Cambridge Chemistry Challenge Lower 6th

June 2021

> Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical A-level papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.
>
> If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

- The time allowed is 90 minutes under exam conditions.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table and necessary constants are included on the next page.

Group Number

Symbol
atomic number
mean atomic mass

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block		d-block										p-block					
1	**H** 1 1.008	**He** 2 4.003																**He** 2 4.003
2	**Li** 3 6.94	**Be** 4 9.01											**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
3	**Na** 11 22.99	**Mg** 12 24.31											**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
4	**K** 19 39.10	**Ca** 20 40.08	**Sc** 21 44.96	**Ti** 22 47.87	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.69	**Cu** 29 63.55	**Zn** 30 65.38	**Ga** 31 69.72	**Ge** 32 72.63	**As** 33 74.92	**Se** 34 78.97	**Br** 35 79.90	**Kr** 36 83.80
5	**Rb** 37 85.47	**Sr** 38 87.62	**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.95	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.42	**Ag** 47 107.87	**Cd** 48 112.41	**In** 49 114.82	**Sn** 50 118.71	**Sb** 51 121.76	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.29
6	**Cs** 55 132.91	**Ba** 56 137.34	* **Lu** 71 174.97	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.84	**Re** 75 186.21	**Os** 76 190.23	**Ir** 77 192.22	**Pt** 78 195.08	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.38	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
7	**Fr** 87	**Ra** 88	+ **Lr** 103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

f-block

Lanthanoids: *	**La** 57 138.91	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.36	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.05
Actinoids: +	**Ac** 89	**Th** 90 232.04	**Pa** 91 231.04	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102

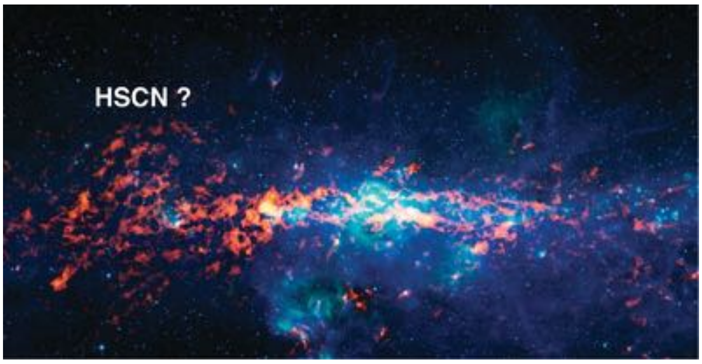
The Avogadro constant $N_A = 6.022 \times 10^{23}\ mol^{-1}$

1. This question is about thiocyanates

Ammonium thiocyanate is formed when ammonia reacts with carbon disulfide, CS_2.

The thiocyanate anion, $[SCN]^-$, can form bonds either via the sulfur (to give thiocyanate compounds), or via the nitrogen (to give isothiocyanates).

Protonation of the nitrogen in $[SCN]^-$ forms isothiocyanic acid. Its isomer, thiocyanic acid was first detected in a large gas cloud in space in 2009 using radio astronomy.



Credit: ESO/APEX & MSX/IPAC/NASA

Sagittarius B2 (Sgr B2) is one of the largest clouds of molecular gas in the Milky Way. It is located close to the supermassive black hole at centre of the galaxy.

When ammonia and carbon disulfide react, two moles of ammonia react with one of carbon disulfide to form one mole of an intermediate compound, **A**. Intermediate compound **A** decomposes on warming to form ammonium thiocyanate and hydrogen sulfide.

(a) **(i)** Draw a dot-and-cross diagram for carbon disulfide and indicate any relevant bond angles.

(ii) Give the overall equation for the reaction between ammonia and carbon disulfide.

(iii) Give the molecular formula for intermediate compound **A**.

The reaction between ammonia and carbon disulfide starts with nucleophilic attack by ammonia on the carbon disulfide to give a reactive species, **X**, which is quickly deprotonated by the second ammonia to give the intermediate compound **A**.

(b) **(i)** Suggest a structure for the reactive species **X**.

(ii) Suggest a structure for the intermediate compound **A**.

The sulfur-carbon bond lengths in isothiocyanic (here denoted $S–C_{iso}$) and in thiocyanic acid ($S–C_{thio}$) are quite different, as are the carbon-nitrogen bond lengths $C–N_{iso}$ and $C–N_{thio}$.

