Chemistry in your cupboard: Calgon

Introduction
Water forms the basis of most cleaning processes. As it seeps through the ground, magnesium and calcium ions dissolve in it. Water containing dissolved minerals is known as hard water. Dissolved minerals reduce the efficiency of cleaning processes and additional cleaning agent is required to compensate for this. Water softeners such as Calgon® may be used to reduce the effect of hard water on appliance efficiency and improve cleaning by removing or masking the effect of dissolved ions.

Links to the curriculum
This section contains information relevant to the following areas of your chemistry curriculum:

- Group 2 elements
- Acids and bases
- Polymerisation

CALGON

Tap water
In the western world, we think of our tap water as being pure. And it is in the sense that it is safe to drink and contains no dangerous micro-organisms - viruses and bacteria - which could make us ill. However, in the chemical sense of being a single substance, it is not pure at all. It will contain materials dissolved from the ground, through which it has seeped between falling as rain (when it has effectively been distilled) and arriving in a reservoir from which it enters the distribution system.

Question 1
Explain why rainwater is ‘effectively distilled’.

Question 2
Even rainwater is not chemically pure when it falls. Suggest what else may be dissolved in it.

These dissolved materials can make a great deal of difference to water's ability as a cleaning solvent - for its use in washing machines and dishwashers, for example. Water containing dissolved minerals is termed ‘hard’ and water softeners such as Calgon® may be used to reduce the effects of this and improve cleaning.

Hard water has two effects on the cleaning efficiency of washing machines and dishwashers. Firstly, inorganic compounds may deposit on the electric elements used to heat up the cleaning water, thereby reducing efficiency. These compounds may also deposit on the articles being cleaned. Secondly, metal ions in the hard water react with...
soap and certain other detergents to form scum, which reduces cleaning power, and deposits on the items to be cleaned. The solution to these problems is to use more cleaning agent.

This is why laundry detergent manufacturers recommend different levels of detergent depending on the water hardness: the higher the water hardness, the more detergent is required, see Figure 1.

![Figure 1: Manufacturers recommend using more detergent in hard water areas](image)

The use of a water softener can reduce the amount of detergent required by up to 40%.

**The taste of water**
Dissolved materials also make a significant difference to water’s taste. If you live in a hard water area, you may never have tasted pure water. If you get the opportunity to taste some distilled or deionised water at school, college or elsewhere try it (with suitable hygiene precautions). You may be surprised.

*Note: Do not taste water that has been treated with Calgon® or other water softening products.*

**How water becomes hard**
Figure 2 shows the water cycle. The time taken between water falling as rain and entering a reservoir can vary from zero (rain falling directly into the reservoir) to thousands of years. So, there may be plenty of time for material to dissolve, even if the rate of dissolving is slow. What materials actually dissolve will depend on the nature of the rock through which the water percolates. Of most importance from the point of view of cleaning are dissolved metal ions, and of these the most relevant are Ca\(^{2+}\), Mg\(^{2+}\) and, to a lesser extent, Fe\(^{3+}\).
When rainwater seeps through limestone rock, it dissolves some of it. This is the origin of limestone caves. Limestone is calcium carbonate, which is pretty insoluble in pure water, but rainwater naturally contains dissolved carbon dioxide which makes it acidic. The following reaction occurs, dissolving limestone as calcium hydrogen carbonate (calcium bicarbonate).

\[ \text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \quad \Delta H -ve \]

A similar reaction can occur with magnesium carbonate.

Rainwater is naturally acidic because of dissolved carbon dioxide, which is normally present in the air and takes part in the equilibria:

\[ \text{H}_2\text{O}(l) + \text{CO}_2(aq) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \]

The acidity of rain is increasing because the level of carbon dioxide in the atmosphere is rising as we burn more fossil fuels. The presence of gases such as sulfur dioxide and nitrogen oxides, also produced by burning fuels, adds to the acidity.

