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| ASI School ID: | | | | |
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2013 AUSTRALIAN SCIENCE OLYMPIAD EXAM CHEMISTRY – SECTIONS A & B

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS

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| Student Name: |
| Home Address: |
| Post Code: |
| Telephone: (.....) Mobile: |
| E-Mail: Date of Birth:/...../..... |
| <input type="checkbox"/> Male <input type="checkbox"/> Female Year 10 <input type="checkbox"/> Year 11 <input type="checkbox"/> Other: |

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| Name of School: State: |
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To be eligible for selection for the Australian Science Olympiad Summer School, students must be able to hold an Australian passport by the time of team selection (March 2014).

The Australian Olympiad teams in Biology, Chemistry and Physics will be selected from students participating in the Australian Science Olympiad Science Summer School.

Please note - students in Yr12 in 2013 are not eligible to attend the 2014 Australian Science Olympiad Science Summer School

Information is collected solely for the purpose of Science Summer School offers. To view the privacy policy:
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| Examiners' Use Only: | | | | | | | | | |
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2013 Australian Science Olympiad Exam

Time Allowed:

Reading Time: 10 minutes

Examination Time: 120 minutes

INSTRUCTIONS

- Attempt ALL questions in ALL sections of this paper.
- Permitted materials: Non-programmable non-graphical calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. **Use a pencil.**
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will not be deducted for incorrect answers.
- Rough working must be done only on pages 26 to 27 of this booklet.
- Relevant data that may be required for a question will be found on page 3.
- Do not staple the multiple choice answer sheet to this booklet.

MARKS

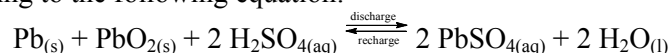
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|-----------|------------------------------|-----------|
| SECTION A | 15 multiple choice questions | 30 marks |
| SECTION B | 3 short answer questions | 90 marks |
| | Total marks for the paper | 120 marks |

SECTION A: MULTIPLE CHOICE
USE THE ANSWER SHEET PROVIDED

1. If a chemist requires 16.0 mole of liquid ethanol (C_2H_5OH) for a chemical reaction, what volume should be used? The density of C_2H_5OH is 0.789 g mL^{-1} .
- 0.0320 L
 - 0.581 L
 - 0.690 L
 - 0.934 L
 - 1.88 L
2. Which of the following pairs of atoms would form a polar covalent bond?
- Na and Br
 - H and Br
 - N and N
 - Br and Br
 - Ca and Br
3. In which species does the underlined element have an oxidation number of +II?
- S O_2Cl_2
 - Fe $(CN)_6^{4-}$
 - H NO_2
 - Ni $(CO)_4$
 - Fe $(CN)_6^{3-}$
4. In which species is the oxidation number for hydrogen different from those in the other four?
- H_2O
 - H_3AsO_4
 - H_3PO_4
 - NH_3
 - H_2
5. Which one of the following transformations from species **A** to species **B** is an oxidation?
- | Species A | Species B |
|--------------|--------------|
| a. VO_3^- | VO_2^+ |
| b. CrO_2 | CrO_4^{2-} |
| c. SO_3 | SO_4^{2-} |
| d. NO_3^- | NO_2^- |
| e. MnO_4^- | Mn^{2+} |

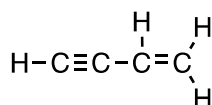
6. Which one of the following species is both a hydrogen-bond donor and a hydrogen-bond acceptor?
- CH_3OCH_3
 - HI
 - CH_4
 - CH_3OH
 - Cl_4
7. Which one of the following bonding features is common to both graphite and diamond?
- a carbon-carbon bond length equal to that in ethane
 - covalent bonds between carbon atoms
 - delocalised electrons
 - each carbon atom is bonded to four other carbon atoms
 - van der Waals forces
8. Which one of the following elements has the lowest second ionisation energy?
- Na
 - Be
 - K
 - He
 - Mg
9. What will happen to the pH of a buffer solution when a small amount of a strong base is added?
- it will increase slightly
 - it will decrease slightly
 - it will remain exactly the same
 - it will become 7.0
 - it will initially increase slightly and then become 7.0
10. In the titration of a 0.1 mol L^{-1} monoprotic acid with 0.2 mol L^{-1} sodium hydroxide (NaOH), using methyl red as indicator, which one of the following statements correctly describes the system at the equivalence point?
- the concentrations of each of the hydroxide ion and hydronium ion (H_3O^+) are equal
 - the number of moles of the hydroxide ion added and the number of moles of the hydronium ion initially present are equal
 - the volume of sodium hydroxide solution added and the volume of acid solution initially present are equal
 - the number of moles of hydroxide ion added and the number of moles of monoprotic acid initially present are equal
 - the indicator is present in two different forms

