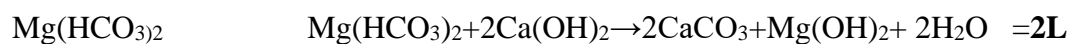


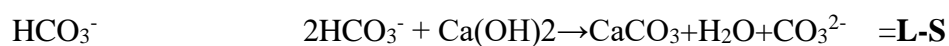
## SOLVED NUMERICAL: HARDNESS OF WATER

### Calculation of equivalents of calcium carbonate

Dissolved Salt/Ion	Molar Mass	Chemical Equivalent	Multiplication factor for converting in to equivalents of CaCO <sub>3</sub>
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162	81	100/162
Mg(HCO <sub>3</sub> ) <sub>2</sub>	146	73	100/146
CaSO <sub>4</sub>	136	68	100/136
CaCl <sub>2</sub>	111	55.5	100/111
MgSO <sub>4</sub>	120	60	100/120
MgCl <sub>2</sub>	95	47.5	100/95
CaCO <sub>3</sub>	100	50	100/100
MgCO <sub>3</sub>	84	42	100/84
CO <sub>2</sub>	44	22	100/44
Ca(NO <sub>3</sub> ) <sub>2</sub>	164	82	100/164
Mg(NO <sub>3</sub> ) <sub>2</sub>	148	74	100/148
HCO <sub>3</sub> <sup>-</sup>	61	61	100/122
OH <sup>-</sup>	17	17	100/34
CO <sub>3</sub> <sup>2-</sup>	60	30	100/60
NaAlO <sub>2</sub>	82	82	100/164
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	342	57	100/114
FeSO <sub>4</sub> .7H <sub>2</sub> O	278	139	100/278
H <sup>+</sup>	1	1	100/2
HCl	36.5	1	100/73



(Temp.Mg)



(e.g., NaHCO<sub>3</sub>)



Note: Substance like NaCl, KCl, Na<sub>2</sub>SO<sub>4</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> etc.do not impart any hardness and therefore, these do not consume any lime or soda. These should not be taken in to consideration for calculating the lime and soda requirements.

**Lime** requirement for softening

$$= 74/100 [\text{Temp. Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2] : \text{All in terms of CaCO}_3 \text{ eq.}]$$

**Soda** requirement for softening

$$= 106/100 [\text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+}) \times \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^-] : \text{All in terms of CaCO}_3 \text{ eq.}]$$

**Q.1** How many grams of FeSO<sub>4</sub> dissolved per litre gives 210.5 ppm of hardness?

**Solution:**

$$\text{FeSO}_4 = \text{CaCO}_3$$

$$56 + 16 + 64 = 136 \text{ gm} = 152 \text{ gm} = 100 \text{ gm}$$

$$\therefore 100 \text{ ppm of hardness} = 152 \text{ ppm of FeSO}_4$$

$$210.5 \text{ ppm of hardness} = 152 \times 210.5 / 100 = 319.96 \text{ ppm of FeSO}_4$$

$$= 319.96 \text{ mg/L or } 0.31996 \text{ gm /L of FeSO}_4$$

**Q.2.** Calculate the temporary and permanent hardness of a sample of water containing:

Mg (HCO<sub>3</sub>)<sub>2</sub> = 7.3 mg/L, Ca (HCO<sub>3</sub>)<sub>2</sub> = 16.2 mg/L, MgCl<sub>2</sub> = 9.5 mg/L, CaSO<sub>4</sub> = 13.6 mg/L

(Atomic weight of Mg and Ca are 24 and 40 respectively.)

**Solution:** Conversion in to CaCO<sub>3</sub> equivalents:

Constituents	Multiplication factor	CaCO <sub>3</sub> equivalents
Mg (HCO <sub>3</sub> ) <sub>2</sub> = 7.3 mg/L	100/146	7.3 x 100/146 = 5 mg/L
Ca (HCO <sub>3</sub> ) <sub>2</sub> = 16.2 mg/L	100/162	16.2 x 100/162 = 10 mg/L
MgCl <sub>2</sub> = 9.5 mg/L	100/95	9.5 x 100/95 = 10 mg/L
CaSO <sub>4</sub> = 13.6 mg/L	100/136	13.6 x 100/136 = 10 mg/L

**Temporary** hardness, due to Mg (HCO<sub>3</sub>)<sub>2</sub> and Ca (HCO<sub>3</sub>)<sub>2</sub>

$$= (5 + 10) \text{ mg/L} = 15 \text{ mg/L or } 15 \text{ ppm}$$

**Permanent** hardness due to MgCl<sub>2</sub> and CaSO<sub>4</sub>

$$= (10 + 10) \text{ mg/L} = 20 \text{ mg/L or } 20 \text{ ppm}$$

**Q.3.** Calculate the temporary and total hardness of a sample of water containing:

Mg (HCO<sub>3</sub>)<sub>2</sub> = 73 mg/L, Ca (HCO<sub>3</sub>)<sub>2</sub> = 162 mg/L, MgCl<sub>2</sub> = 95 mg/L, CaSO<sub>4</sub> = 136 mg/L

(Atomic weight of Mg and Ca are 24 and 40 respectively.)

