Hardness of water



• Hardness of water is the characteristic of preventing lather formation of water with soap. Generally salts like chlorides, bicarbonates and sulfates of Ca²⁺, Mg²⁺ and Fe²⁺ make water hard.

Hard water is water in which some kind of salt (Ca²⁺, Mg²⁺, Fe³⁺, SO₄²⁻, and HCO₃⁻) has been dissolved. Normal Water Hard Water



Allows Lather Formation with Soap

Prevents Lather Formation with Soap

Hardness of water



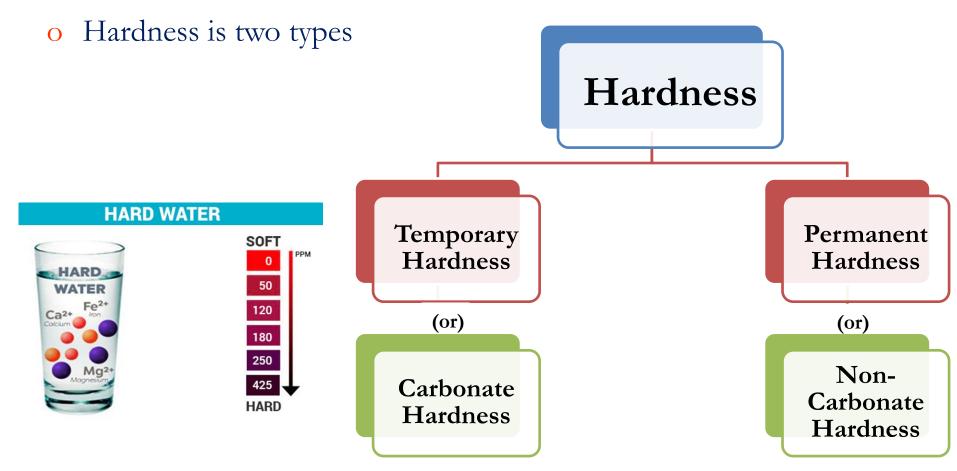
O This hard water on treatment with soap which is stearic or palmitic acid salts of sodium or potassium causes white precipitate formation of calcium or magnesium stearate or palmitate.

$$2C_{17}H_{35} COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$$
 Sodium stearate (soap) Calcium stearate (insoluble)

O Thus the cause of hardness is the precipitation of the soap and hence prevents lathering at first. When the hardness causing ions are removed as insoluble soaps, water becomes soft and forms lather.



o Hardness of water is due to dissolved salts of mainly calcium and magnesium as well as iron and other heavy metals.





a) Temporary Hardness or Carbonate Hardness:

- Due to dissolved bicarbonates of calcium and magnesium and carbonates of iron and other heavy metals. Hence it is also called as carbonate hardness.
- Can be easily removed by boiling, where insoluble carbonates and hydroxides get precipitated at the bottom of the vessel, this it removes the hardness

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

$$Mg(HCO_3)_2 \xrightarrow{Heat} MgCO_3 + CO_2$$



a) Temporary Hardness or Carbonate Hardness:

- > CaCO₃ is completely in-soluble in water.
- Whereas, MgCO₃ is slightly soluble in water but heating causes its hydrolysis into the much less soluble Mg(OH)₂.

$$MgCO_3 + H_2O \longrightarrow Mg(OH)_2 + CO_2$$

So simple boiling and filtration of water remove temporary hardness.



b) Permanent Hardness or non-carbonate Hardness:

- This kind of hardness is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals.
- Permanent Hardness cannot be removed by simple boiling.
- Can be removed through zeolite, Lime-soda, ion-exchange processes.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaCl$$

Difference between Temporary Hardness and Permanent Hardness



Sr. No	Temporary hardness	Permanent hardness
1	Type of hardness which can be	Type of hardness which cannot be
	removed by simple techniques	removed by simple techniques such as
	such as boiling is known as	boiling is known as Permanent
	temporary hardness	hardness
2	It is due to bicarbonates of Ca,Mg	It is due to other salts hence known as
	and carbonates of Mg hence	carbonate hardness
	known as carbonate hardness	
3	It is due to Ca(HCO ₃) ₂ ,	It is due to CaCl ₂ ,MgCl ₂ ,CaSO ₄ ,
	Mg(HCO ₃) ₂ , MgCO ₃	MgSO ₄ ,Ca(NO ₃) ₂ , Mg(NO ₃) ₂ ,FeC ₁₂ , &FeSO ₄
4	It is known as alkaline hardness	It is known as non alkaline hardness
5	It is removed by boiling not by	It is removed by chemicals lime and
	chemicals	soda
6	Ca(HCO ₃) ₂ → CaCO ₃ +CO ₂ +2H ₂ O	CaSO ₄ + Na ₂ CO ₃ → CaCO ₃ +Na ₂ SO ₄
	Mg(HCO ₃) ₂ → Mg(OH) ₂ +2CO ₂	

Units of Hardness



- Both temporary and permanent hardness are expressed in mg/L (ppm) as equivalent of CaCO₃
- The choice of CaCO₃ is due to the fact that
 - O It is the most insoluble salt in water
 - O Besides, its molecular weight is 100 and equivalent weight is 50

Hardness

Equivalent of $CaCO_3 = \frac{Mass \text{ of hardness}}{producing \text{ substance}} \mathbf{x}$

Molecular weight of CaCO₃

Molecular weight of hardness producing substance





A sample hard water contains,

8.1 mg/L Ca(HCO₃)₂ ; 7.5 mg/L Mg(HCO₃)₂; 13.6 mg/L CaSO₄; 12.0 mg/L MgSO₄ and 2.0 mg/L MgCl₂.

