Hardness

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Hard and soft water

Soft water forms a lather easily with soap.

Hard water needs more soap to form a lather, adding additional cost to cleaning processes.

This is because dissolved chemicals in the hard water react with soap to form a scum.

SOAP

Soap molecules have two distinctly different ends;

HYDROPHOBIC

“water hating”

HYDROPHILIC

“water liking”

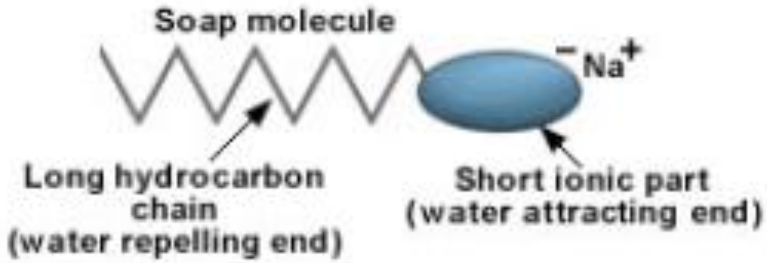
CHAIN OF CARBON ATOMS

attracts oil and grease

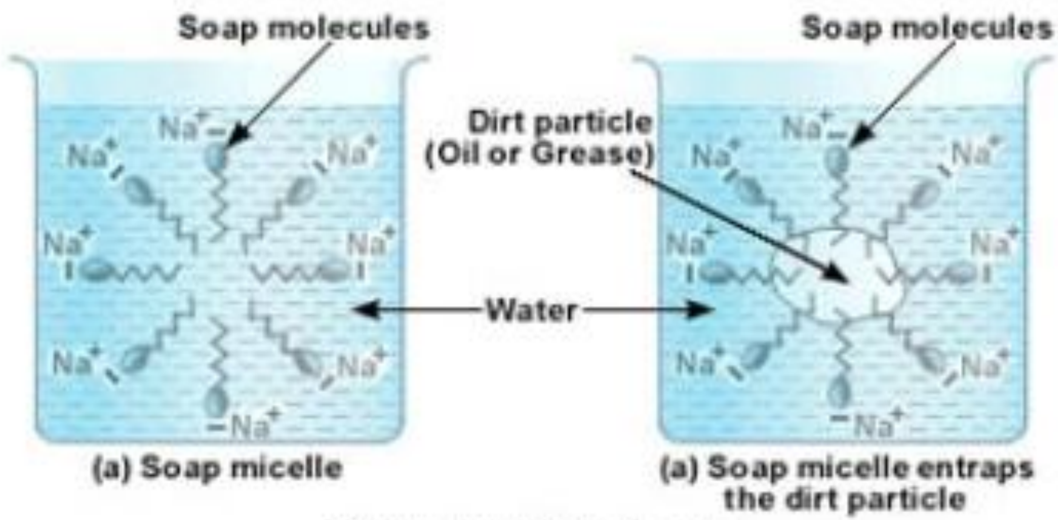
attracts water

When soap is placed in hard water, it reacts with the calcium and magnesium ions to produce an unsightly, insoluble grey scum.

The scum is a calcium compound and is thus removed from the water.
When all the hardness has been removed, the soap can act in the normal way.



Representation of a soap molecule.



Cleansing action of soap

Limescale

When hard water is heated, the dissolved calcium hydrogen carbonate decomposes to form solid calcium carbonate.

These deposits of calcium carbonate are called **limescale**.

calcium hydrogen carbonate	➔	**calcium carbonate**	+	**water**	+	**carbon dioxide**
$Ca(HCO_3)_2 (aq)$	➔	$CaCO_3 (s)$	+	$H_2O (l)$	+	$CO_2 (g)$

Limescale can block pipes and coat the heating elements in kettles, washing machines and heaters.

Limescale is a poor heat conductor, and reduces the efficiency of appliances.