A second source of hardness is the dissolution of other calcium and magnesium salts, such as chlorides and sulfates, in rainwater. Here acidity does not play an important role. One common rock is anhydrite, calcium sulfate:

\[ \text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq) \]
Temporary and permanent hardness

The reaction

$$\text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \quad \Delta H -ve$$

is exothermic in the forward direction, and Le Chatelier's principle predicts that at high temperatures, the equilibrium will move to the left.

This is what happens inside kettles, dishwashers and washing machines and results in the formation of a deposit of calcium carbonate on their heating elements, Figure 3. This is usually called limescale in everyday language. Limescale reduces heat transfer from the element to the water and makes the appliance less efficient.

Figure 3a: The effects of limescale: a new heating element

Figure 3b: The effects of limescale: a heating element with limescale deposit

It can also deposit on clothes making them feel rough. Figure 4 shows the effect of deposition of limescale on fibres of clothing.
Because the calcium ions are removed from solution (as solid calcium carbonate) by heating the water, the type of hardness where the negative ion is the hydrogencarbonate ion is called **temporary hardness**.

The hardness caused by calcium (and magnesium) salts other than hydrogencarbonates is not affected by heating and is therefore called **permanent hardness**.

**Question 3**

a) Write the expression for the equilibrium constant $K_c$ for the equilibrium

$$\text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(aq) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \quad \Delta H \text{-ve}$$

Remember how to deal with the concentrations of solids and pure liquids.

b) What are the units of the equilibrium constant in the previous question?

c) Apart from changing the temperature, what other ways can you suggest of reducing $[\text{Ca}^{2+}(aq)]$?

**How hard is your tap water?**

Water companies routinely monitor the hardness of water in their areas.
Question 4
On the map in Figure 5, the units of water hardness are given as ‘mg/l of calcium carbonate equivalent’. Another unit often used is ‘mg/l of calcium’.

100 mg/l as calcium carbonate equivalent is the same as 40 mg/l of calcium. Use the formula of calcium carbonate (CaCO$_3$) and the relative atomic masses (Ca = 40; C = 12; O = 16) to explain why these two measurements are equivalent.

1 mg/l is the equivalent of 1 mg dm$^{-3}$.

Question 5
The method of reporting hardness as ‘calcium carbonate equivalent’ makes the assumption that all the calcium ions in the water are derived from (or associated with) carbonate ions, i.e. that all the calcium is actually part of calcium carbonate.

If a sample of water contained 272 mg/l (272 mg dm$^{-3}$) of calcium sulfate (CaSO$_4$), how would this be reported as ‘calcium carbonate equivalent’? (Relative atomic mass S= 32)

Calgon® is formulated to soften water and reduce the effects of hardness in a number of ways that reinforce each other – they are synergistic. It prevents the deposition of limescale in four ways called technically ion exchange, neutralisation, suspension and regrowth inhibition. Find out more about these below.
Ion exchange
Calgon® contains compounds called zeolites. These are aluminosilicate minerals whose structures have large numbers of ‘holes’ or ‘tunnels’ giving them an enormous surface area. The structures are made up of notional Si\(^{4+}\) ions linked by oxygen atoms. Some of the silicon ions are replaced by aluminium ions. However, aluminium forms Al\(^{3+}\) ions and so, to keep the structure neutral, each one must be associated with another, singly charged, ion, usually Na\(^{+}\). These sodium ions can be exchanged for other ions such as calcium or magnesium.

**Question 6**
Explain why aluminium forms Al\(^{3+}\) ions and silicon might form Si\(^{4+}\) ions.

**Question 7**
The silicon atoms do not in fact form true Si\(^{4+}\) ions, there is a degree of covalent bonding with the oxygen atoms in the structure. Explain why true Si\(^{4+}\) ions are unlikely to form.

**Question 8**
Explain why Si\(^{5+}\) and Al\(^{4+}\) will never form.

To keep the charges balanced, two Na\(^{+}\) ions are exchanged for each Ca\(^{2+}\) or Mg\(^{2+}\), Figure 6. Thus, zeolites remove the ions that cause hardness from the washing water.