To calculate the hardness and express in CaCO₃ equivalents:

Constituent	Multiplication	CaCO ₃ equivalents	Hardness
	factor		
$Ca(HCO_3)_2 = 8.1 \text{ mg/L}$	100/162	$8.1 \times 100/162 = 5.0 \mathrm{mg/L}$	Υ
$Mg(HCO_3)_2 = 7.5 \text{ mg/L}$	100/146	$7.5 \times 100/146 = 5.14 \text{ mg/L}$	Temporary
$CaSO_4 = 13.6 \text{ mg/L}$	100/136	$13.6 \times 100/136 = 5.0 \text{ mg/L}$	
$MgSO_4 = 12.0 \text{ mg/L}$	100/120	12.0 x 100/120 =10.0 mg/L	Permanent
$MgCl_2 = 2.0 \text{ mg/L}$	100/95	$2.0 \times 100/95 = 2.11 \text{ mg/L}$	





Temporary hardness of water

due to
$$Ca(HCO_3)_2$$
 and $Mg(HCO_3)_2 = 5.0 + 5.14$
= **10.14 mg/L or ppm CaCO₃ eq.**

Permanent hardness of water

due to
$$CaSO_4$$
, $MgSO_4$ and $MgCl_2 = 5.0 + 10.0 + 2.11$
= 17.11 mg/L or ppm $CaCO_3$ eq.

Total hardness of water =
$$10.14 + 17.11$$

= 27.25 mg/L or ppm CaCO₃ eq.





Calculate the temporary and total hardness of a water sample containing

$$Mg(HCO_3)_2 = 73mg/L$$

$$Ca(HCO_3)_2 = 162mg/L$$

$$MgCl_2 = 95mg/L$$

$$CaSO_4 = 136 mg/L$$

Molecular weight

$$Mg(HCO_3)_2 = 146$$

$$Ca(HCO_3)_2 = 162$$

$$MgCl_2 = 95$$

$$CaSO_4 = 136$$





Solution: calculation of CaCO₃ equivalents:

Constituent	Multiplication factor	CaCO ₃ equivalent
$Mg(HCO_3)_2 = 73mg/L$	100/146	73X100/146= 50mg/L
$Ca(HCO_3)_2 = 162mg/L$	100/162	162X100/162=100mg/L
$MgCl_2 = 95mg/L$	100/95	95X100/95= 100mg/L
CaSO ₄ =136mg/L	100/136	136X100/136= 100mg/L

[∴] Temporary hardness of water due to Mg(HCO₃)₂ and Ca(HCO₃)₂ =

$$=100 + 50 = 150 \text{mg/L}$$
 or ppm.

Total hardness of water= 50+100+100+100=350 mg/L or ppm.





Calculate the temporary and total hardness of a water sample containing

$$Mg(HCO_3)_2 = 83 \text{ mg/L}$$

$$Ca(HCO_3)_2 = 134 \text{ mg/L}$$

$$CaSO_4 = 124 \text{ mg/L}$$

$$MgCl_2 = 84 mg/L$$

$$CaCl_2 = 94 \text{ mg/L}$$

Molecular weight

$$Mg(HCO_3)_2 = 146$$

$$Ca(HCO_3)_2 = 162$$

$$CaSO_4=136$$

$$MgCl_2 = 95$$

$$CaCl_2 = 111$$





Constituent	Multiplication factor	CaCO ₃ equivalent
$Mg(HCO_3)_2 = 83 \text{ mg/L}$	100/146	56.8
$Ca(HCO_3)_2 = 134 \text{ mg/L}$	100/162	82.7
$CaSO_4 = 124 \text{ mg/L}$	100/136	91.2
$MgCl_2 = 84 \text{ mg/L}$	100/95	88.4
$CaCl_2 = 94 \text{ mg/L}$	100/111	84.7

- \circ Temporary hardness = 56.8 + 82.7 = 139.5 mg/L or ppm CaCO₃ equiv.
- \circ **Permanent hardness** = 91.2 + 88.4 + 84.7 = 264.3 mg/L or ppm CaCO₃ equiv.
- O Total hardness = 139.5 + 264.3 = 403.8 mg/L or ppm CaCO₃ equiv.





Calculate total, carbonate and non-carbonate hardness of 1L water sample which contains $CaCl_2 = 25.4 \text{ ppm}$; $MgSO_4 = 23.6 \text{ ppm}$; $MgCl_2 = 32 \text{ ppm}$; $Ca(HCO_3)_2 = 33.9 \text{ ppm}$; $Mg(HCO_3)_2 = 12.7 \text{ ppm}$ and NaCl = 17 ppm.

(Atomic masses of Ca = 40; Cl = 35.45; S = 32; O = 16; C = 12; Mg = 24 and Na = 23)



Total hardness = 105.8 ppm

Permanent hardness = 76.2 ppm

Temporary hardness = 29.6 ppm