Hardness of Turkey's water supplies

Water Hardness Rating

mg/L as $CaCO_3$	Degree of Hardness
0-75	Soft water
75-150	Moderately hard water
150-300	Hard water
>300	Very hard water

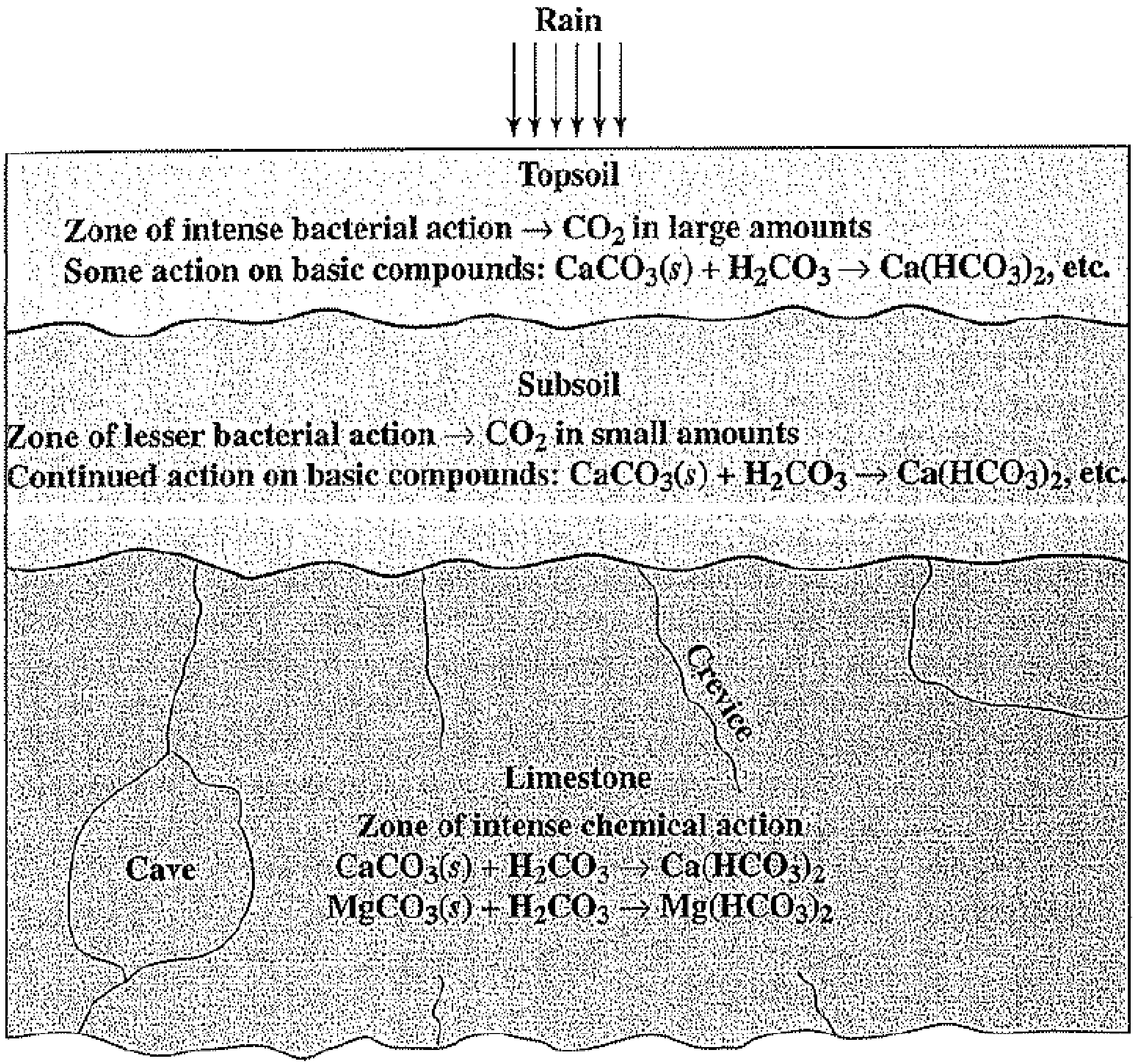
*Hardness is normally expressed in terms of CaCO3 as is alkalinity

Causes

Cations causing hardness	Anions
Ca^{2+}	HCO_3^-
Mg^{2+}	SO_4^{2-}
Sr^{2+}	Cl^-
Fe^{2+}	NO^-
Mn^{2+}	SiO_3^{2-}

Principle cations causing hardness in water and the major anions associated with them

Source of Hardness



Public Health Significance of Hard Water

Hard water can be good for health:

- calcium is needed for healthy bones and teeth
- magnesium is needed for effective metabolism.