11. The most common batteries used in cars are lead-acid batteries that can be discharged and recharged according to the following equation:



When discharging, which species is the reducing agent?

- $\text{Pb}_{(s)}$
 - $\text{PbO}_{2(s)}$
 - $\text{H}^+_{(aq)}$
 - $\text{SO}_4^{2-}_{(aq)}$
 - $\text{PbSO}_{4(aq)}$
12. How many π -electrons are in a molecule of but-3-yn-1-ene? The structure of but-1-en-3-yne is shown below:



- 3
 - 6
 - 8
 - 10
 - 20
13. Which of the following changes takes place when 500 mL of water is added to 500 mL of 1 mol L⁻¹ acetic acid?
- pH increases, percentage ionisation increases
 - pH increases, percentage ionisation does not change
 - pH decreases, percentage ionisation does not change
 - pH decreases, percentage ionisation decreases
 - pH does not change, percentage ionisation increases
14. For a spontaneous reaction to occur at constant temperature and pressure, the Gibbs free energy (ΔG) must be negative. The Gibbs free energy combines two thermodynamic parameters into the Gibbs equation: $\Delta G = \Delta H - T\Delta S$ where, ΔH is the change in enthalpy and ΔS is the change in entropy. What conditions of ΔH and ΔS for a chemical reaction will **always** give a spontaneous reaction?
- ΔH positive, ΔS positive
 - ΔH positive, ΔS negative
 - ΔH negative, ΔS positive
 - ΔH negative, ΔS negative
 - none of the above
15. The chloride of element **J** does not react with water nor will dissolve in it. Which one of the following elements could **J** be?
- aluminium
 - carbon
 - hydrogen
 - magnesium
 - sodium

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

Question 16

Tracey, an Australian Chemistry Olympiad tutor wishes to determine the ascorbic acid ($C_6H_8O_6$) content of a Vitamin C tablet. Tracey comes across a method that involves a non-aqueous titration - that is, a titration that uses a liquid other than water as the solvent. The method describes the determination of ascorbic acid with copper(II) perchlorate ($Cu(ClO_4)_2$) using acetonitrile (CH_3CN) as the solvent.

Having searched every nook and cranny of the labyrinthine store rooms of the Monash University laboratories Tracey concludes that there is no $Cu(ClO_4)_2$ to be found. Not to be deterred, however, Tracey decides to synthesise her own sample of $Cu(ClO_4)_2$. Tracey finds a bottle labelled copper(II) carbonate. She forms a suspension of 2.50 g of its content in water and subsequently adds an excess of aqueous perchloric acid solution ($HClO_4$). The resulting mixture is heated gently until bubble formation ceases and subsequently cooled and filtered to afford crystalline copper(II) perchlorate.

a) Assuming that the contents of the bottle is pure copper(II) carbonate, calculate the theoretical yield in grams of copper(II) perchlorate.

b) Give the oxidation state of each of the following:

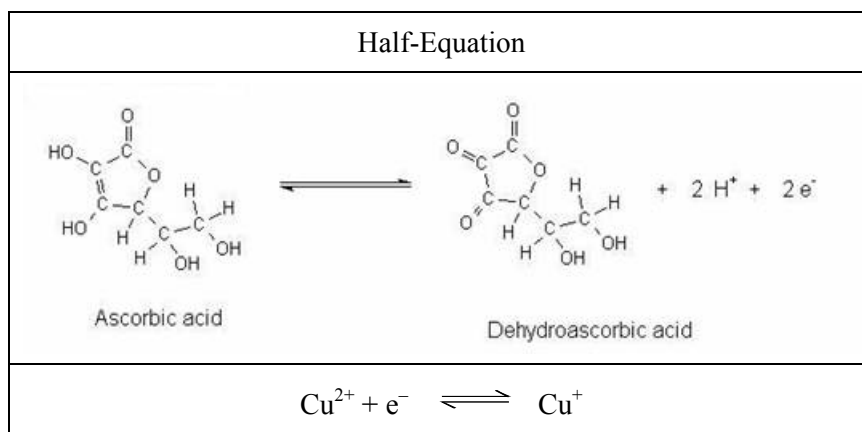
i) oxygen in perchloric acid ($HClO_4$)

ii) chlorine in perchloric acid (HClO_4)

c) Identify the gas that is eliminated on heating.

The non-aqueous titration involves the titration of an ascorbic acid in acetonitrile solution with a copper(II) perchlorate solution. At equivalence the titration solution contains copper(I) ions and dehydroascorbic acid. [There is **no** copper(II) nor ascorbic acid present.]

The half-equations for the reaction are as follows:



d) Circle the **oxidation** half-equation in the table above.

e) State how the half-equation you labelled in d) above can be identified as the oxidation half-equation.

f) Write the overall redox equation for the reaction occurring in the titration. [You may use **Asc** and **DAsc** as shorthand for **ascorbic acid** and **dehydroascorbic acid**, respectively.]

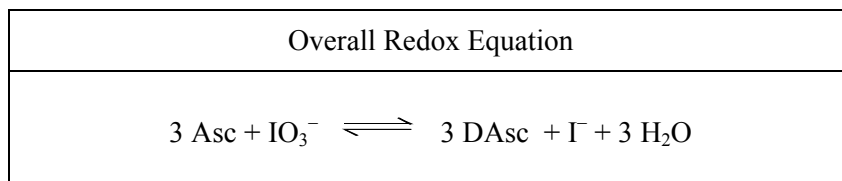
Tracey makes up a copper(II) perchlorate solution by dissolving 3.131 g of the synthesised copper(II) perchlorate in acetonitrile in a 500.0 mL volumetric flask. Tracey also dissolves one Vitamin C tablet in acetonitrile in a 250.0 mL volumetric flask. 20.00 mL aliquots of this ascorbic acid solution are titrated with the copper(II) perchlorate solution until equivalence. The average titre value is 25.95 mL.

g) Calculate the mass of ascorbic acid in the Vitamin C tablet using the results of the non-aqueous titration.

Tracey notes that the mass of ascorbic acid calculated from the above procedure is significantly different to that reported by the manufacturer. Tracey therefore decides to use the more familiar technique of iodometry to check her result.

One Vitamin C tablet is dissolved in water in a 100.0 mL volumetric flask. Tracey takes 10.00 mL aliquot of this solution and adds to each an excess of potassium iodide (KI) and 20.00 mL of a 0.02510 mol L⁻¹ solution of potassium iodate (KIO₃). The iodate reacts with the ascorbic acid and then the excess iodate reacts with iodide to form iodine. The liberated iodine is titrated with a standardised solution of 0.1930 mol L⁻¹ sodium thiosulfate (Na₂S₂O₃). In this second reaction the thiosulfate ion (S₂O₃²⁻) is oxidised to the tetrathionate ion (S₄O₆²⁻).

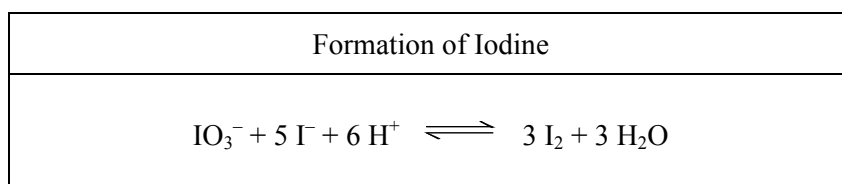
The overall redox equation for the reaction between the iodate (IO₃⁻) ions and ascorbic acid is as follows:



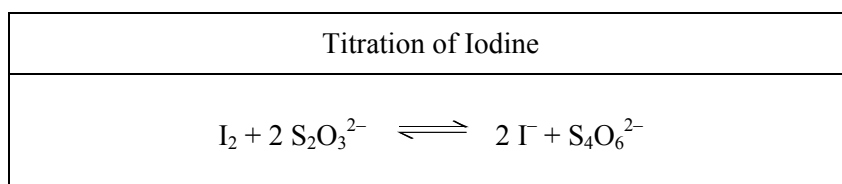
h) Write the oxidation half-equation and the reduction half-equation for the reaction between iodate ions and ascorbic acid.

| |
|--------------------------|
| Oxidation Half-Equation: |
| |
| Reduction Half-Equation: |
| |

Iodine is formed by the reaction between excess iodate ions and iodide ions. The equation for the reaction is as follows:



The equation for the reaction for the titration of iodine with sodium thiosulfate solution is as follows:



The average volume of sodium thiosulfate solution required to reach endpoint was 12.77 mL.

i) Calculate the mass of ascorbic acid in the Vitamin C tablet using the results of the iodometric titration.

Perplexed by her differing results Tracey does some research using the internet and finds out that the copper(II) perchlorate commonly exists as a hydrate. That is, the formula of Tracey's product is $\text{Cu}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, where x is an integer.

j) Determine the value of x .

Question 17

An astute young chemist was suddenly struck with a strange compulsion to find out the density of caesium metal. Knowing that caesium reacts with water, she knew her experiments would have to be water-free.

She found a 500 mL beaker that weighed 234.10 g. She filled it to the brim with kerosene, which consists mainly of the hydrocarbon dodecane ($C_{12}H_{26}$). Kerosene has a density of 0.7493 g cm^{-3} . The beaker with kerosene was found to weigh 633.70 g.

Now, she knew that beakers were not meant to be used for quantitative measurements of volumes. She realised, however, that she could calculate the volume of the beaker using the data she had just acquired.

a) What was the volume of the beaker?

Said chemist then carefully placed a sample of solid caesium in the beaker and some of the kerosene overflowed out of the beaker. She then weighed the beaker and it turned out to weigh 717.49 g. When she removed the caesium and reweighed the beaker with less kerosene in it, she found that it weighed 575.57 g.

b) What did the sample of solid caesium weigh?

c) What volume of kerosene was lost?

d) What is the density of caesium?

When removing the caesium sample, however, some kerosene spilled out because the beaker was so full.

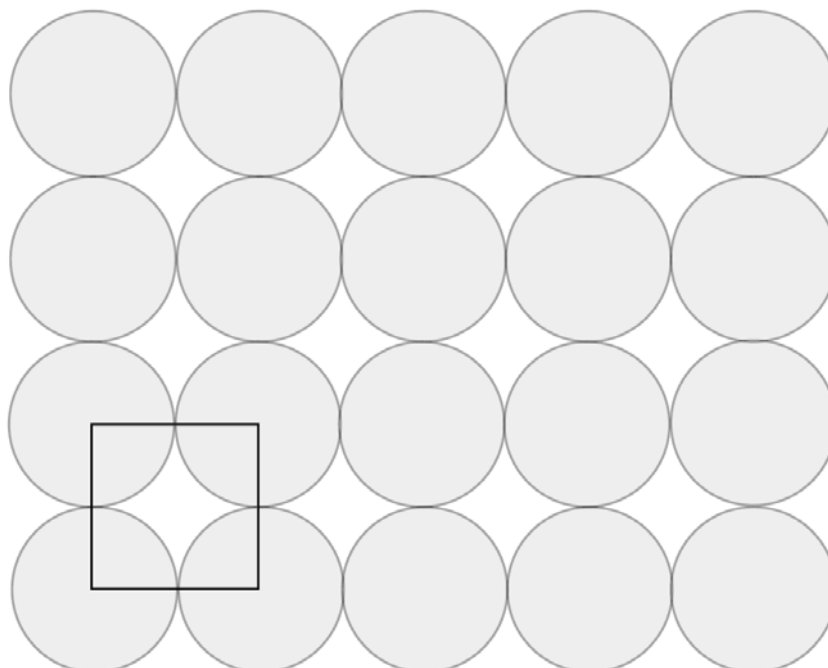
e) How would this affect her calculated density of caesium?

