1. What is the total hardness of sample of water which has the following impurities in mg/L. $Ca(HCO_3)_2 = 162$, $CaCl_2 = 22.2$, $MgCl_2 = 95$, NaCl = 20.

Step I : Calculation of CaCO₃ equivalent

Constituents	Quantity	Molecular Weight	Multiplication Factor	CaCO ₃ Equivalent
Ca(HCO ₃) ₂	162 mg/L	162	100/162	162 X 100/162 = 100 mg/L
CaCl ₂	22.2 mg/L	111	100/111	22.2 X 100/111 = 20 mg/L
MgCl ₂	95 mg/L	95	100/95	95 X 100/95 = 100 mg/L

Step II: Calculation of Temporary hardness

Temporary hardness = Hardness due to $Ca(HCO_3)_2 = 100 \text{ mg/L}$

Step III : Calculation of Permanent hardness

Permanent hardness = Hardness due to CaSO₄ and MgCl₂

$$= 20 + 100 = 120 \text{ mg/L}$$

Step IV: Calculation of Total hardness

Total hardness = Temporary Hardness + Permanent Hardness

Problems for Practice

2. Calculate all types of hardness of water sample containing: $Ca(HCO_3)_2 = 81 \text{ ppm}$, $MgSO_4 = 60 \text{ ppm}$, $MgCO_3 = 42 \text{ ppm}$, $Ca(NO_3)_2 = 82 \text{ ppm}$.

Temporary Hardness: 100 ppm, Permanent Hardness: 100 ppm, Total: 200 ppm.

3. Classify the following salts into temporary and permanent hardness causing salts and also calculate their calcium carbonate equivalents. $Ca(HCO_3)_2 = 16.2 \text{ mg/L}$, $MgSO_4 = 1.2 \text{ mg/L}$, $FeCl_2 = 12.7 \text{ mg/L}$, NaCl = 94 mg/L

Temporary Hardness: 10 ppm, Permanent Hardness: 11 ppm.

Various Steps Involved are

- Preparation of Standard hard water
- Standardization of EDTA (SHW)
- Titration of Sample Hard Water (HW)
- Titration of Boiled Hard Water (BHW)

Calculations:

Let V_1 ml of EDTA solution = 50 ml standard hard water.

Let V_2 ml of EDTA solution = 50 ml unknown sample of hard water.

Let V_3 ml of EDTA solution = 50 ml boiled hard water.

Step I – Determination of Strength of EDTA solution.

1 ml of SHW = 1 mg of $CaCO_3$

:. 50 ml of SHW = 50 mg of $CaCO_3$ -----(1)

Also 50 ml standard hard water = V_1 ml of EDTA solution -----(2)

From equation (1) and (2),

 V_1 ml of EDTA solution = 50 mg of CaCO₃

 \therefore 1 ml of EDTA solution = 50/V₁ mg of CaCO₃ equivalent.

Step II – Determination of total hardness.

50 ml of HW = V_2 ml of EDTA solution -----(3) But, 1 ml of EDTA solution = $50/V_1$ mg of CaCO₃ equivalent

- ∴ V_2 ml of EDTA solution = $\frac{50 \text{ X } V_2}{V_1}$ mg of CaCO₃ equivalent————(4) From equation (3) and (4)
- ∴ 50 ml of Sample hard water contains = $\frac{50 \text{ X V}_2}{V_1}$ mg of CaCO₃ equivalent
- $\text{$:$ 1000 ml of Sample hard water contains} = \frac{50 \text{ X V}_2 \text{ X 1000}}{\text{V}_1 \text{ X 50}} \text{ mg of CaCO}_3 \text{ equivalent}$

$$=\frac{V_2 \times 1000}{V_1} \text{ mg/L}$$

Total Hardness
$$=\frac{V_2 \times 1000}{V_1} \text{ mg/L}$$

Step III – Determination of Permanent hardness.

