Name _____ Date _____

GRCI CHEMISTRY

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Double Replacement

HARD WATER

The deposition of scale in boilers and kettles, the inability to properly wash clothes in the presence of sufficient soap, the formation of bathtub rings and the inability to raise suds from soap are all caused by the presence of the metal **ions of calcium and magnesium**: Ca^{2+} and Mg^{2+}. It is these metal ions that cause the **"hardness"** of water. When soap is placed in hard water a reaction takes place which forms an insoluble scum.

Sources of the hardness are **calcium carbonate**, $CaCO_3$ (limestone) and **magnesium carbonate**, $MgCO_3$ (in dolomite along with $CaCO_3$) in the land over which surface water flows. Both **calcium carbonate** and **magnesium carbonate** are insoluble in water. However, a soluble calcium or magnesium compound is formed when there is **carbon dioxide** dissolved in rain **water**. An example of the reaction for **calcium carbonate** follows:

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \qquad (1)$$

Calcium carbonate + water + carbon dioxide ➡ calcium hydrogen carbonate

The soluble **calcium hydrogen carbonate** forms ions when it dissolves.

$$Ca(HCO_3)_2 \rightarrow Ca^{2+} + 2\ HCO_3^- \qquad (2)$$

calcium hydrogen carbonate ➡ calcium ion + hydrogen carbonate ion

Due to the fact that **calcium hydrogen carbonate** dissolves the compound can be transported along with the water. The insoluble **calcium ions** in **calcium carbonate** would never move (or be dissolved in water) except for the fact that **carbon dioxide and water** together can react with **calcium carbonate**.

An insoluble scum forms when soap, **sodium stearate**, $NaC_{17}H_{35}COO$, reacts with $Ca(HCO_3)_2$ in a <u>double replacement reaction</u>.

sodium stearate + calcium hydrogen carbonate ➡ sodium hydrogen carbonate + calcium stearate (3)

Calcium stearate is a scum which precipitates and sticks to bathtubs.

The compound $Ca(HCO_3)_2$ is easily decomposed, even in solution. If the hard water is boiled, or even heated (as in a hot water tank) reaction **(1)** is reversed. This releases the CO_2 and precipitates the $CaCO_3$ as scale. Due to this reaction we call it **temporary hardness**. Any temporary hard water that has been boiled will have lost its hardness because it has lost the soluble $Ca(HCO_3)_2$. The same reactions take place with $Mg(HCO_3)_2$. If reaction **(1)**, involving $CaCO_3$ and $MgCO_3$, was the only source of hardness then a simple heating of temporary hard water would get rid of the hardness.

Natural waters also pick up **calcium sulphate**, $CaSO_4$ and **calcium chloride**, $CaCl_2$ which are both soluble and are not affected by heating. Both of these compounds react in a double replacement reaction similar to reaction **(3)** to form scum but heating will not rid the water of this hardness. This is called **permanent hardness.**

The difficulties with hard water (both types) have led to water softening. Water softeners work by removing the Ca^{2+} and Mg^{2+} ions by a method called ion exchange. There are two compounds (ion exchange resins) which are used for trapping the Ca^{2+} and Mg^{2+} ions. They are **sodium zeolite** and **sodium sulphonated polystyrene**. **Zeolite** and **sulphonated polystyrene** are very complex and we will use short forms to represent them: **Ze^{2-} and Sp^{2-}** respectively. Unlike most sodium compounds **sodium zeolite** and **sodium sulphonated polystyrene** will not dissolve in water.

How does the softener work? The following is an example. In operation the hard water is passed through a column packed with **sodium zeolite.** The following double replacement reaction occurs.

$$Na_2Ze + CaSO_4 \rightarrow Na_2SO_4 + CaZe \qquad (4)$$

sodium zeolite + calcium sulphate ➡ sodium sulphate + calcium zeolite

The Na_2SO_4 dissolves and flows out of the softener while the CaZe is trapped because it is insoluble. The **sodium ions** have been replaced by the **calcium ions**. An increased concentration of **sodium ions** appears in the water that comes out of the water softener. **Sodium ions** do not make water soft. (*Recent research has shown that hard water is beneficial to health and the availability of excess **sodium ions** can be harmful. It is not recommended that one drink soft water.*)

Needless to say, a point is eventually reached when all of the **sodium ions** in the softener have all been replaced by the **calcium or magnesium ions** so that hard water will be unaffected. At this point, it is necessary to recharge the resin by stripping off the hardness ions. This is done by flushing the softener tank with concentrated **sodium chloride** solution, which is obtained by directing a flow of water through the second tank containing salt crystals. The following double replacement reaction occurs.

$$CaZe + 2\,NaCl \rightarrow CaCl_2 + Na_2Ze \qquad (5)$$

calcium zeolite + sodium chloride ➡ calcium chloride + sodium zeolite

The **calcium chloride** is washed down the drain usually at night when we don't need water for washing etc.

In recent years the use of soap has decreased in favour of detergents. Detergents in contrast to soaps do not form precipitates with the ions of calcium and magnesium. The need for totally softened water is lessened. But detergents caused an environmental problem because detergents worked best if they contained "**phosphates**" which encouraged the growth of algae which can lead to a destruction of aquatic life.

Questions

1. What ions cause the hardness of water?

2. What compounds found in soil react to form compounds of **calcium** and **magnesium** which cause hardness?

3. (a) Using reaction (**1**) as an example, write out the balanced chemical equation which shows **magnesium carbonate** turned into soluble **magnesium hydrogen carbonate**.

   (b) This kind of reaction is called a **composition reaction** not a **simple composition reaction**. Please explain why?

4. Write out the balanced chemical equation for reaction (**3**).

5. (a) What is the chemical name of a scum, which is named in this article, that forms when hard water reacts with soap?

   (b) Knowing the ions which make water hard, state the name of another chemical which is also a bathtub scum.

6. What method is effective for removing temporary hardness from water?

7. What chemicals cause permanent hardness?

8. Using equation (**4**) as an example write out the balanced equation for the reaction of **sodium zeolite** and **calcium hydrogen carbonate**?

9. Using equation (**5**) as an example write out the balanced equation for the reaction of **sodium chloride** and **calcium sulphonated polystyrene**, **CaSp**.

10. What chemicals are wash down the drain when the water softener is being recharged?