She then realised that she could calculate the size of the caesium atoms if she knew how the caesium atoms were packed together. She looked it up, and came across the term “unit cell”. Apparently, in 1850, Auguste Bravais gave the following definition of a unit cell as a division of space which meets the following criteria:

- The unit cell is the smallest repeating unit of the pattern
- Opposite edges/faces of the cell are parallel
- The edges of the unit cell connect equivalent points.

She noticed that in 2D, she could draw unit cells on some rather antiquated wallpaper patterns she found. She found the following unit cell for the following pattern (see Figure 1 below) of an infinite grid of circles arranged in a square.

Figure 1:



She also noticed that inside the cell, there were four quarter-circles. That made one complete circle that was contained in the cell.

Our brilliant young chemist realised she could draw a large number of different unit cells for this pattern, but only 2 were highly symmetric and intuitive.

f) On Figure 1 above, draw a different symmetric unit cell for this pattern.

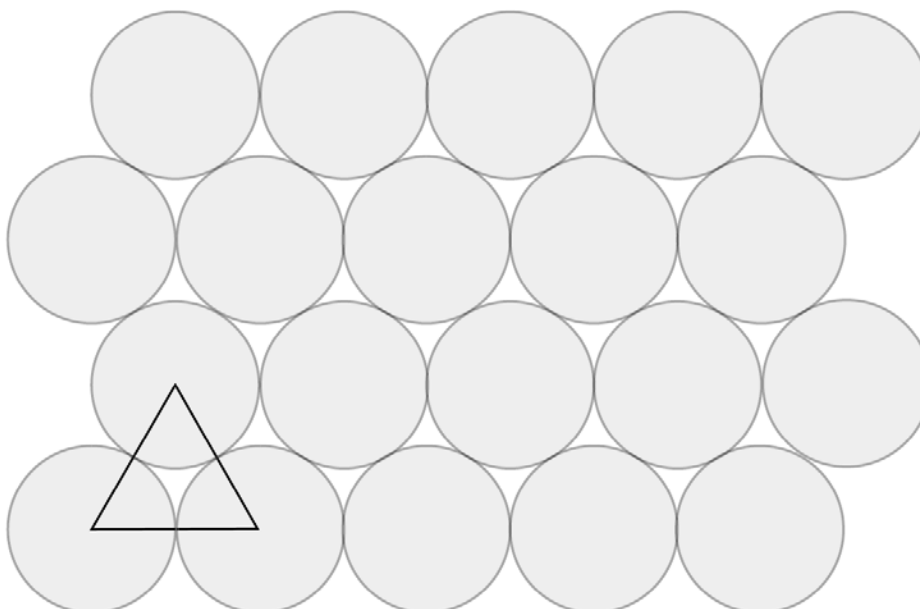
g) What percentage of the square cell is being occupied by circles?

[Area of a circle = πr^2 where r is the radius of the circle.]



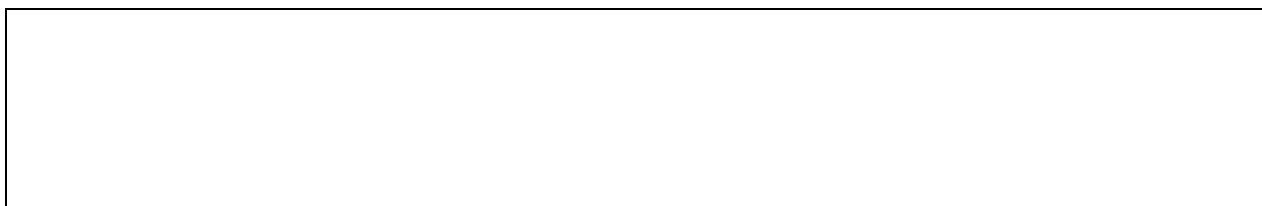
She then happened upon another equally horrendous sample of wallpaper, whilst visiting her aunt, and drew the following unit cell on it (see Figure 2).