50 ml of BHW = V_3 ml of EDTA solution -----(5) But, 1 ml of EDTA solution = $50/V_1$ mg of CaCO₃ equivalent

- ∴ V_3 ml of EDTA solution = $\frac{50 \times V_3}{V_1}$ mg of CaCO₃ equivalent————(6) From Equation (5) and (6)
- ∴ 50 ml of Boiled hard water contains = $\frac{50 \text{ X V}_3}{V_1}$ mg of CaCO₃ equivalent
- $\text{$\stackrel{.}{.}$ 1000 ml of Boiled hard water contains} = \frac{50 \text{ X V}_3 \text{ X 1000}}{\text{V}_1 \text{ X 50}} \text{ mg of CaCO}_3 \text{ equivalent}$

$$=\frac{V_3 X 1000}{V_1} mg/L$$

Permanent Hardness =
$$\frac{V_3 \times 1000}{V_1} \text{ mg/L}$$

Step IV: Determination of temporary hardness

Temporary Hardness = Total hardness – Permanent hardness.

$$= \frac{V_2 \times 1000}{V_1} - \frac{V_3 \times 1000}{V_1}$$

Temporary Hardness =
$$\frac{1000(V_2 - V_3)}{V_1}$$

Problems for practice

1. 50 ml of standard hard water containing 1 mg of pure $CaCO_3$ per ml consumed 20 ml of EDTA solution. 50 ml of the given water sample required 25 ml of same EDTA solution. 50 ml of the boiled sample required 15 ml of EDTA solution. Calculate total, permanent and temporary hardness of water sample.

Temp. Hard. = 500 ppm, Perm. Hard. = 750, Total Hard. = 1250 ppm

2. 0.28 g of CaCO₃ was dissolved in HCl and solution is made up to 1 litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution. 100 ml hard water required 33 ml of same EDTA solution on titration. After boiling 100 ml of this was required 10 ml of EDTA solution on titration. Calculate the temporary and permanent hardness of water.

Temp. Hard. = 230 ppm, Perm. Hard. = 100, Total Hard. = 330 ppm

3. Calculate the hardness of water sample whose 20 ml required 30 ml of EDTA solution. 10 ml $CaCl_2$ solution (300 mg $CaCO_3$ per 200ml) required 20 ml of EDTA solution.

Total Hardness = 1125 ppm

Problem 1

20 ml of EDTA solution = 50 ml standard hard water.

25 ml of EDTA solution = 50 ml unknown sample of hard water.

15 ml of EDTA solution = 50 ml boiled hard water.

 \therefore 50 ml of SHW = 50 mg of CaCO₃ -----(1)

Also 50 ml standard hard water = 20 ml of EDTA solution -----(2)

From equation (1) and (2),

20 ml of EDTA solution = 50 mg of CaCO₃

 \therefore 1 ml of EDTA solution = 50/20 = 2.5 mg of CaCO₃ equivalent.

Step II – Determination of total hardness.

50 ml of HW = 25 ml of EDTA solution -----(3) But, 1 ml of EDTA solution = 2.5 mg of CaCO₃ equivalent

- ∴ 25 ml of EDTA solution = $2.5 \times 25 = 62.5 \text{ mg}$ of CaCO₃ equivalent—————(4) From equation (3) and (4)
 - \therefore 50 ml of Sample hard water contains = 62.5 mg of CaCO₃ equivalent
 - ∴ 1000 ml of Sample hard water contains = $\frac{1000 \text{ X } 62.5}{50}$ mg of CaCO₃ equivalent

= 1250 mg/L or ppm

Total Hardness = 1250 ppm

Step III – Determination of Permanent hardness.

50 ml of BHW = 15 ml of EDTA solution -----(5) But, 1 ml of EDTA solution = 2.5 mg of CaCO₃ equivalent

- ∴ 15 ml of EDTA solution = $2.5 \times 15 = 37.5 \text{ mg}$ of CaCO₃ equivalent—————(6) From Equation (5) and (6)
- $∴ 50 ml of Boiled hard water contains = <math>\frac{1000 \text{ X } 37.5}{50} \text{ mg of CaCO}_3 \text{ equivalent}$
 - \therefore 1000 ml of Boiled hard water contains = 750 mg of CaCO₃ equivalent

$$=750 \text{ ppm}$$

Permanent Hardness = 750 ppm

Step IV: Determination of temporary hardness

Temporary Hardness = Total hardness – Permanent hardness.

$$= 1250 - 750$$

Temporary Hardness = 500 ppm

Problem 2

28 ml of EDTA solution = 100 ml standard hard water.