![Figure 6: Part of the structure of a zeolite showing one of the ‘tunnels’. Blue represents Al\(^{3+}\) and red represents Si\(^{4+}\) (Courtesy of moleculesieve.org)](Image)

Calgon is a registered trade mark of the Reckitt Benckiser group of companies.
Last reviewed by Reckitt Benckiser in 2013.
Neutralisation (1 of 3)

Essentially this removes calcium ions from solution so that the equilibrium

$$\text{CaCO}_3(s) + H_2O(l) + CO_2(aq) \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^-(aq)$$

cannot move to the left and deposit calcium carbonate.

Calcium ions may be removed using a complexing agent. A complexing agent is a negatively charged ion that wraps itself around the $Ca^{2+}$ ion forming dative covalent (co-ordinate) bonds with it and effectively removing it from solution. These are sometimes called ‘sequestering agents’ - sequester meaning ‘to seclude, isolate or set apart’ according to the Oxford English Dictionary.

One of the complexing agents used in Calgon® is sodium citrate (sodium 2-hydroxypropane-1,2,3-tricarboxylate).

![Figure 7: Structure of the citrate 3- ion.](image)

The structural formula of the citrate 3- ion is shown in Figure 7 and a 3D representation in Figure 8. Make sure that you can relate the two representations of the citrate ion to one another.

![Figure 8: 3D representation of the citrate 3- ion](image)
In the 3D representation, carbon atoms are coloured grey, oxygen red and hydrogen white. You may find it helpful to make a model of the citrate ion using a ball and stick modelling kit such as Molymod™ to help you understand how this complexing works.

Neutralisation (2 of 3)
The citrate 3- ion is often written Cit³⁻ for short. The three O's can twist round to enfold a Ca²⁺ ion (remember that there is free rotation about single bonds). They are attracted to the ion electrostatically and can use their lone pairs of electrons to form dative (coordinate bonds) with it.

Question 9
a) What will be the charge on the complex ion formed from the citrate ion and a calcium ion?
b) Will it be attracted to a hydrogen carbonate ion?

Question 10
Would you expect the citrate/calcium ion to be soluble in water? Explain your answer.

The effect of complexing the Ca²⁺ ion is to keep it dissolved in the water rather than being deposited as calcium carbonate. Mg²⁺ ions will be complexed in the same way.

Question 11
Write the electron arrangement (1s², 2s² etc) of a Ca atom and Ca²⁺ ion. What noble gas configuration does Ca²⁺ have?
What empty orbitals might be used on the Ca²⁺ ion to accept lone pair electrons from the citrate ion?

Question 12
The two C-O bond lengths in the COO⁻ groups of sodium citrate are identical rather than one shorter than the other. Explain this observation.

Question 13
Considering its electronic structure and the formation of complexes, in what ways will Mg²⁺
a) resemble a Ca²⁺ ion?
b) differ from a Ca²⁺ ion?

Another typical complexing agent in Calgon® is sodium tripolyphosphate, Figure 9.
Figure 9: Structure of the tripolyphosphate ion.

The structural formula of the tripolyphosphate ion is shown in Figure 9 and a 3-D representation in Figure 10.

Figure 10: 3D representation of the tripolyphosphate ion

Make sure that you can relate the two representations of the phosphate ion to one another. In the 3D representation, phosphorus atoms are coloured orange and the oxygen red. You may find it helpful to make a model of the phosphate ion using a ball and stick modelling kit such as Molymod™ to help you understand how this complexing works.