Some studies have also shown that people living in hard water areas are less likely to suffer from heart disease.

Disadvantages of Hard Water-(Again)

Soap is less effective in hard water because the calcium ions react with the stearate ions in soap to form a precipitate, calcium stearate ("soap scum").

When temporarily hard water is heated, calcium carbonate ("scale") is formed. This solid can reduce the efficiency of tea kettles and block hot water pipes.

Methods of Determination

1. Complete Cation Analysis

- Most accurate

- Calculation of the hardness caused by each ion is performed by use of the general formula:

$$\text{Hardness (mg/L) as } CaCO_3 = M^{2+} \text{ (mg/L)} \times \frac{50}{\text{EW of } M^{2+}}$$

where M^{2+} represents any divalent metallic ion and EW represents equivalent weight

Measurement of individual cations

Calculation from concentration of divalent cations.

* Atomic Absorption Specttroscopy (AAS)
* Inductively Coupled Plasma (ICP)
* Ion Chromatography
* Ion Specific Electrodes (ISE)

Example of Complete Cation Analysis

* Calculate the hardness of a water sample with the following analysis:

Cation	Concentration (mg/L)	Anion	Concentration (mg/L)
Na^+	20	Cl^-	40
Ca^{2+}	15	SO_4^{2-}	16
Mg^{2+}	10	NO_3^-	1
Sr^{2+}	2	Alkalinity	50