33 ml of EDTA solution = 100 ml unknown sample of hard water.

10 ml of EDTA solution = 100 ml boiled hard water.

Step I – Determination of Strength of EDTA solution.

1 ml of SHW = 0.28 mg of CaCO₃

:. 100 ml of SHW = 28 mg of $CaCO_3$ -----(1)

Also 100 ml standard hard water = 28 ml of EDTA solution -----(2)

From equation (1) and (2),

28 ml of EDTA solution = 28 mg of CaCO₃

 \therefore 1 ml of EDTA solution = 28/28 = 1 mg of CaCO₃ equivalent.

Step II – Determination of total hardness.

100 ml of HW = 33 ml of EDTA solution -----(3) But, 1 ml of EDTA solution = 1 mg of CaCO₃ equivalent

- \therefore 33 ml of EDTA solution = 1 X 33 = 33 mg of CaCO₃ equivalent————(4) From equation (3) and (4)
 - \therefore 100 ml of Sample hard water contains = 33 mg of CaCO₃ equivalent
 - ∴ 1000 ml of Sample hard water contains = $\frac{1000 \text{ X} 33}{100}$ mg of CaCO₃ equivalent

= 330 mg/L or ppm

Total Hardness = 330 ppm

Step III – Determination of Permanent hardness.

100 ml of BHW = 10 ml of EDTA solution -----(5) But, 1 ml of EDTA solution = 1 mg of CaCO₃ equivalent

- ∴ 10 ml of EDTA solution = $10 \times 1 = 10 \text{ mg}$ of CaCO₃ equivalent—————(6) From Equation (5) and (6)
- ∴ 100 ml of Boiled hard water contains = $\frac{1000 \text{ X } 10}{100}$ mg of CaCO₃ equivalent

 \therefore 1000 ml of Boiled hard water contains = 100 mg of CaCO₃ equivalent

Permanent Hardness = 100 mg/L

Permanent Hardness = 100 ppm

Step IV: Determination of temporary hardness

Temporary Hardness = Total hardness – Permanent hardness.

$$= 330 - 100$$

Temporary Hardness = 230 ppm

Problem 3

Calculate the hardness of water sample whose 20 ml required 30 ml of EDTA solution. 10 ml $CaCl_2$ solution (300 mg $CaCO_3$ per 200ml) required 20 ml of EDTA solution.

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20 ml of EDTA solution = 10 ml standard hard water. ------ (1)
30 ml of EDTA solution = 20 ml unknown sample of hard water. ------(2)
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- \therefore 200 ml of SHW = 300 mg of CaCO₃
- \therefore 1 ml of SHW = 1.5 mg of CaCO₃
- \therefore 10 ml of SHW = 15 mg of CaCO₃ -----(3)

From equation (1) and (3), 20 ml of EDTA solution = 15 mg of CaCO₃

 \therefore 1 ml of EDTA solution = 15/20 = 0.75 mg of CaCO₃ equivalent.

Step II – Determination of total hardness.

30 ml of EDTA solution = 20 ml unknown sample of hard water. -----(2) But, 1 ml of EDTA solution = 0.75 mg of CaCO₃ equivalent

- ∴ 30 ml of EDTA solution = $0.75 \times 30 = 22.5 \text{ mg}$ of CaCO₃ equivalent—————(4) From equation (2) and (4)
 - \therefore 20 ml of Sample hard water contains = 22.5 mg of CaCO₃ equivalent
 - ∴ 1000 ml of Sample hard water contains = $\frac{1000 \text{ X } 22.5}{20}$ mg of CaCO₃ equivalent

= 1125 mg/L or ppm

Total Hardness = 1125 ppm

Problem 4

0.5 g of CaCO₃ was dissolved in dilute HCl and diluted to 500 ml, 50 ml of this solution required 45 ml of EDTA solution for titration. 50 ml of hard water sample required 15 ml of EDTA solution for titration. 50 ml of same water sample on boiling, filtering requires 10 ml EDTA solution. Calculate the temporary, permanent and total hardness in ppm.

