2013 Australian Science Olympiad Exam
Solutions

SECTION A

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

SECTION B

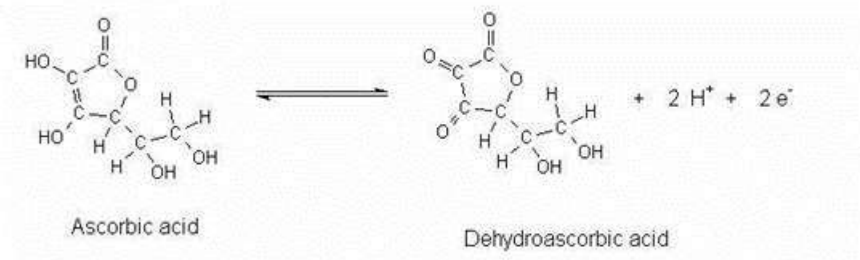
QUESTION 16

(a)
$n(CuCO_3) = 2.50\ g/123.56\ g\ mol^{-1} = 0.02023\ mol$
$n(Cu(ClO_4)_2) = 0.02023\ mol$
$m(Cu(ClO_4)_2) = 0.02023 \times 262.45\ g\ mol^{-1} = \mathbf{5.31\ g}$

(b)
i) –II
ii) +VII

(c)
CO_2

(d)

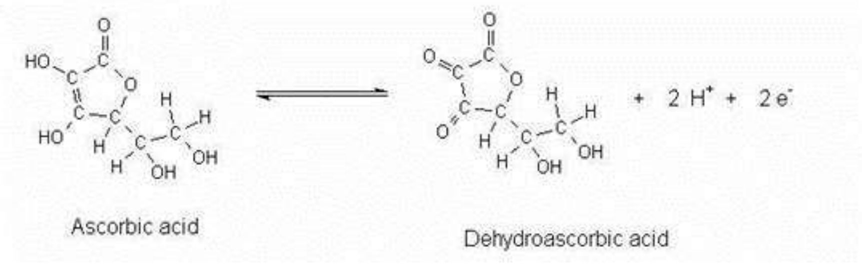


(e) Loss of electrons or electrons are products in the ascorbic acid half-equation.

(f)
$Asc + 2\ Cu^{2+} \rightarrow DAsc + 2\ Cu^{+} + 2H^{+}$

(g)
$v(Cu^{2+}) = 0.02595$ L
$[Cu^{2+}] = 3.131$ g÷(262.45 g mol^{-1}÷0.500 L = 0.02386 mol L^{-1}
$n(Cu^{2+}) = 0.02595$ L × 0.02386 mol L^{-1}
$n(Cu^{2+}) = 6.1916 \times 10^{-4}$ mol
$n(Asc) = 6.1916 \times 10^{-4} / 2$
$n(Asc) = 3.096 \times 10^{-4}$ mol
$n(Asc)_{total} = 3.096$ x $10^{-4} \times 250/20$
$n(Asc)_{total} = 3.870 \times 10^{-3}$ mol
$m(Asc)_{total} = 3.870 \times 10^{-3} \times 176.124)$
$m(Asc)_{total}$ = **0.6816 g**

(h)
Oxidation half-equation:



Ascorbic acid Dehydroascorbic acid

Reduction half-equation:
$IO_3^- + 6 H^+ + 6 e^- \rightarrow I^- + 3 H_2O$

(i)
$n(S_2O_3) = 0.1930$ mol $L^{-1} \times 0.01277$ L = 2.4646×10^{-3} mol
$n(I_2) = 2.4646 \times 10^{-3} \div 2 = 1.2323 \times 10^{-3}$ mol
$n(IO_3^-)_{excess} = n(I_2) \div 3 = 1.2323 \times 10^{-3}$ mol ÷ 3 = 4.1077×10^{-4} mol
$n(IO_3^-)_{total} = 0.02510$ mol $L^{-1} \times 0.02000$ L = 5.020×10^{-4} mol
$n(IO_3^-)_{\text{consumed by ascorbic acid}} = 5.020 \times 10^{-4}$ mol – 4.1077×10^{-4} mol = 9.1230×10^{-5} mol
n(ascorbic acid)$_{\text{10.00 mL aliquot}}$ = $n(IO_3^-)_{\text{consumed by ascorbic acid}} \times 3 = 9.1230 \times 10^{-5}$ mol × 3 = 2.73698×10^{-4} mol
n(ascorbic acid)$_{\text{100.0 mL sample}}$ = $2.73698 \times 10^{-4} \times 10 = 2.73698 \times 10^{-3}$ mol
m(ascorbic acid) = 2.73698×10^{-3} mol × 176.124 g mol^{-1} = **0.4820 g**