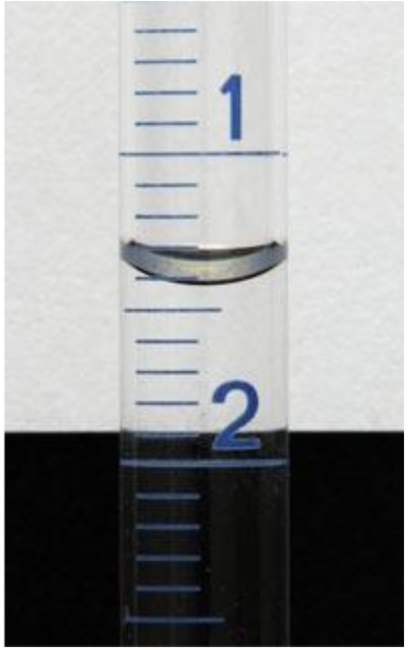
Example of Complete Cation Analysis

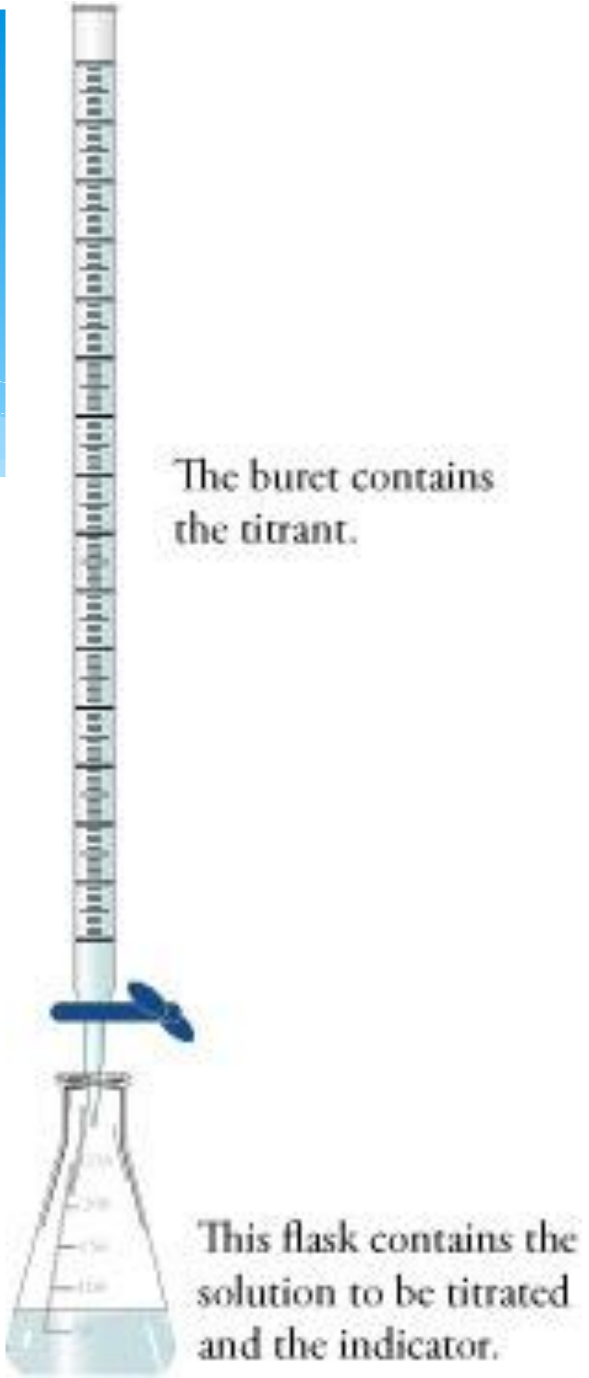
Cation	**EW**	**Hardness, mg/L as $CaCO_3$**
Ca^{2+}	20.0	(15)(50)/(20.0) = 37.5
Mg^{2+}	12.2	(10)(50)/(12.2) = 41.0
Sr^{2+}	43.8	(2)(50)/(43.8) = 2.3
		Total hardness = 80.8

Methods of Analysis

2. Titrimetric Method

* Burette