(c) **(i)** Clearly showing all the bonds present, draw the structure of isothiocyanic acid, the product formed on protonating $[SCN]^-$ on the nitrogen.

(ii) Clearly showing all the bonds present, draw the structure of thiocyanic acid, the product formed if $[SCN]^-$ is protonated on the sulfur.

(iii) Arrange the four bonds $S–C_{iso}$, $S–C_{thio}$, $C–N_{iso}$, and $C–N_{thio}$ in order of INCREASING bond length.

Ammonium thiocyanate has two nitrogen atoms in very different environments, one in the ammonium cation, the other in the thiocyanate anion. However, on warming, it isomerises to form a covalent molecule, compound **C**, in which both nitrogen atoms are in an equivalent environment.

(d) Suggest a structure for compound **C**.

Mercury(II) thiocyanate, prepared by mixing ammonium thiocyanate and mercury(II) nitrate, became a popular chemical amusement in the 19th century. When compressed into pellets and ignited the compound smoulders with a blue flame and gradually produces a large quantity of a low-density, solid foam – the 'serpent'. However, the toxicity of some of the products has led to a decrease in its use as an example of scientific entertainment!

During the reaction, the compound decomposes to form three products: mercury(II) sulfide, carbon disulfide, and a polymer consisting of carbon and nitrogen only.

The blue flame is produced from the **combustion of the carbon disulfide**, and the heat produced in this combustion is sufficient to keep the reaction proceeding.

THERE'S a new toy called Pharaoh's serpent, which is all the rage just now. It consists of a small cone, about the size of a large pastile, covered with tin foil. On lighting the apex a writhing and seemingly endless coil, something like a pale puff adder, pours from it. The toy has two advantages : it is a very amusing surprise, and as it is of a poisonous nature you can, if you are an old bachelor and hate children, take them to your friends' houses and make a clean sweep of their growing families, by allowing the youngsters to inhale the fumes or put the serpents in their mouths.

From the satirical magazine 'FUN' Oct 28, 1865.

(e) (i) Write an equation for the complete combustion of 1 mole of CS_2.

(ii) Calculate the standard enthalpy of combustion of CS_2, given the following data:

$\Delta_f H°$ (CS_2) = +89.4 kJ mol^{-1}
$\Delta_c H°$ (C) = –393.5 kJ mol^{-1}
$\Delta_c H°$ (S) = –297.5 kJ mol^{-1}.

(iii) Write a balanced equation for the decomposition of mercury(II) thiocyanate, giving the empirical formula of the polymer of carbon and nitrogen.

The composition of the serpent ash formed after the mercury(II) thiocyanate has reacted has recently been investigated using a technique called *Thermal Gravimetric Analysis* (TGA). TGA slowly heats a small amount of material and monitors the percentage mass loss as various gaseous products are released as the material decomposes. Different decompositions occur at different temperatures and, by measuring the mass loss at different temperatures, conclusions can be drawn about the composition of the original material.
When a small amount of the serpent ash was heated, a mass loss of 78.5% occurred in the temperature range 245 – 370 °C. This is less than expected but this large mass loss can only be equated with the removal of one of the compounds from the serpent ash, albeit incompletely.

(f) Calculate the percentage mass loss you would expect for the loss of each of the mercury(II) sulfide and the polymer of carbon and nitrogen from the serpent ash, and hence identify which compound is removed upon heating through this temperature range.

The polymer of carbon and nitrogen that is formed in this demonstration is one of a family of carbon nitrides (**CN**). These materials are currently being investigated as photocatalysts for the production of hydrogen from water using the energy in visible light. The **CN** example in this question can be synthesised in a variety of ways, including starting from calcium cyanamide, $CaCN_2$. On mixing with a weak acid, calcium cyanamide forms the neutral molecule with formula CH_2N_2, simply called cyanamide. Three molecules of cyanamide can form a cyclic trimer, melamine (and no other products). Melamine contains a 6-membered ring consisting of alternating C and N atoms.

(g) **(i)** Draw the structure of the CN_2^{2-} ion and state the bond angle between the bonds.

(ii) Suggest **two** possible structures for cyanamide.

(iii) Suggest a structure for melamine.

When melamine is subjected to TGA analysis, the first mass loss, 6.75%, is associated with a dimerisation process and the loss of a single molecule.

