THE INSTITUTE OF EDUCATION

Chemistry

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Higher Level

2020-21

Hardness in Water

HARDNESS IN WATER

In some parts of Ireland when soap is put into water, lather is produced, however in other parts of Ireland instead of lather, a scum is produced. This 'scum' is caused by hardness present in the water supply.

This hardness is caused by Ca^{2+} and Mg^{2+} ions.

The equation to represent this formation of scum due to hardness is:

$$2C_{17}H_{35}COONa + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca(\downarrow) + 2Na^{+}$$

sodium stearate (soap) — calcium stearate (scum)

The Ca^{2+} (or Mg^{2+}) ions that cause the hardness in the water combine with soap to form the scum and sodium ions (these sodium ions do not cause hardness). Lather will only be produced when all of the calcium ions are gone and so a lot of soap needs to be used.

HARD WATER **Defn – hard water is water that does not form a lather easily with soap.**

There are two types of hardness depending on the cause.

1. **Temporary hardness** – this is caused by the presence of **calcium hydrogencarbonate**. This type of hardness enters the water when carbonic acid (acid rain) reacts with limestone in the ground.

$$H_2CO_3 + CaCO_3 \rightarrow Ca(HCO_3)_2$$

carbonic acid — limestone — calcium hydrogencarbonate

This type of hardness can be removed by **boiling.** The calcium hydrogencarbonate that causes the temporary hardness is soluble in water but when heated it forms insoluble calcium carbonate which is responsible for the 'fur' or 'scale' that coats the elements of kettles, washing machines, dishwashers or can build up and block pipes. The equation to show that temporary hardness can be removed by boiling is:

$$Ca(HCO_3)_2 \xrightarrow{BOIL} CaCO_3(\downarrow) + H_2O + CO_2$$

soluble — insoluble scale

2. **Permanent hardness** – this is caused by the presence of **calcium sulfate**, $CaSO_4$, or **magnesium sulfate**, $MgSO_4$.
   This type of hardness cannot be removed by boiling, as **sulfates do not decompose on heating.**

METHODS OF REMOVING BOTH TYPES OF HARDNESS

1. **Distillation** – the water is boiled off through a Liebeg condenser and the hydrogencarbonates and sulfates remain in the flask. This is too expensive on a large scale.
2. **Addition of washing soda crystals**, $Na_2CO_3.10H_2O$. The carbonate ions in the washing soda crystals react with the calcium ions that cause the hardness (both temporary and permanent) and thus remove them.

$$Na_2CO_3 + Ca^{2+} \rightarrow CaCO_3 + 2Na^+$$

3. **Ion exchange resins** –

(a) A domestic resin can be represented by Na_2R. When the hard water passes through these resins, the calcium ions that cause the hardness are 'swapped' with the sodium ions in the resin, thereby removing the cause of hardness as the calcium ions remain in the resin.

$$Na_2R + Ca^{2+} \rightarrow CaR + 2Na^+$$

Eventually the resin becomes full of calcium ions and so must be soaked in a concentrated solution of sodium chloride which will replace the calcium ions in the resin with sodium ions. Then it is ready for use again.

(b) Another type of resin will remove all of the ions in the water (not just the calcium/magnesium ions) to produce <u>'deionised' water</u>. This involves two resins, a cation exchange resin and an anion exchange resin. The cation exchange resin contains H^+ ions which will swap with any positive ions in the water, thus removing the positive ions. The anion exchange resin contains OH^- ions which will swap with any negative ions in the water, thus removing the negative ions. The H^+ ions combine with the OH^- ions to produce water.

Cation exchange resin - $RH + \text{cation} \rightarrow \text{H}^+ + spent\ \text{resin}$

Anion exchange resin - $ROH + anion \rightarrow OH^- + spent\ \text{resin}$

Then - $H^+ + OH^- \rightarrow H_2O$

DEIONISED WATER VERSUS DISTILLED WATER

Deionised water	**Distilled water**
No ions	No ions
Has dissolved gases and organic material	No dissolved gases and organic material

Advantages of hard water

1. Tastes better.
2. Contains calcium, which is good for bones and teeth.
3. Good for the brewing industry (better beer!)