    * A piece of glassware designed to deliver known amounts of liquid into another container

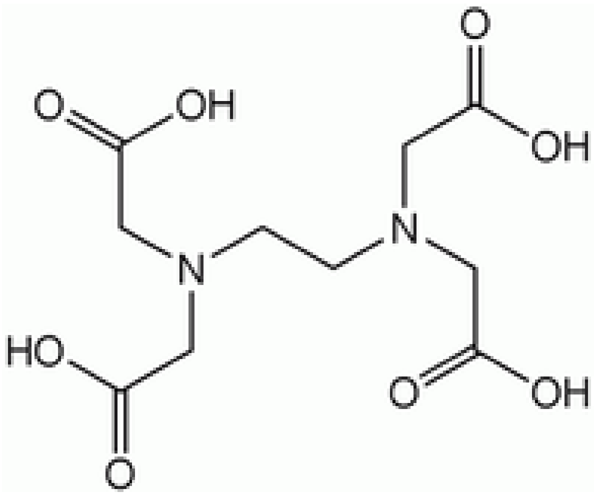


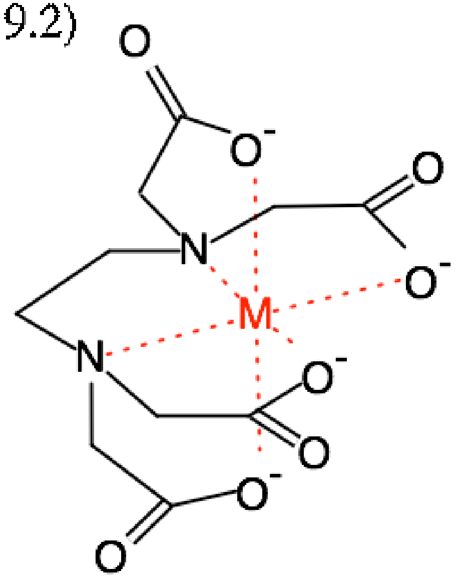


EDTA

* Ethylenediaminetetracetic acid
* Chelating agent
  * Substance whose molecules can form several bonds to a single metal ion
  * Forms extremely stable complex ions with Ca2+, Mg2+