Neutralisation (3 of 3)

When low levels of sodium tripolyphosphate are used, insoluble calcium and magnesium salts of tripolyphosphate, e.g. \(\text{Ca}_5\left(\text{P}_3\text{O}_{10}\right)_2\), are formed which precipitate out.

\[
2\text{Na}_5\text{P}_3\text{O}_{10(aq)} + 5\text{Ca}^{2+}_{(aq)} \rightarrow \text{Ca}_5(\text{P}_3\text{O}_{10})_2(s) + 10\text{Na}^+_{(aq)}
\]

At higher concentrations of sodium tripolyphosphate, a soluble 1:1 complex \([\text{CaP}_3\text{O}_{10}]^{3-}\) is formed. This effect it is known as the threshold effect.

\[
\text{Na}_5\text{P}_3\text{O}_{10(aq)} + \text{Ca}^{2+}_{(aq)} \rightarrow [\text{CaP}_3\text{O}_{10}]^{3-}_{(aq)} + 5\text{Na}^+_{(aq)}
\]

It is therefore important that the concentration of sodium tripolyphosphate is sufficient to form the soluble complex rather than the insoluble salt.
In some countries, the use of phosphates is restricted because they can cause eutrophication in high concentrations. This is the overgrowth of plants in watercourses with consequent lack of oxygen in the water which kills fish. So formulations of the same brand may well be different in different areas.

**The pH of the solution**

Many cleaning products act best in somewhat alkaline solution.

This is because alkalis:

- emulsify grease by reacting with insoluble fatty acids to form ionic salts which are soluble. Figure 11 shows how insoluble fatty acids react with hydroxide ions and are broken down into soluble ions which can then form ionic salts.

\[
\text{Figure 11: Breaking down insoluble fatty acids into soluble ions}
\]

- protect the metal of washing machines and dishwashers from acid corrosion
- help to reduce re-deposition of dirt that has been removed by coating particles of it with negatively charged hydroxide ions – this means the dirt particles repel each other and remain in suspension rather than clumping together to form large aggregates which would tend to precipitate out onto clothes *etc*

**Question 14**

Grease contains long chain fatty acids such as \(\text{CH}_3(\text{CH}_2)_{14}\text{COOH}\). These are weak acids.

a) Write the equation for the reaction of \(\text{CH}_3(\text{CH}_2)_{14}\text{COOH}\) with a hydroxide ion, \(\text{OH}^-\).

b) Explain why the product is more soluble than the original fatty acid.
c) Explain what is meant by a weak acid. Remember how to deal with the concentrations of solids and pure liquids.

**Question 15**
An aqueous solution of sodium citrate will have an alkaline pH. Explain this observation. Use Na\(_3\)Cit to represent sodium citrate.

**Suspension and regrowth inhibition**

**Suspension**
Another important ingredient of Calgon® is polycarboxylate. This is a polymer based on the monomer whose non-systematic name is acrylic acid. Its skeletal formula is shown in Figure 12.

![Structure of acrylic acid](image)

**Figure 12: Structure of acrylic acid**

**Question 16**

a) What is the systematic name of acrylic acid.

b) Draw the displayed formula of acrylic acid (one that shows every atom and every bond).

c) What type of polymer will be formed by acrylic acid?

d) What feature of the acrylic acid molecule gives rise to this type of polymerisation?

A short section of a polyacrylate (polycarboxylate) molecule is shown in Figure 13.

![A section of a polyacrylate molecule](image)

**Figure 13: A section of a polyacrylate molecule**

This polymer can also complex metal ions in the same way as can citrate ions.

Notice that in solution COOH groups of the polymer exist as COO\(^-\) ions. These ions can form a coating around any calcium carbonate that has formed in the wash mixture and hold it in suspension. This stops it depositing on parts of the machine, such as the heater, or on fibres of clothing.
This is similar to the complexing effect of citrate and phosphate ions on Ca$^{2+}$, but as the polymer molecule is larger, it can hold larger aggregates of limescale in suspension. Figure 14 shows this schematically.

![Polymer coating limescale](image)

Figure 14: Suspension inhibition. The polymer coats the limescale particle and prevents its deposition

**Regrowth inhibition**
This works in the same way as discussed above. Calcium carbonate will not deposit on parts of the machine that become coated with polyacrylate.