(j)
n(ascorbic acid)$_{\text{in sample}}$ = 2.73698×10^{-3} mol
n(ascorbic acid)$_{\text{original}}$ = 2.73698×10^{-3} mol × (20/250) = 2.1895×10^{-4} mol
$n(Cu^{2})_{original} = 2.1895 \times 10^{-4}$ mol × 2 = 4.3790×10^{-4} mol
$c(Cu(C\ell O_4)_2)_{original} = 4.3790 \times 10^{-4}$ mol ÷ 0.02595 L = 1.6875×10^{-2} mol L^{-1}
$n(Cu(C\ell O_4)_2)_{\text{in Tracey's solution}} = 1.6875 \times 10^{-2}$ mol $L^{-1} \times 0.500$ L = 8.4375×10^{-3} mol
Molar mass$(CuC\ell O_4)_2 \bullet x\ H_2O$ = 3.131 g ÷ 8.4375×10^{-3} mol = 371.08 g mol^{-1}
Molar mass difference = 371.08 – 262.45 = 108.63 g mol^{-1}
x = 108.63 ÷ 18.016 = 6.02

Therefore x = 6

QUESTION 17

Questions (a) to (e) were meant to appeal to basic concepts of weight, volume and density. The fact that all the data was given all at once, and not divided up between the relevant questions meant that students were required to think about which pieces of data to use for each calculation. This, of course, requires understanding what is physically happening in the problem. Many students seemed to struggle with this.

It should be emphasised that equations are not the lords and masters of physical chemistry, despite their preponderance in this field. Rather, understanding what is happening in a chemical sense (as opposed to a mathematical sense) is equally as important. Whilst the rest of Question 17 was well-done by many who are sufficiently proficient in mathematics, these first five parts were in general poorly done, considering their simplicity and fundamental nature.

(a) Mass of kerosene in beaker = 633.70 × 234.10 = 399.60 g
Volume of beaker = Volume of kerosene
= 399.60 ÷ 0.7493 = **533.3 mL** (4 s.f.)
Beakers are not pieces of volumetric glassware. Do not be surprised if they hold a very different volume to what they indicate.

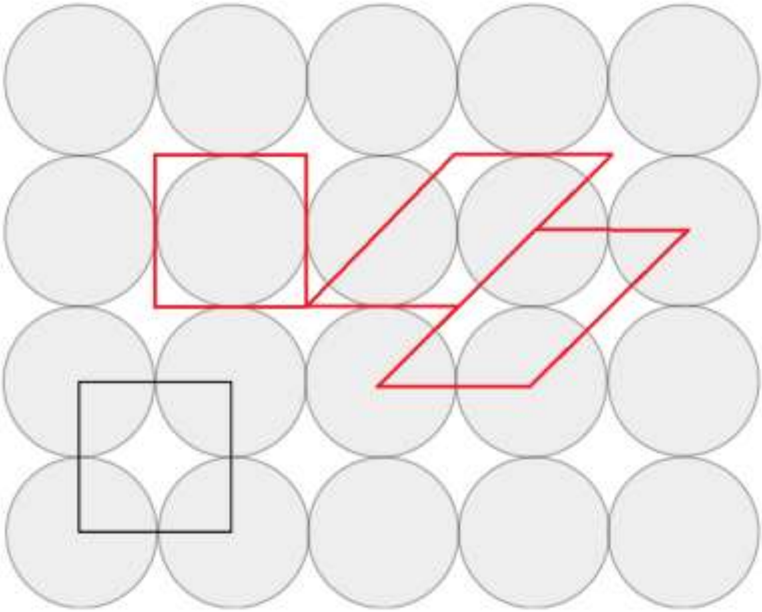
(b) Mass of caesium = 717.49 g - 575.57 g = **141.92 g**

(c) m(lost kerosene) = 633.7 g - 575.57 g = 58.13 g
So Volume(lost kerosene) = 58.13 g ÷ 0.7493 g cm^{-3} = **77.58 mL**

(d) ρ(caesium) = m(caesium) ÷ V(caesium)
= 141.92 g ÷ 77.58 mL
=**1.829 g mL^{-1}**

(e) Less kerosene remains during final weighing step, so she calculates more kerosene lost and overestimates the volume of the caesium. Hence she underestimates the density.