$$M^{2+} + EDTA \rightarrow [M \cdot EDTA]_{complex} \quad (19.2)$$

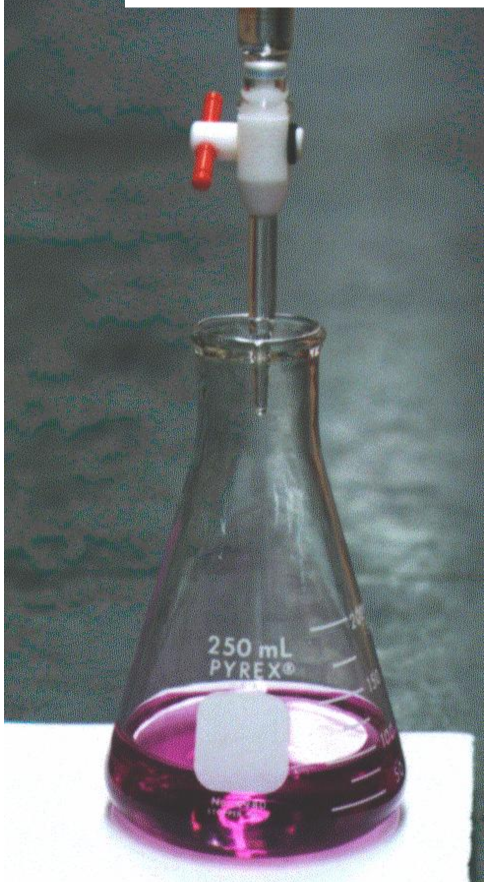


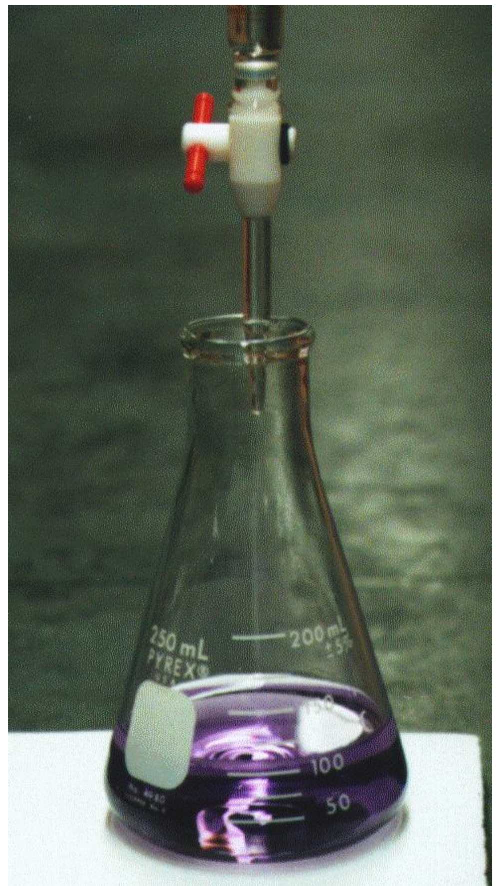


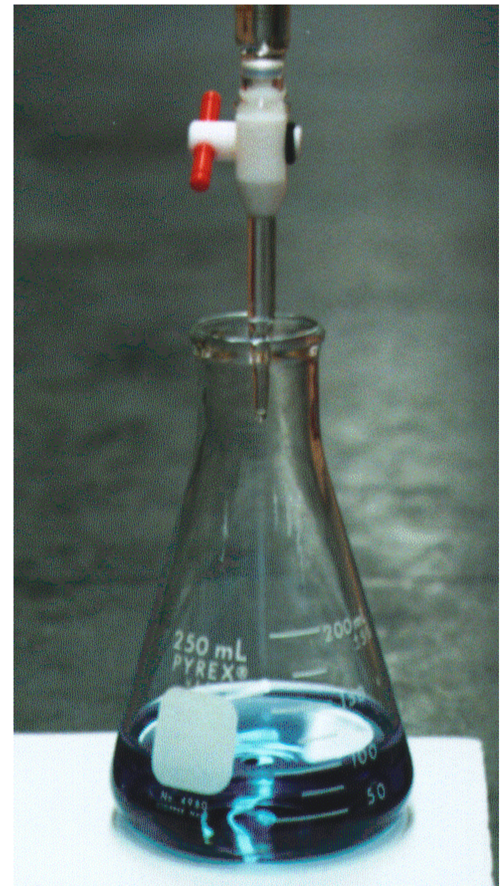
EBT

* Eriochrome Black T
  * Indicator

$$\underset{\text{Blue}}{M^{2+} + \text{Eriochrome Black T}} \rightarrow \underset{\text{Wine red}}{(\text{M} \cdot \text{Eriochrome Black T})_{\text{complex}}} \qquad (19.3)$$







$$\text{Hardness (EDTA) mg CaCO}^3\text{/L} = \frac{A \times N \times 50{,}000}{\text{mL sample}}$$

Where:
A = mL EDTA titrant (6.4)
N = normality of EDTA titrant

- 50.0 mL tap water sample.
- 13.75 mL EDTA used in the titration.
  a) Calculate the moles of EDTA used.
  b) Calculate the molarity of metal ion present in the tap water sample (Remember: EDTA binds to metal ions on a 1:1 molar ratio).
  c) Find the ppm calcium ion concentration in the sample based on your results from question b).

Types of Hardness

* With respect to metallic ion
  * Calcium Hardness
  * Magnesium hardness
* With respect to the anions associated with metallic ions
  * Carbonate hardness
  * Noncarbonate hardness

Calcium – Magnesium Hardness

* Ca , Mg cause greatest portion of hardness.
* Amount of Mg^{2+} should be known for lime soda ash softening.
* Ca-Mg → Calculated from complete analysis
* Total hard.– Calcium hard. = Magnesium hard.