(h) **(i)** Calculate the relative molar mass of the molecule lost when melamine dimerises.

(ii) What molecule, **M**, accounts for the 6.75% mass lost when melamine dimerises?

(iii) Suggest a possible structure for the dimer consistent with this mass loss.

Further polymerisation of melamine produces a number of different structures that are known as graphitic carbon nitrides, **g-CN**. Elemental analysis of all of these compounds always shows some small amount of residual hydrogen in the formula, which cannot be easily removed by increasing the amount of polymerisation.

(j) In your answer booklet, tick one of the following answers that most simply explains the presence of this hydrogen:

Hydrogen gas is easily absorbed from the atmosphere in between the layers of **g-CN**.

Polymerisation reactions inevitably leave some hydrogen attached to N-atoms at the edges of the sheets of **g-CN**.

g-CN is very reactive and reacts with atmospheric moisture to attach hydrogen atoms.

There are contaminants in the original melamine that contain hydrogen and these react with the **g-CN**.

(k) Calculate the empirical formula of the **g-CN** that could ultimately be formed on heating melamine if all of the H atoms were lost in the form of molecule **M** from part **(h)**.

2. This question is about oxidation, reduction and ferrets

The term 'oxidation' was first used to suggest processes when oxygen was introduced into a substance, but later came, more generally, to be associated with the loss of electrons from species.

The term 'reduction' was initially used when metal oxides were 'reduced' to the metal since the overall mass was found to decrease in the process.

'Oxidation states' are the hypothetical charges that atoms would have if the bonds in the compounds were totally ionic with no covalent contribution; this assumption is never true in real compounds.

(a) **(i)** Calculate the percentage decrease in mass when copper(II) oxide is reduced to copper metal.

(ii) Give two equations for the production of copper metal from copper(II) oxide and carbon.

(iii) What is the minimum theoretical mass of carbon needed to produce 100g of copper?

The maximum possible oxidation state for an element could occur if all the outermost electrons, the so-called valence electrons, were used in bonding. The maximum number of valence electrons is equal to the group number for Groups 1 to 11, and the group number minus 10 for elements from Groups 12 to 18. Note the maximum possible oxidation state is not always achievable.

(b) Each of the following elements forms an **oxide exhibiting the theoretical maximum oxidation** state for that element. Give the formula for each oxide.

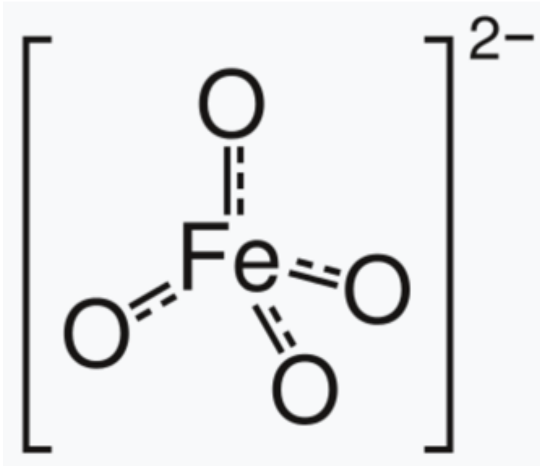
xenon (Xe)	polonium (Po)	chlorine (Cl)
niobium (Nb)	osmium (Os)	yttrium (Y)

A commonly occurring unit in chemistry consists of an element associated with four oxygen atoms, and possibly a charge. An example is the tetrahedral sulfate ion, SO_4^{2-}.

(c) **(i)** Given that the following elements all form either molecules or ions by uniting with four oxygen atoms **with the element in its maximum theoretical oxidation state**, give the formula for each ion or molecule.

bromine (Br)	chromium (Cr)	arsenic (As)	germanium (Ge)
technetium (Tc)	thallium (Tl)	iridium (Ir)	ruthenium (Ru)

(ii) One of the molecules or ions above cannot have a tetrahedral structure; which one?



The ferrate ion (above left) is easily confused with the ferret animal (above right).

Another tetrahedral oxyanion is the ferrate ion, FeO_4^{2-} which contains iron in its so-far highest obtained oxidation state of +VI. This has been proposed as a powerful 'green' oxidising agent, since it produces harmless iron compounds when it reacts. Potassium ferrate is prepared industrially from iron(III) chloride, potassium hydroxide and chlorine. An aqueous solution of potassium ferrate will eventually decompose to give an alkaline solution, a precipitate of iron(III) oxide, and a colourless, odourless gas.