(f)



In red are the three unit cells we accepted. When writing the question, the red square was the intended answer. Trust students to come up with correct answers that you have never even considered! These three satisfy the three constraints of a unit cell as stated above. Students who drew unit cells that still tiled to give the pattern were given some credit. Technically, any translational equivalent of these three unit cells also satisfies the conditions, but the question asked for a highly symmetrical unit cell.

(g) Side of square = 2r

Hence A(square) = $(2r)^2 = 4r^2$

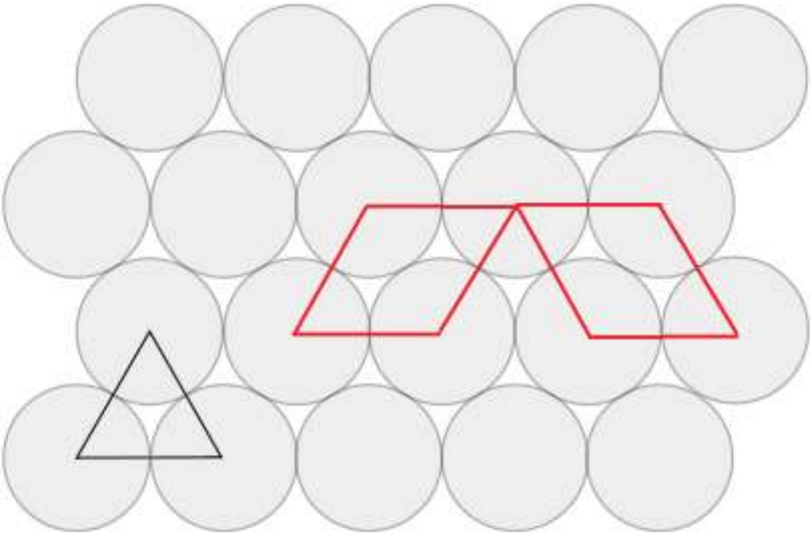
Using the given unit cell, total amount of circle inside the square is 4 × ¼ of a circle.

Hence A(circle) = $1 \times \pi r^2$ and percentage occupied by circles is.

$$\frac{\pi r^2}{4r^2} \times 100 = \frac{\pi}{4} \times 100 \approx \mathbf{78.5}\%$$

(h) Opposite edges of the cell are NOT parallel.

(i)



In red are the two main unit cells we accepted. In fact, any translational variation of these two unit cells still satisfies the requirements (they still connect equivalent points!)

(j) Circle total = $\frac{60°+120°+60°+120°}{360°}$ = 1 circle

Area of triangle = $\frac{\sqrt{3}}{4} \times (side)^2$

The rhombus on the diagram is made of 2 equilateral triangles

A(rhombus)=$2 \times \frac{\sqrt{3}}{4} \times (2r)^2 = 2\sqrt{3}r^2$

So percentage occupied is

$$\frac{\pi r^2}{2\sqrt{3}r^2} = \frac{\pi}{2\sqrt{3}} \approx \mathbf{90.7}\%$$

(k) **2**

(l) radius + diameter + radius = 4r

(m) Diagonal of the cube is 4r (from part l)

Pythagoras in 3D says $a^2 + a^2 + a^2 = (4r)^2$, where a is the side length of the cube.

Therefore, $4r = a\sqrt{3}$

Volume of the 2 spheres in cell = $2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$

Volume of the cube with sides a is $a^3 = \left(\frac{4r}{\sqrt{3}}\right)^3 = \frac{64r^3}{3\sqrt{3}}$

Percentage occupied is therefore:

$$\frac{V_{spheres}}{V_{cube}} = \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}}r^3} = \frac{\sqrt{3}}{8}\pi$$

This corresponds to about **68.01%** efficiency of packing.

(n) 1 cm^3 of caesium weighs 1.87 g.
1.87g =1.87 ÷ 132.905 = 14.07 mmol
Number of atoms = 14.07 mmol × N_A atoms (where $N_A = 6.022 \times 10^{23}$ is Avogadro's constant)
=8.47×10^{21} atoms

(o) Each cell contains 2 atoms. So number of cells = $8.47 \times 10^{21} \div 2$
= **4.24×10^{21} unit cells**.

(p) i) Volume of each unit cell = $\frac{1\ cm^3}{4.24 \times 10^{21}\ cells}$ = 2.36×10^{-22} cm^3.