**Solution:** Conversion in to CaCO<sub>3</sub> equivalents:

Constituents	Multiplication factor	CaCO <sub>3</sub> equivalent
--------------	-----------------------	------------------------------

Mg (HCO <sub>3</sub> ) <sub>2</sub> = 73mg/L	100/146	73x100/146= 50mg/L
Ca (HCO <sub>3</sub> ) <sub>2</sub> =162 mg/L	100/162	162X100/162=100 mg/L
MgCl <sub>2</sub> = 95mg/L	100/95	95X100/95=100 mg/L
CaSO <sub>4</sub> = 136 mg/ L	100/136	136X100/136=100 mg/L

Temporary hardness, due to Mg (HCO<sub>3</sub>)<sub>2</sub> and Ca (HCO<sub>3</sub>)<sub>2</sub>

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

**Total hardness** = Temporary + permanent

$$= (150) \text{ mg/L} + (200) \text{ mg/L} = 350 \text{ mg/L or } 350 \text{ ppm}$$

**Q.4.** Calculate the quantity of lime and soda required for softening 50,000 litres of water containing following salts per litre: Ca (HCO<sub>3</sub>)<sub>2</sub>=8.1 mg/L, Mg (HCO<sub>3</sub>)<sub>2</sub>= 7.5mg/L, CaSO<sub>4</sub>= 13.6 mg/L, MgSO<sub>4</sub>= 12.0 mg/L, MgCl<sub>2</sub>= 2.0 mg/L and NaCl=4.7 mg/L.

**Solution:** Conversion in to CaCO<sub>3</sub> equivalents:

Constituents	Multiplication factor	CaCO <sub>3</sub> equivalent
Ca (HCO <sub>3</sub> ) <sub>2</sub> =8.1 mg/L	100/162	8.1X100/162=5.0 mg/L
Mg (HCO <sub>3</sub> ) <sub>2</sub> = 7.5mg/L	100/146	7.5X100/146=5.14 mg/L
CaSO <sub>4</sub> = 13.6 mg/L	100/136	13.6X100/136=10.0 mg/L
MgSO <sub>4</sub> = 12.0 mg/L	100/120	12.0X100/120=10.0 mg/L
MgCl <sub>2</sub> = 2.0 mg/L	100/95	2.0X100/95=2.11 mg/L

**Lime** requirement for 50,000 L water:

$$= 74/100 [ \text{Ca(HCO}_3)_2 + 2 \times \text{Mg (HCO}_3)_2 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent} ] \times \text{vol. of water}$$

$$= 74/100 [ 5.0 + 2 \times 5.14 + 10.0 + 2.11 ] \text{ mg/L} \times 50,000 \text{ L}$$

$$= 74/100 [ 27.39 \text{ mg/L} ] \times 50,000 \text{ L} = 10,13,430 \text{ mg}$$

$$= 10,13,430 \text{ mg} \times 10^{-6} \text{ kg} = 1.0134 \text{ kg}$$

**Soda** requirement for 50,000 L water:

$$= 106/100 [ \text{CaSO}_4 + \text{MgSO}_4 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ equivalent} ] \times \text{vol. of water}$$

$$= 106/100 [ 5.0 + 10.0 + 2.11 ] \text{ mg/L} \times 50,000 \text{ L}$$

$$= 106/100 [ 17.11 \text{ mg/L} ] \times 50,000 \text{ L} = 9,06,830 \text{ mg}$$

$$= 9,06,830 \text{ mg} \times 10^{-6} \text{ kg} = 0.9068 \text{ kg}$$

**Q.5.** A water sample on analysis gave the following data:

$$\text{Ca}^{2+} = 30 \text{ mg/L}, \text{Mg}^{2+} = 24 \text{ mg/L}, \text{CO}_2 = 24 \text{ mg/L}, \text{HCl} = 50 \text{ mg/L}, \text{K}^+ = 10 \text{ mg/L}$$

Calculate the quantities of lime (90% pure) and soda (94% pure) required to softened one million litres of water sample.