**Other ingredients**
The ingredients of Calgon® dual action tablets are shown in Table 1.

<table>
<thead>
<tr>
<th>Ingredients:</th>
</tr>
</thead>
<tbody>
<tr>
<td>SODIUM CITRATE</td>
</tr>
<tr>
<td>SODIUM POLYACRYLATE</td>
</tr>
<tr>
<td>SODIUM SULFATE</td>
</tr>
<tr>
<td>CELLULOSE</td>
</tr>
<tr>
<td>PEG-130 - PEG-150</td>
</tr>
<tr>
<td>AQUA</td>
</tr>
<tr>
<td>PEG-200</td>
</tr>
<tr>
<td>COLORANT</td>
</tr>
</tbody>
</table>

Table 1: Ingredients of Calgon® dual action tablets
The ingredients of other formulations of Calgon®, such as that in Figure 16, can be found at the Reckitt Benckiser website:


**Figure 16: One of the formulations of Calgon**

**PEG**

PEG is short for polyethyleneglycol. This is a family of polymers with the formula HO(CH₂CH₂O)nH. They help bind together the ingredients into a tablet which does not crumble and also have the effect of reducing the formation of dust during manufacture.

Polyethyleneglycols are made from epoxyethane, which is in turn made from ethene by catalytic oxidation with the oxygen from air. Epoxyethane has the formula

\[
\begin{align*}
H_2C & \quad CH_2 \\
\end{align*}
\]

The number after PEG is its approximate relative molecular mass. So PEG 200 has \( M_r = 200 \).

**Sodium sulfate**

Sodium sulfate is added to Calgon® as a so-called filler. It does not have any water softening effect. It is used to bulk out the active ingredients so that it is easier to measure out the required quantity. So a spoonful, for example, might contain the correct amount of the active ingredients.

**Other ingredients**

In tablet formulations of Calgon®, cellulose is added. This swells when it is exposed to water and helps the tablet to break up when added to the wash.
Aqua is shorthand for water and colours are also added to make the product look attractive and distinctive.

**Experimental work**
The following are some suggestions for experimental work to support the above material.

*Figure 17: Experimental work in a school laboratory*

If the water in your area is soft, samples of hard water can be made as follows (taken from the CLEAPSS Recipe Card):

**Permanently hard water**
Measure 0.45 g of calcium sulfate-2-water and add it to 1000 cm$^3$ of water in a bottle and leave it overnight to dissolve.

**Temporary hard water**
Filter 130 cm$^3$ of freshly-made calcium hydroxide solution. Bubble carbon dioxide though the solution so that calcium carbonate first precipitates and then, as more carbon dioxide is passed, re-dissolves to form calcium hydrogen carbonate. Dilute this clear solution to 1000 cm$^3$.

**Demonstrating the mineral content of hard water**
Evaporate a few drops of tap water, hard water and distilled (or de-ionised) water on a watch glass and note the deposits formed.
Testing water hardness
This can be done by adding soap solution to various water samples. For full instructions see http://www.rsc.org/learn-chemistry/resource/res00000426/testing-the-hardness-of-water.

Demonstrating the threshold effect
Apparatus and chemicals
1 beaker 2 dm$^3$
1.5 dm$^3$ of distilled or de-ionised water
0.99 g of calcium chloride-2-water (EYE IRRITANT)
3.5 g of potassium tripolyphosphate (SKIN/EYE IRRITANT, POSSIBLY HARMFUL IF SWALLOWED)

Method
Eye protection should be used while handling the solid salts.

Using a magnetic stirrer
- fill the beaker with 1.5 dm$^3$ of distilled or de-ionised water
- add 0.99 g of calcium chloride-2-water
- stir until the salt is completely dissolved
- add 1.5 g of potassium tripolyphosphate
- stir for 30 seconds, the solution will become opaque because of the formation of the insoluble salt of phosphate and calcium
- after 30 seconds add 2 g of potassium tripolyphosphate and keep stirring, the solution will turn back to clear

Further information
Calgon® is sold in the UK by Reckitt Benckiser (www.calgon.co.uk/). There are other branded products which work in a similar way.

Acknowledgements
The Royal Society of Chemistry wishes to thank Chris Jones, Fabio Costiniti and Liliana Oliva of Reckitt Benckiser for help in preparing this material.