Figure 2:



She then realised that it wasn't a proper unit cell.

h) Why is it not a proper unit cell?

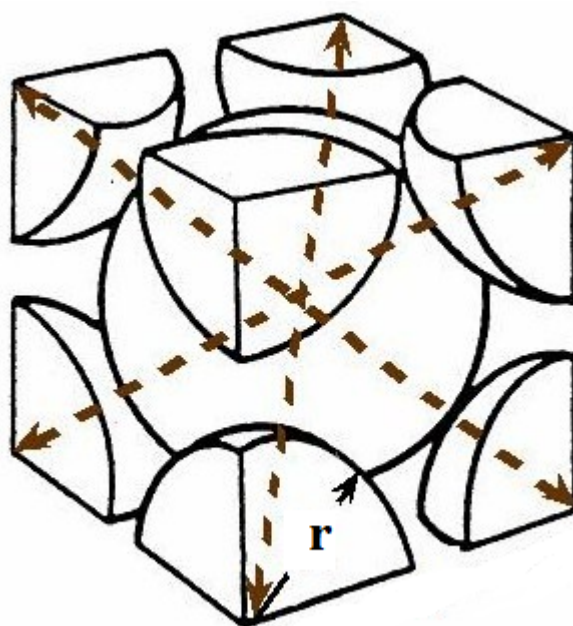


i) On Figure 2 above, draw a valid unit cell for this pattern.

j) What percentage of your unit cell is occupied by circles?

Now, our protagonist wanted to start thinking in three-dimensions. After all, real crystals could be modelled as spheres being packed together. She found out that caesium atoms pack together in what chemists describe as “body centred cubic”, or “bcc” packing. In the BCC packing, every single atom is in direct contact with eight neighbouring atoms at the same time. After a quick search on the internet, she found this image of the BCC unit cell (see Figure 3):

Figure 3:



The unit cell is described by a cube. There are eight atoms arranged at the eight vertices of this cube. And in the centre of the “body” of the cube lay one whole atom. The central atom touches all eight other atoms simultaneously.

Each of the atoms on the corner were cut off because they lay partially outside of the cube, so only a fraction of these corner atoms are counted in the unit cell, just like the corner circles in her 2D wallpaper unit cells.

k) How many spherical atoms in total are actually inside the unit cell?

l) If the radius of each atom is 'r' (as shown on Figure 3), what is the length of each of the three diagonals shown in the diagram?



Our chemist remembered from her maths classes that Pythagoras' theorem in three-dimensions, says that the length of the diagonal of a cube is $L = \sqrt{a^2 + a^2 + a^2} = a\sqrt{3}$. She also remembered in her maths class that the volume of a sphere radius r was given by $V = \frac{4}{3}\pi r^3$.

m) What percentage of the cubic unit cell would be occupied by spheres?



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Now, our adventurous young chemist realised she had enough information to work out the radius of a caesium atom. She found a new block of caesium, and carefully measured its density to be 1.87 g cm^{-3} .
[If you are unable to get an answer for part m), use 70.00% in your subsequent calculations.]

n) How many atoms of caesium are in 1.00 cm^3 of caesium?

o) Knowing that caesium atoms pack in BCC cells, how many unit cells does 1.00 cm^3 of caesium contain?

p) i) What is the volume of each unit cell?

ii) Hence, find the radius of each caesium atom.



Emboldened by her success at finding the radius of the caesium atom, our young chemist decided to try and find the radius of the Cs^+ cation. She then started thinking about the salt caesium chloride, a common non-toxic chemical with a density of 3.99 g cm^{-3} . She found that the crystal structure was exactly the same as BCC, except that the central atom was a caesium cation, and the corner atoms were chloride anions.

q) How many chloride anions are there in each unit cell?



Our chemist, however, immediately ran into a problem. She didn't know the radius of the chloride anion, so she could never solve for the radius of the caesium cation.