- Types of Hardness

1) Temporary:- or Carbonate Hardness

Water that contains bicarbonate of calcium and magnesium or of both

- removed by boiling

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$

2) Permanent :- or Non- Carbonate Hardness

Contains chlorides or sulphates of calcium or magnesium or of both

- Can not be removed by boiling

$$CaCl_2 \rightarrow Ca^{+2} + 2Cl^{-1}$$

$$MgSO_4 \rightarrow Mg^{+2} + SO_4^{-2}$$

Carbonate and Noncarbonate Hardness

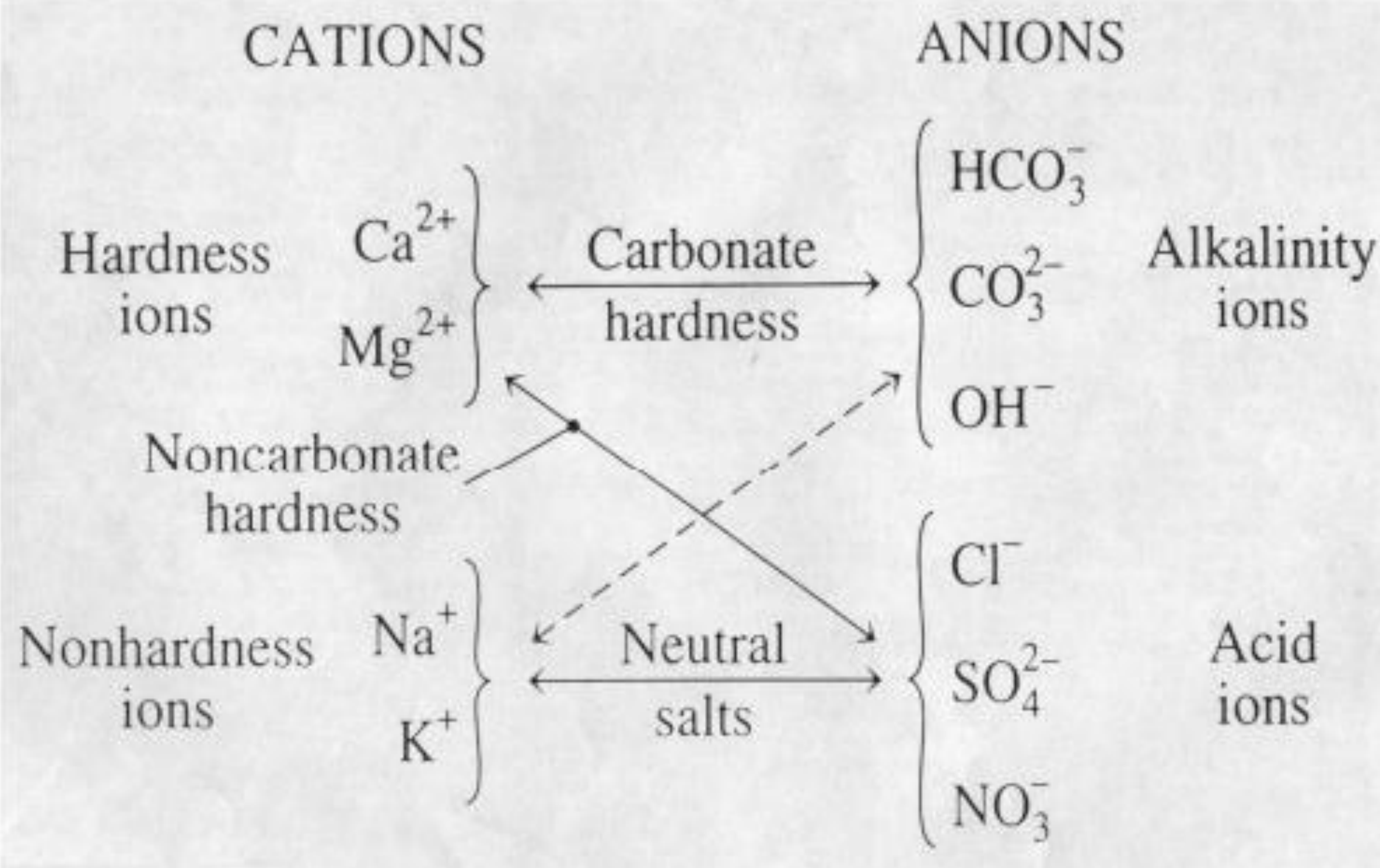
When alkalinity < total hardness,

$$\text{Carbonate hardness (in mg/L)} = \text{alkalinity (in mg/L)} \qquad (19.5)$$

When alkalinity ≥ total hardness,

$$\text{Carbonate hardness (in mg/L)} = \text{total hardness (in mg/L)} \qquad (19.6)$$

$$\text{Noncarbonate hardness (NCH)} = \text{total hardness} - \text{carbonate hardness} \qquad (19.9)$$



Major cations and associated anions

Example

A sample of water having a pH of 7.2 has the following concentrations of ions

Ca^{2+}	40 mg/L
Mg^{2+}	10 mg/L
Na^{+}	11.8 mg/L
K^{+}	7.0 mg/L
HCO_3^{-}	110 mg/L
SO_4^{2-}	67.2 mg/L
Cl^{-}	11 mg/L

Construct a bar chart of the ions in term of mg/L $CaCO_3$

Calculate the TH, CH, NCH, Alkalinity

Solution

Ion	Conc. mg/L	M.W. mg/mmol	z	Eq. Wt. mg/meq	Conc. meq/L	Conc. mg/L as $CaCO_3$
Ca^{2+}	40.0	40.1	2	20.05	1.995	99.8
Mg^{2+}	10.0	24.3	2	12.15	.823	41.2
Na^{+}	11.8	23.0	1	23.0	.51	25.7
K^{+}	7.0	39.1	1	39.1	.179	8.95
HCO_3^{-}	110.0	61.0	1	61.0	1.80	90.2
SO_4^{2-}	67.2	96.1	2	48.05	1.40	69.9
Cl^{-}	11.0	35.5	1	35.5	.031	15.5

Check The ionic balance:

Σ(cations) = Σ(anions)