Disadvantages of hard water

1. 'Dirty' looking scum produced with soap.
2. Wastes soap.
3. Produces 'scale' that can block pipes and made the heating elements useless.

EXPERIMENT – ESTIMATION OF THE TOTAL HARDNESS IN A WATER SAMPLE USING EDTA.

Theory behind the experiment – as we have already learned, hardness in water is caused by the presence of calcium and magnesium hydrogencarbonates or sulfates. This hardness can be removed by titrating the hard water sample against a standard solution of **ethylenediaminetetraacetic acid, EDTA** for short. We use the disodium salt of the acid when doing the titration. This can be represented by the formula Na_2H_2X . When the disodium salt reacts with the calcium and magnesium ions a complex is formed, thus removing the hardness as follows:

$$Na_2H_2X + Ca^{2+} \rightarrow \underbrace{CaH_2X}_{\text{complex}} + 2Na^+$$

The sodium ions that are released do not cause hardness. As we can see from the equation EDTA and calcium ions react in **a 1:1 ratio**. The following points must be learned for the titration.

- The **indicator** in the titration is **Eriochrome Black T (or Solochrome Black T).** This is a black powder. When this indicator is added to a water sample containing hardness a **wine/ red colour** is observed. When all the hardness has been removed a **blue colour** is observed. So the colour change to indicate the end point is wine/red to blue.
- The end point of this titration is difficult to detect and so must be carried out at a particular pH. A solution called a **buffer solution of pH 10** is added to the water sample in the conical flask to give the required pH.
- EDTA is **stored** in a **plastic container** as it has the ability to extract metal ions from glass if left in a glass container for too long.
- Even though the hardness is caused by the presence of calcium and magnesium hydrogencarbonates or sulfates, for simplicity sake we attribute **all hardness** as being caused by **calcium carbonate**, $CaCO_3$ which has a Mr of 100.

Apparatus – pipette, burette, conical flask, retort stand, buffer solution pH 10, wash bottle with deionised water.

Materials – water sample, EDTA solution (0.01M), Erichrome Black T.

Method –

1. The burette was washed with deionised water to clean it and then with some of the 0.01M EDTA solution to prevent dilution of the solution.
2. The burette was then filled using a funnel observing the usual precautions.
3. This was then clamped vertically.
4. The pipette was washed with some deionised water to clean it and then with the water sample to prevent dilution of the sample.
5. 25 cm^3 of the hard water sample were pipetted into the conical flask by touching the tip of the pipette off the inside of the conical flask.

6. 1 cm^3 of the buffer solution of pH 10 was added into the conical flask.
7. A pinch of Erichrome Black T was then added into the conical flask also.
8. The solution in the conical flask is now a wine/red colour due to hardness present.
9. The titration was carried out in the usual manner.
10. The endpoint of the titration occurred when the wine/red solution in the conical flask turned blue. This was repeated two more times.

Results –

Rough titration	**15.4** cm^3
1st titre	15.2 cm^3
2nd titre	15.3 cm^3

Average titre = 15.25 cm^3

Water sample	**EDTA**
$V_1 = 25cm^3$	$V_2 = 15.25cm^3$
$M_1 = x$	$M_2 = 0.01M$
$n_1 = 1$	$n_2 = 1$

$$\frac{V_1 \times M_1}{n_1} = \frac{V_2 \times M_2}{n_2}$$

$$\frac{25 \times x}{1} = \frac{15.25 \times 0.01}{1}$$

$x = 0.0061 mol/l$ of $CaCO_3$

$moles \times M_r(CaCO_3) = grams$

$0.0061 \times 100 = 0.61 g/l$ of $CaCO_3$

Multiply by 1000 to get mg/l

$0.61 \times 1000 = 610 mg/l$

Since 1mg/l = 1 p.p.m. then

610 p.p.m. is the total hardness in the water sample.