The Royal Society of Chemistry gratefully acknowledges that this project was initially supported by Reckitt Benckiser in 2007. Reckitt Benckiser conducted a final review in 2013 so please note that certain information may be out of date.
QUESTIONS AND ANSWERS

Question 1: Explain why rainwater is 'effectively distilled'.
Water is evaporated from the sea by the heat of the sun. It then condenses at the lower temperatures found high up in the atmosphere.

Question 2: Even rainwater is not chemically pure when it falls. Suggest what else may be dissolved in it.
All of the gases present in the air may be dissolved in rainwater. Particularly significant is carbon dioxide as it is quite soluble. Its presence makes rainwater naturally acidic. Gases caused by human activities will also be present. These include sulfur dioxide, from burning fossil fuels, and nitrogen oxide, from the combination of nitrogen and oxygen at the high temperatures in internal combustion engines and other combustion processes.

Question 3
a) Write the expression for the equilibrium constant $K_c$ for the equilibrium

$$\text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3^-(\text{aq}) \quad \Delta H^\text{<0}$$

Remember how to deal with the concentrations of solids and pure liquids.

$$K_c = \frac{[\text{Ca}^{2+}(\text{aq})]_\text{eqm}[\text{HCO}_3^-(\text{aq})]_\text{eqm}^2}{[\text{CO}_2(\text{aq})]_\text{eqm}}$$

Remember that the concentrations of pure liquids (water) and solids (calcium carbonate) cannot change and by convention they are incorporated into the value of the equilibrium constant.

b) What are the units of the equilibrium constant in the previous question?
$\text{mol}^2 \text{dm}^{-6}$

c) Apart from changing the temperature, what other ways can you suggest of reducing $[\text{Ca}^{2+}(\text{aq})]$?
Reducing the concentration of carbon dioxide.

Question 4
On the map in Figure 5, the units of water hardness are given as 'mg/l of calcium carbonate equivalent'. Another unit often used is 'mg/l of calcium'.

100 mg/l as calcium carbonate equivalent is the same as 40 mg/l of calcium. Use the formula of calcium carbonate ($\text{CaCO}_3$) and the relative atomic masses ($\text{Ca} = 40; \text{C} = 12; \text{O} = 16$) to explain why these two measurements are equivalent. 1 mg/l is the equivalent of 1 mg dm$^{-3}$.

The relative molecular mass (relative formula mass) of calcium carbonate is $40 + 12 + (3 \times 16) = 100$ and the relative atomic mass of calcium is 40. So every 100 mg of calcium carbonate contains 40 mg of calcium. This is, of course, present as Ca$^{2+}$ ions, not calcium atoms!
Question 5
The method of reporting hardness as ‘calcium carbonate equivalent’ makes the assumption that all the calcium ions in the water are derived from (or associated with) carbonate ions, *ie* that all the calcium is actually part of calcium carbonate.

If a sample of water contained 272 mg/l (272 mg dm$^{-3}$) of calcium sulfate (CaSO$_4$), how would this be reported as ‘calcium carbonate equivalent’? (Relative atomic mass S = 32)
The relative molecular mass (relative formula mass) of calcium sulfate is 40 + 32 + (4 x 16) = 136. So 136 mg CaSO$_4$ contain 40 mg Ca, the same as 100 mg CaCO$_3$. So the calcium carbonate equivalent of 272 mg CaSO$_4$ would be 200 mg/l.

Question 6
Explain why aluminium forms Al$^{3+}$ ions and silicon might form Si$^{4+}$ ions.
Silicon has four electrons in its outer shell, aluminium has three.

Question 7
The silicon atoms do not in fact form true Si$^{4+}$ ions, there is a degree of covalent bonding with the oxygen atoms in the structure. Explain why true Si$^{4+}$ ions are unlikely to form.
A great deal of energy would be required to remove four electrons from the silicon atom.