**Solution:** Conversion in to CaCO<sub>3</sub> equivalents:

Constituents	Multiplication factor	CaCO <sub>3</sub> equivalent
Ca <sup>2+</sup> = 30 mg/L	100/40	30x100/40=75.0 mg/L
Mg <sup>2+</sup> =24 mg/L	100/24	24x100/24=100.0 mg/L
CO <sub>2</sub> =24mg/L	100/44	24x100/44=54.5 mg/L
HCl=50 mg/L	100/73	50x100/73=68.5 mg/L

**Lime** requirement:

$$=74/100[\text{Mg}^{2+}+\text{CO}_2 +\text{HCl as CaCO}_3 \text{ eq.}] \times \text{Vol.of water} \times (100\% \text{ purity})$$

$$=74/100[(100+54.5+68.5) \text{ mg/L}] \times 106 \text{ L} \times (100/90)$$

$$=74/100[223\text{mg/L}] \times 106 \text{ L} \times (100/90)=(74 \times 223 \times 106)/90 \text{ mg}$$

$$=1.834 \times 108 \text{ mg} =1.834 \times 102 \text{ kg}=183.4 \text{ kg}$$

**Soda** requirement:

$$=106/100[\text{Ca}^{2+}+\text{Mg}^{2+} + \text{HCl as CaCO}_3 \text{ eq.}] \times \text{Vol.of water} \times (100\% \text{ purity})$$

$$=106/100[(75+100+68.5) \text{ mg/L}] \times 106 \text{ L} \times (100/94)$$

$$=106/100[243.5\text{mg/L}] \times 106 \text{ L} \times (100/94)=(106 \times 243.5 \times 106)/94 \text{ mg}$$

$$=2.946 \times 108 \text{ mg}=2.946 \times 102 \text{ kg}=294.6 \text{ kg}$$

**Q.6.** A water sample on analysis gave the following data:

Ca<sup>2+</sup>=30 mg/L, Mg<sup>2+</sup>=18mg/L, K<sup>+</sup>= 19.5 mg/L, CO<sub>2</sub>=11mg/L, HCO<sub>3</sub><sup>-</sup> = 122 mg/L, Cl<sup>-</sup>=35.5 mg/L, SO<sub>4</sub><sup>2-</sup> =48mg/L

- Calculate the total hardness and alkalinity of water sample
- Calculate lime-soda required for softening one litre of this sample of hard water

**Solution:** Conversion in to CaCO<sub>3</sub> equivalents:

Constituents	Multiplication factor	CaCO <sub>3</sub> equivalent
Ca <sup>2+</sup> =30 mg/L	100/40	30x100/40=75 mg /L
Mg <sup>2+</sup> =18mg/L	100/24	18x 100/24=75 mg /L
CO <sub>2</sub> =11mg/L	100/44	11x 100/44=25 mg/L
HCO <sub>3</sub> <sup>-</sup> = 122 mg/L	100/122	122x 100/122 = 100 mg /L

- Total hardness= (75+75) mg/L=150 mg/L or 150 ppm

Alkalinity present = (HCO<sub>3</sub><sup>-</sup> -CO<sub>2</sub> ) = (100-25) mg/L = 75 mg/L or 75 ppm

- Lime requirement =74 /100[ Mg<sup>2+</sup> + CO<sub>2</sub> +HCO<sub>3</sub><sup>-</sup> as CaCO<sub>3</sub> eq.]

$$= 74/100[75+25+100] \text{ mg /L} = 148 \text{ mg/L}$$

$$\begin{aligned}\text{Soda requirement} &= 106/100[\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ as CaCO}_3 \text{ eq.}] \\ &= 106/100[75+75-100] \text{ mg /L} = 53 \text{ mg/L}\end{aligned}$$

**Q.7.** 100 ml of water sample has a hardness equivalent to 12.5 ml of 0.08N  $\text{MgSO}_4$ . What is its hardness in ppm?

**Solution:** 100 ml of water sample = 12.5 ml of 0.08N  $\text{MgSO}_4$

$$\begin{aligned}&= 12.5 \times 0.08 \text{ ml of 1N MgSO}_4 \\ &= 1 \text{ ml of 1N MgSO}_4 = 1 \text{ ml of 1N CaCO}_3 \text{ eq.} \\ &= 0.001 \text{ L of 1N CaCO}_3 \text{ eq.} \\ &= 0.001 \times 50 \text{ g CaCO}_3 \text{ eq.} \\ &= 0.05 \text{ g CaCO}_3 \text{ eq. (or 50 mg CaCO}_3\text{)}\end{aligned}$$

Therefore, 1000 ml (or /L) of water sample =  $50 \text{ mg CaCO}_3 \text{ eq.} \times 1000 \text{ ml} / 100 \text{ ml}$   
 $= 500 \text{ mg CaCO}_3 \text{ eq.}$

Hence, the hardness of water sample is 500 mg  $\text{CaCO}_3$  eq. Per litre or 500 ppm.