175.6 = 175.6 mg/L as $CaCO_3$ O.K

3.51 = 3.23 meq/L O.K

Note: (error in the range of ± 10% is accepted)

Note: one check is enough (either as {mg/L as CaCO3 } or as {meq/L})

- Total Hardness = Σ $(Ca^{2+}) + (Mg^{2+}) = 99.8 + 41.2$

TH =141 mg/L as $CaCO_3$

or → TH= 1.995 + 0.823 = 2.818 meq/L

- Carbonate Hardness

  the portion of the hardness associated with carbonate or bicarbonate

  - Alkalinity = 90.1 mg/L as $CaCO_3$

    TH = 141 mg/L as $CaCO_3$

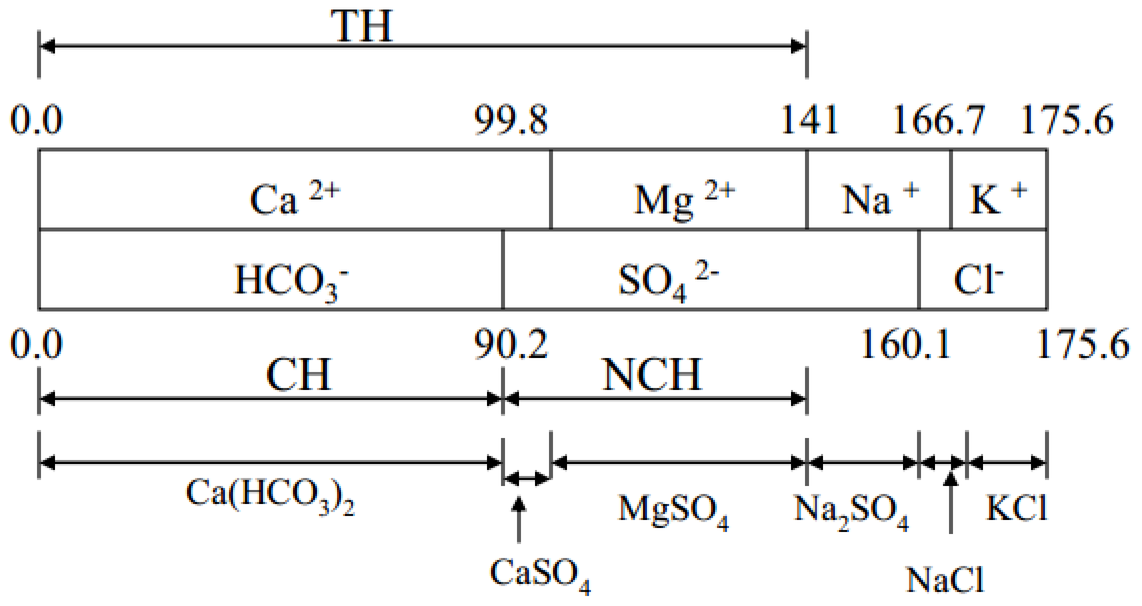
    CH = 90.2 mg/L as $CaCO_3$

  - Non-carbonate Hardness:

    NCH = TH - CH

    = 141 - 90.1= 50.9 mg/L as $CaCO_3$

Construct the bar chart of the ions in term of mg/L $CaCO_3$



Note: the chemicals at the lower line of the bar graph is called the **hypothetical combination** of positive and negative ions in the water sample

Pseudo- Hardness

* When there is Na+ → interfere with normal behaviour of soap.
* Na^+ is not a hardness causing cation.
* High concentration of Na^+ → Pseudo-Hardness

Application of Hardness Data

* Suitability of water for domestic industrial use
* Softening process

Hard water chemicals

Fill in the missing infomation in the table

compound	formula	temporary or permanent?
magnesium hydrogen carbonate	?	?
calcium hydrogen carbonate	$Ca(HCO_3)_2$	temporary
magnesium sulfate	$MgSO_4$	?
calcium sulfate	?	permanent

$Mg(HCO_3)_2$ **$CaSO_4$** **Ca_2SO_4** **$Mg(HCO_2)_3$**

temporary **permanent**

? C solve