Our enthusiastic young chemist then did some research and realised that a rather famous chemist, Linus Pauling, proposed that the ratio of the radii of two ions would be determined by the INVERSE ratio of their effective nuclear charge (Z_{eff}). For example, Pauling said that for the salt NaF:

$$\frac{\text{radius}(\text{Na}^+)}{\text{radius}(\text{F}^-)} = \frac{Z_{\text{eff}}(\text{F}^-)}{Z_{\text{eff}}(\text{Na}^+)}$$

r) If the effective nuclear charges of Cs^+ and Cl^- are 9.25 and 5.75 respectively, what would be the radius of both ions calculated by our aspiring young chemist?

Question 18

Ultraviolet-visible (UV-vis) spectroscopy measures the absorbance of compounds, typically in solution. The structures that give rise to colour are called chromophores. Most metal ions in solution bond to six water molecules to give a complex, which is a chromophore.

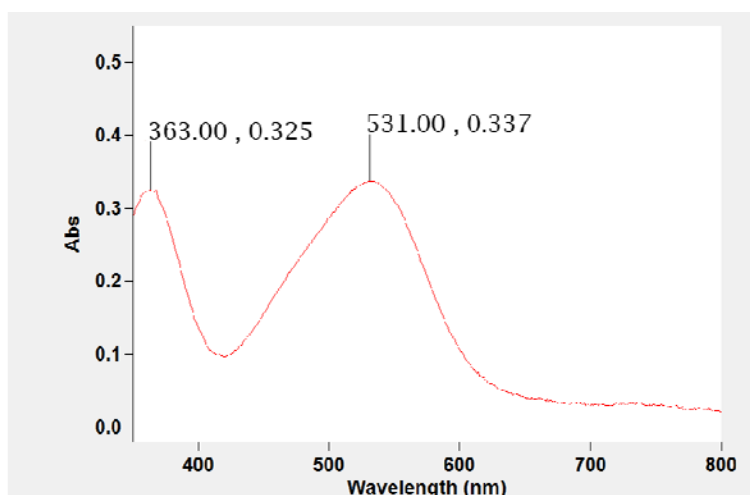
Metal ions, however, do not bond only to water molecules. Ammonia and chloride ions also commonly bond to metal ions, giving coloured complexes. One example of this is the pentaamminechlorocobalt(III) cation, which is a cobalt(III) ion with five ammonia molecules and one chloride ion bonded to it.

a) What is the overall charge on the pentaamminechlorocobalt(III) cation?

A common unit in spectroscopy is the wavenumber which has the dimensions of cm^{-1} . It is the inverse of the wavelength expressed in centimetres. It is commonly used as it is directly proportional to the energy of a transition, which will commonly be measured to occur at a certain wavelength.

The UV-vis spectrum (that is, a plot of absorbance versus wavelength) of a solution of the pentaamminechlorocobalt(III) ion is shown below in Figure 1.

Figure 1: UV-visible spectrum for the pentaamminechlorocobalt(III) ion.

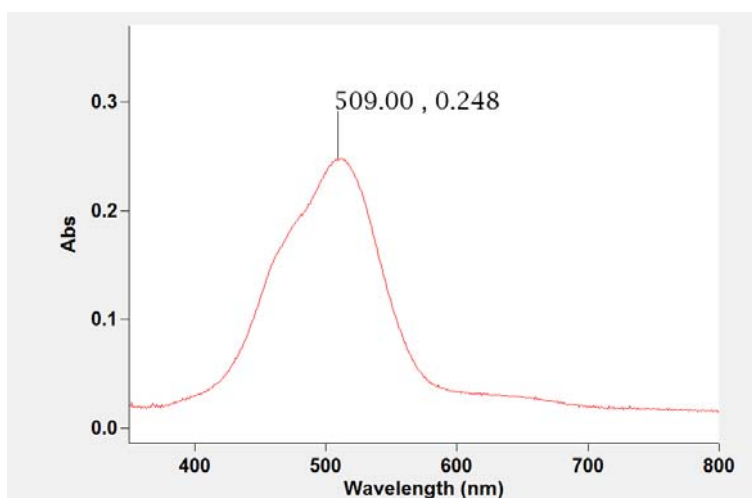


b) Convert the wavelength of each of the two peaks in Figure 1 into wavenumbers.

c) Which one of the peaks in Figure 1 corresponds to the transition of lowest energy?