(d) **(i)** Balance the following equation for the preparation of potassium ferrate:

$$\_\_FeCl_3 + \_\_KOH + \_\_Cl_2 \longrightarrow \_\_K_2FeO_4 + \_\_KCl + \_\_H_2O.$$

(ii) Give an equation for the decomposition of aqueous potassium ferrate solution.

(iii) The speed at which potassium ferrate decomposes strongly depends on the pH of the solution. How would you expect the rate of decomposition to vary at the following three pHs? Arrange the pHs in order from the slowest-expected reaction to fastest.

pH 4 pH 7 pH 10

One possible use of potassium ferrate is for the removal of manganese(II) ions from drinking water. In this process, potassium ferrate reacts with Mn^{2+} ions in water to form insoluble iron oxide and manganese oxide which can be removed by filtration. The potential health impacts from Mn^{2+} ions in water is an area of active research; some studies have found manganese exposure through drinking water to be associated with lower IQ scores in school-aged children, and higher incidence of hyperactive behaviours.

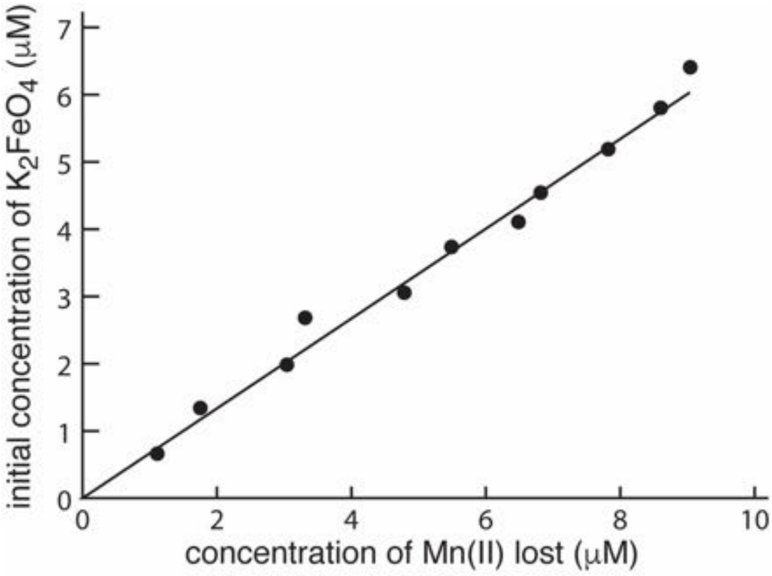
An experiment to investigate the oxidation of aqueous Mn^{2+} ions at their typical concentrations found in drinking water was recently carried out as follows:

- A sample of a concentrated potassium ferrate stock solution was added to 750 ml of buffered solutions of Mn^{2+} ions (present in excess).
- The reaction was allowed to proceed for 45 minutes.
- The solution was filtered to remove solid products.
- The concentration of Fe and Mn species in the filtrate was measured using a mass spectrometer.
- The proportions of the reacting species were determined.

(e) (i) Given the concentration of Mn(II) was 9.6 μM [1 μM = 1 × 10^{-6} mol dm^{-3}], calculate what mass of manganese(II) sulfate-monohydrate is contained in the 750 ml sample. Give your answer in mg.

(ii) An 8.0 ml stock solution of potassium ferrate was added to a buffered Mn(II) solution as described above. The initial concentration of potassium ferrate in the resulting solution was 9.6 μM. Calculate the concentration of the potassium ferrate stock solution in μM.

The concentrations of the Mn^{2+} ions that reacted with certain concentrations of the added potassium ferrate were measured and reported in the following graph:



Knowing the proportions in which the reactants combine, and the fact that iron(III) ions are formed, the researchers were able to work out the oxidation state of the manganese in the product.

(f) (i) What is the combining molar ratio of ferrate ions : Mn(II) ions? (Give your answer in whole numbers.)

(ii) Assuming the reaction takes place with the reactants in the whole-number ratio above, how many electrons are formally transferred during the reaction?

(iii) What is the oxidation state of the manganese in the product?

(iv) Given oxides of manganese and iron are two of the products formed in the reaction, suggest an equation for the reaction between aqueous potassium ferrate and manganese(II) chloride.

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