Y
asymmetric deformation 2 (doubly degenerate)		Y

(l) Now consider SOCl_2 . How many absorptions in the IR spectrum would you expect for SOCl_2 ?

5 (accepted 4-6)

(m) CF_3 has the following T-shaped structure. It has six vibrational modes, none of which are degenerate. How many of these will be IR active?

6