**Q.8.** 100 ml of a sample of hard water neutralizes exactly 12 ml of 0.12 N HCl using methyl orange as indicator. What kind of hardness is present? express the same in terms of  $\text{CaCO}_3$  equivalent.

**Solution:** Hardness is temporary, since methyl orange does not give the value for permanent hardness.

$$\begin{aligned}100 \text{ ml of sample} &= 12 \text{ ml of 0.12 N HCl} \\ &= 12 \times 0.12 \text{ ml of 1N HCl} \\ &= 1.44 \text{ ml of 1 N HCl or 1N CaCO}_3 \text{ eq.} \\ &= 1.44 \times 10^{-3} \text{ L} \times 50 \text{ g CaCO}_3 \text{ eq. L}^{-1} \\ &= 0.072 \text{ g CaCO}_3 \text{ eq. or 72 mg CaCO}_3 \text{ eq.}\end{aligned}$$

Hence, 1000 ml (or 1 L) of water =  $72 \text{ mg CaCO}_3 \text{ eq.} \times 1000 \text{ ml} / 100 \text{ ml} = 720 \text{ mg CaCO}_3 \text{ eq.}$

**Temporary hardness of water is 720 ppm**

**Q.9.** 0.5 g of  $\text{CaCO}_3$  was dissolved in HCl and the solution made up to 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA and after boiling and filtering required 10 ml of EDTA solution. Calculate the hardness.

**Solution:** 500 ml of SHW = 0.5 g or 500mg  $\text{CaCO}_3$  eq.

Hence, 1 ml SHW = 1mg  $\text{CaCO}_3$

Now 48 ml of EDTA = 50 ml SHW = 50 mg  $\text{CaCO}_3$  eq.

Therefore, 1 ml of EDTA = 50/48 mg CaCO<sub>3</sub> eq.

(i) Calculation of the total hardness of water:

50 ml hard water = 15 ml EDTA = 15 x (50/48) mg CaCO<sub>3</sub> eq.

$$= 15.625 \text{ mg CaCO}_3 \text{ eq.}$$

Hence, 1000 ml of hard water = 15.625 x 1000/50 mg CaCO<sub>3</sub> eq.

$$= 312.5 \text{ mg /L CaCO}_3 \text{ eq.}$$

Therefore, **total hardness = 312.5 mg /L or 312.5 ppm**

(ii) Calculation of non-carbonate hardness:

50 ml boiled hard water = 10 ml EDTA

$$= 10 \times (50/48) \text{ mg CaCO}_3 \text{ eq.}$$

$$= 10.417 \text{ mg CaCO}_3 \text{ eq.}$$

Hence, 1000 ml boiled hard water = 10.417 x 1000 /50 mg CaCO<sub>3</sub> eq.

$$= 208.3 \text{ mg CaCO}_3 \text{ eq.}$$

Therefore, non-carbonate hardness = 208.3 mg/L or 208.3 ppm

**Hence, carbonate hardness = (312.5-208.3) = 104.2 ppm**

**Q.10.** A water sample contains the following impurities: Ca<sup>2+</sup>=20 ppm, Mg<sup>2+</sup>=18 ppm, HCO<sub>3</sub><sup>-</sup>=183ppm and SO<sub>4</sub><sup>2-</sup>=24ppm. Calculate the amount of lime and soda needed for softening.

(Atomic weight of Mg and Ca are 24 and 40 respectively.)

**Solution:** Conversion in to CaCO<sub>3</sub> equivalents:

Constituents	Multiplication factor	CaCO <sub>3</sub> equivalent
Ca <sup>2+</sup> = 20 ppm	100/40	20x100/40=50 ppm
Mg <sup>2+</sup> =18 ppm	100/24	18x100/24=75 ppm
HCO <sub>3</sub> <sup>-</sup> =183ppm	100/122	183x100/122=150 ppm

**Lime** requirement:

$$= 74/100 [\text{perm. Mg}^{2+} + \text{HCO}_3^- \text{ as CaCO}_3 \text{ equivalent}]$$

$$= 74/100 [75+150] \text{ ppm} = 166.5 \text{ ppm or mg/L}$$

**Soda** requirement:

$$= 106/100 [\text{perm. Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- \text{ as CaCO}_3 \text{ equivalent}]$$

$$= 106/100 [50+75-150] \text{ ppm} = \text{Negative or Nil}$$