Question 8
Explain why Si$^{5+}$ and Al$^{4+}$ will never form.
To form either of these ions would mean removing an electron from an inner shell as well as removing all the outer electrons. This would require an enormous amount of energy.

Question 9
a) What will be the charge on the complex ion formed from the citrate ion and a calcium ion?
-1

b) Will it be attracted to a hydrogencarbonate ion?
No, both are negatively charged.

Question 10
Would you expect the citrate/calcium ion to be soluble in water? Explain your answer.
Yes. It is charged, and also has several oxygen atoms which can form hydrogen bonds with water molecules as well as an –OH group which can also do this.

Question 11
Write the electron arrangement (1s$^2$, 2s$^2$ etc) of a Ca atom and Ca$^{2+}$ ion. What noble gas configuration does Ca$^{2+}$ have?
What empty orbitals might be used on the Ca$^{2+}$ ion to accept lone pair electrons from the citrate ion?
Ca atom - 1s², 2s², 2p⁶, 3s², 3p⁶, 4s²; Ca²⁺ ion - 1s², 2s², 2p⁶, 3s², 3p⁶. The Ca²⁺ ion has the same electron configuration as Ar.

The 4s and 3d orbitals can be used to accept lone pair electrons from the citrate ion.

**Question 12**
The two C=O bond lengths in the COO⁻ groups of sodium citrate are identical rather than one shorter than the other. Explain this observation.

The electrons in the π orbital of the C=O are delocalised over the whole O=C-O system giving two bonds of length intermediate between C-O and C=O.

**Question 13**
Considering its electronic structure and the formation of complexes, in what ways will Mg²⁺ resemble a Ca²⁺ ion?
- resemble a Ca²⁺ ion?
- differ from a Ca²⁺ ion?
  - It has a noble gas electron configuration.
  - It is smaller (as it has one fewer full shell of electrons). It has no d orbitals of energy suitable to form bonds with the complexing agent.

**Question 14**
Grease contains long chain fatty acids such as CH₃(CH₂)₁₄COOH. These are weak acids.

a) Write the equation for the reaction of CH₃(CH₂)₁₄COOH with a hydroxide ion, OH⁻.

\[
\text{CH₃(CH₂)₁₄COOH} + \text{OH}⁻ \rightleftharpoons \text{CH₃(CH₂)₁₄COO}⁻ + \text{H₂O}
\]

b) Explain why the product is more soluble than the original fatty acid.

The product is a negative ion rather than a neutral molecule. It will therefore be hydrated by and form hydrogen bonds with water molecules more effectively than a neutral molecule consisting largely of a non-polar hydrocarbon.

c) Explain what is meant by a weak acid.

A weak acid is one that is only partially dissociated in solution,

\[e.g. \text{CH₃(CH₂)₁₄COOH}_{(aq)} \rightleftharpoons \text{CH₃(CH₂)₁₄COO}⁻_{(aq)} + \text{H}⁺_{(aq)}\]

**Question 15**
An aqueous solution of sodium citrate will have an alkaline pH. Explain this observation. Use Na₃Cit to represent sodium citrate.

Sodium citrate is the salt of a weak acid, citric acid, with a strong alkali (sodium hydroxide). So acid hydrolysis will take place, eg

\[
\text{Na₃Cit}_{(aq)} + \text{H₂O}_{(l)} \rightleftharpoons \text{Na}⁺_{(aq)} + \text{OH}⁻_{(aq)} + \text{Na₂HCit}_{(aq)}
\]

The free OH⁻ ions make the solution alkaline.

**Question 16**
a) What is the systematic name of acrylic acid.

Propenoic acid
b) Draw the displayed formula of acrylic acid (one that shows every atom and every bond).

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{C} \overset{\text{C}}{\text{O}} \overset{\text{C}}{\text{O}} \overset{\text{C}}{\text{O}} \\
\text{H} \\
\end{array}
\]

c) What type of polymer will be formed by acrylic acid?
An addition polymer

d) What feature of the acrylic acid molecule gives rise to this type of polymerisation?
\( \text{C} = \text{C} \)