Therefore, side length of each cell = $\sqrt[3]{2.36 \times 10^{-22}}$ = 6.18×10^{-8} cm = 6.18×10^{-10} **m = 6.18 Å.**

ii) We have already know that 4r = a$\sqrt{3}$
So 4r = $\sqrt{3} \times 6.18$ Å
Therefore, **r = 2.68 Å.**

(q) 1 chlorine atom. It's actually 8 × $1/_8$ bits of atoms

(r) There are multiple ways to do this problem, but the way presented below is probably the most intuitive and easily followed. It is not the quickest way.

The density of CsCl is 3.99 g cm^{-3}
$= \frac{3.99}{168.36}$ mol cm^{-3} where MW(CsCl) = 132.905 + 35.45 = 168.36 g mol^{-1}
= $\frac{3.99 \times N_A}{168.36}$ cells cm^{-3}, since each CsCl pair constitutes 1 cell.
$V_{cell} = \left(\frac{3.99 \times N_A}{168.36}\right)^{-1} = \frac{168.36}{3.99 \times N_A}$ cm^3 $cell^{-1}$
So side length of the cell = $\sqrt[3]{\frac{168.36}{3.99 \times N_A}} = a$
Now, consider the diagonal of the cell. Length is $2r_{Cs+} + 2r_{Cl-}$
Then using the 3D Pythagoras theorem again, $2(r_{Cs+} + r_{Cl-}) = a\sqrt{3}$
Therefore $r_{Cs+} + r_{Cl-} = \frac{\sqrt{3}}{2}a$
But according to Pauling:

$$\frac{r_{Cs+}}{r_{Cl-}} = \frac{5.75}{9.25}$$

Then

$$r_{Cl-} + \frac{5.75}{9.25} r_{Cl-} = \frac{\sqrt{3}}{2} a$$

So therefore, $r_{Cl-} = 0.5340a$
And hence $r_{Cs+} = \left(\frac{\sqrt{3}}{2} - 0.5340\right) a = 0.3320a$

Substituting for a:
r_{Cs+} = 1.37 Å
r_{Cl-} = 2.24 Å

QUESTION 18

(a) The ammonia molecules are uncharged, the chloride ion has a charge of 1– and the cobalt ion has a charge of 3+, so the complex will have a charge of 2+.

(b) 363 nm = 3.63×10^{-7} m = 3.63×10^{-5} cm; $\frac{1}{3.63 \times 10^{-5}} = 2.75 \times 10^{4}$ cm^{-1}

531 nm = 5.31×10^{-7} m = 5.31×10^{-5} cm; $\frac{1}{5.31 \times 10^{-5}} = 1.88 \times 10^{4}$ cm^{-1}

(c) Lowest energy peak is the 531 nm or 1.88×10^{4} cm^{-1} peak (energy increases with increasing wavenumber).

(d) i) 509 nm

ii) 0.248

iii) L mol^{-1} cm^{-1} (or M^{-1} cm^{-1}). As A is dimensionless, the units for molar absorptivity must be the inverse of those for the product of concentration and volume.

iv) Molar mass of $Co(NO_3)_2 \cdot 6H_2O$ = 58.63 + 2 × 14.01 + 6 × 16.00 + 6 × (2 × 1.008 + 16.00) = 290.746 g mol^{-1}

$n(Co(NO_3)_2 \cdot 6H_2O) = \frac{0.1446\ g}{290.746\ g\ mol^{-1}} = 4.973 \times 10^{-4}$ mol

(For simplicity, hydrated ions will be shown without their waters of hydration throughout the rest of this question, e.g. $[Co(H_2O)_6]^{2+} = Co^{2+}$)

$[Co^{2+}] = \frac{4.973 \times 10^{-4}\ mol}{0.01\ L} = 4.973 \times 10^{-2}$ mol L^{-1}

v) $\varepsilon = \frac{A}{cl} = \frac{0.248}{4.973 \times 10^{-2}\ M\ cm} = 4.99$ M^{-1} cm^{-1}

(e) i) Looking at the absorbances of the standard solutions, Ni^{2+} does not absorb at 576 nm so any absorbance at 576 nm is entirely due to Cr^{3+}. Similarly, Cr^{3+} does not absorb at 718 nm so any absorbance at 718 nm is entirely due to Ni^{2+}. We can use this information and the absorbances and concentrations of the standard solutions to calculate the extinction coefficients at each wavelength:

As Cr^{3+} does not absorb at 718 nm: $\varepsilon_{\text{Ni-718 nm}} = \frac{0.750}{0.04814\ M\ cm} = 15.6$ M^{-1} cm^{-1}

As Ni^{2+} does not absorb at 576 nm: $\varepsilon_{\text{Cr-576 nm}} = \frac{0.480}{0.03703\ M\ cm} = 13.0$ M^{-1} cm^{-1}

We can then calculate the Ni^{2+} and Cr^{3+} concentrations in the unknown:

$[Ni^{2+}] = \frac{0.400}{15.6\ M^{-1}cm^{-1}} = 0.0257$ mol L^{-1}

$[Cr^{3+}] = \frac{0.100}{13.0\ M^{-1}cm^{-1}} = 7.71 \times 10^{-3}$ mol L^{-1}

ii) m(Ni) = 0.0257 mol L^{-1} × 58.69 g mol^{-1} = 1.51 g L^{-1}

m(Cr) = 7.71×10^{-3} mol L^{-1} × 52.00 g mol^{-1} = 0.401 g L^{-1}

$\%(Ni) = \frac{1.51}{1.51+0.401} \times \frac{100}{1} = 79.0\ \%$

$\%(Cr) = 100 - 79.0 = 21.0\ \%$ (or $\frac{0.401}{1.51+0.401} \times \frac{100}{1}$)

(f) This is a similar situation to part (e), but with the added complication that both species absorb at both wavelengths. The key step is to realise that the absorbance of the unknown solution at each wavelength is due to absorbance from **both** vanadium and chromium ions at that wavelength. For example at 450 nm:

$A_{450\text{ nm}} = A_{V\text{-}450\text{ nm}} + A_{Cr\text{-}450\text{ nm}}$

And since $A = \varepsilon c\ell$, with $\ell = 1$ cm we can write:

$A_{450\text{ nm}} = \varepsilon_{V\text{-}450\text{ nm}}[V^{3+}] + \varepsilon_{Cr\text{-}450\text{ nm}}[Cr^{3+}]$, or

$0.500 = \varepsilon_{V\text{-}450\text{ nm}}[V^{3+}] + \varepsilon_{Cr\text{-}450\text{ nm}}[Cr^{3+}]$

Similarly, at 625 nm, we can write:

$0.350 = \varepsilon_{V\text{-}625\text{ nm}}[V^{3+}] + \varepsilon_{Cr\text{-}625\text{ nm}}[Cr^{3+}]$

We can calculate extinction coefficients for both species at both wavelengths (which for simplicity we will assign letters **A**-**D**):

$\varepsilon_{V\text{-}450\text{ nm}} = \frac{0.270}{0.04228\ M\ cm} = 6.39\ M^{-1}\ cm^{-1} = \mathbf{A}$

$\varepsilon_{V\text{-}625\text{ nm}} = \frac{0.200}{0.04228\ M\ cm} = 4.73\ M^{-1}\ cm^{-1} = \mathbf{B}$

$\varepsilon_{Cr\text{-}450\text{ nm}} = \frac{0.630}{0.03617\ M\ cm} = 17.4\ M^{-1}\ cm^{-1} = \mathbf{C}$

$\varepsilon_{Cr\text{-}625\text{ nm}} = \frac{0.44}{0.03617\ M\ cm} = 12.2\ M^{-1}\ cm^{-1} = \mathbf{D}$

This leaves us with two equations in two unknowns:

$0.500 = \mathbf{A}[V^{3+}] + \mathbf{C}[Cr^{3+}] \qquad (1)$

$0.350 = \mathbf{B}[V^{3+}] + \mathbf{D}[Cr^{3+}] \qquad (2)$

Solving these simultaneously will give $[V^{3+}]$ and $[Cr^{3+}]$. For example:

(1) × **D** : 0.500**D** = **AD**[V^{3+}] + **CD**[Cr^{3+}]   (3)
(2) × **C** : 0.350**C** = **BC**[V^{3+}] + **CD**[Cr^{3+}]   (4)

(3) − (4): 0.500**D** – 0.350**C** = (**AD**–**BC**)[V^{3+}]

So [V^{3+}] = $\frac{0.500\boldsymbol{D}-0.350\boldsymbol{C}}{\boldsymbol{AD}-\boldsymbol{BC}}$ = 2.94×10^{-3} mol L^{-1}

[Cr^{3+}] can then be obtained by a similar method, or by substitution into either equation (1) or (2):

[Cr^{3+}] = 2.76×10^{-2} mol L^{-1}