Cobalt(II) nitrate hexahydrate dissolves in water to give hexaaquacobalt(II) cations, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, and nitrate anions. The UV-visible spectrum was recorded and is shown in Figure 2 below.

Figure 2: The UV-visible spectrum for the hexaaquacobalt(II) ion, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



d) i) What is the wavelength of maximum absorbance?

ii) What is the maximum absorbance?

The Beer-Lambert law relates the absorbance (A) of a solution, which is a dimensionless (has no units) quantity, to the concentration (c , in mol L^{-1}), path length (ℓ , in cm) and molar absorptivity (ϵ), which is specific to a compound at a certain wavelength. As an equation, the Beer-Lambert law is written as:
 $A = \epsilon c \ell$.

iii) What is the unit of molar absorptivity?

iv) The solution giving rise to the absorption spectrum in Figure 2 was prepared by dissolving 0.1446 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water and making up to the mark of a 10.00 mL volumetric flask. What is the concentration of the hexaaquacobalt(II) cations, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, in the solution in mol L^{-1} ?

v) What is the molar absorptivity (ϵ) of the hexaaquacobalt(II) ion in the solution described in iv) above, given that the path length is 1.00 cm (which you may assume for the rest of question 18) and that the effect of the nitrate ion on absorbance is negligible?

Nichrome is an alloy of nickel and chromium which is used in resistors. When a current is passed through a nichrome wire while it is bathed in acid, the nichrome wire dissolves into solution forming hexaaqua metal ions. Before the concentration of each of the hexaaquanickel(II) ions and the hexaaquachromium(III) ions can be determined, they must be calibrated against a standard solution.

A standard solution of a solution containing hexaaquanickel(II) ions was prepared. A second standard solution containing hexaaquachromium(III) ions was also prepared. The absorbance of each of these solutions was measured at 576 nm and 718 nm and the results are summarised in the table below:

| Species | Concentration (mol L ⁻¹) | Absorbance at 576 nm | Absorbance at 718 nm |
|--|--------------------------------------|----------------------|----------------------|
| [Ni(H ₂ O) ₆] ²⁺ | 0.04814 | 0.000 | 0.750 |
| [Cr(H ₂ O) ₆] ³⁺ | 0.03703 | 0.480 | 0.000 |

The solution of the Nichrome wire, which contains both the [Ni(H₂O)₆]²⁺ and [Cr(H₂O)₆]²⁺ ions, gave an absorbance of 0.100 at 576 nm and 0.400 and 718 nm.

e) i) Determine the concentration of hexaaquachromium(III) and hexaaquanickel(II) ions in the nichrome solution.

ii) What is the percentage composition by mass of nichrome in terms of nickel and chromium assuming that these are the only two elements present?

Chromium-vanadium is a popular alloy steel for springs that are required to withstand a large number of operating cycles.

Two standard solutions were prepared. One contained a solution of hexaaquavanadium(III) ions and the other contained a solution of hexaaquachromium(III) ions. The absorbance of each solution was measured at 450 nm and 625 nm and the results are summarised in the table below.

| Species | Concentration (mol L ⁻¹) | Absorbance at 450 nm | Absorbance at 625 nm |
|--|--------------------------------------|----------------------|----------------------|
| [V(H ₂ O) ₆] ³⁺ | 0.04228 | 0.270 | 0.200 |
| [Cr(H ₂ O) ₆] ²⁺ | 0.03617 | 0.630 | 0.440 |

A solution of a chromium-vanadium alloy, which contains both the [V(H₂O)₆]³⁺ and [Cr(H₂O)₆]²⁺ ions, gave an absorbance of 0.500 at 450 nm and 0.350 at 625 nm.

f) Calculate the concentration (in mol L⁻¹) of both the [V(H₂O)₆]³⁺ and [Cr(H₂O)₆]²⁺ ions in the mixture.

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Integrity of Competition

If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.