45 ml of EDTA solution = 50 ml standard hard water.

15 ml of EDTA solution = 50 ml unknown sample of hard water.

10 ml of EDTA solution = 50 ml boiled hard water.

Step I – Determination of Strength of EDTA solution.

500 ml of SHW = 500 mg of $CaCO_3$

:. 50 ml of SHW = 50 mg of $CaCO_3$ -----(1)

Also 50 ml standard hard water = 45 ml of EDTA solution -----(2)

From equation (1) and (2),

45 ml of EDTA solution = 50 mg of CaCO₃

 \therefore 1 ml of EDTA solution = 50/45 = 1.11 mg of CaCO₃ equivalent.

Step II – Determination of total hardness.

50 ml of HW = 15 ml of EDTA solution -----(3) But, 1 ml of EDTA solution = 1.11 mg of CaCO₃ equivalent

- ∴ 15 ml of EDTA solution = 15 X 1.11 = 16.66 mg of $CaCO_3$ equivalent ----(4) From equation (3) and (4)
 - \therefore 50 ml of Sample hard water contains = 16.66 mg of CaCO₃ equivalent

∴ 1000 ml of Sample hard water contains =
$$\frac{1000 \text{ X } 16.66}{50}$$
 mg of CaCO₃ equivalent

$$= 333 \text{ mg/L or ppm}$$

Total Hardness = 333 ppm

Step III – Determination of Permanent hardness.

50 ml of BHW = 10 ml of EDTA solution -----(5) But, 1 ml of EDTA solution = 1.11 mg of CaCO₃ equivalent

- ∴ 10 ml of EDTA solution = $10 \times 1.11 = 11.1 \text{ mg}$ of CaCO₃ equivalent—————(6) From Equation (5) and (6)
 - \therefore 50 ml of Boiled hard water contains = 11.1 mg of CaCO₃ equivalent

∴ 1000 ml of Boiled hard water contains =
$$\frac{1000 \text{ X } 11.1}{50}$$
 mg of CaCO₃ equivalent

∴ 1000 ml of Boiled hard water contains = 222 mg of CaCO₃ equivalent

Permanent Hardness = 222 mg/L

Permanent Hardness = 222 ppm

Step IV: Determination of temporary hardness

Temporary Hardness = Total hardness – Permanent hardness.

$$= 333 - 222$$

Temporary Hardness = 111 ppm

7. 50 ml sample of water required 7.2 ml of N/20 disodium EDTA for titration. After boiling and filtration, the same volume required 4 ml of EDTA. Calculate both the types of hardness in it.

$$\frac{1}{20} N EDTA solution = 0.05 N EDTA$$

1000 ml of 1 N EDTA Solution = 50 g of CaCO₃

∴ 1 ml of 0.05 N EDTA Solution =
$$\frac{50 \times 0.05}{1000}$$
 = 0.0025 g of CaCO₃

Now, 50 ml of hard water required 7.2 ml of 0.05 N EDTA.

∴ 50 ml of hard water =
$$0.0025 \times 7.2 = 0.018 \text{ gms}$$
 of CaCO₃
= 18 mgs of CaCO₃

1000 ml of hard water = 360 mgs of $CaCO_3$

Total Hardness = 360 ppm of CaCO₃

Now, 50 ml of Boiled hard water required 4.0 ml of 0.05 N EDTA.

 \therefore 50 ml of hard water = 0.0025 X 4 = 0.01 gms of CaCO₃

= $10 \text{ mgs of } CaCO_3$

1000 ml of hard water = 200 mgs of $CaCO_3$

Permanent Hardness = $200 \text{ mgs of } CaCO_3$

Temporary Hardness = $360 - 200 = 160 \text{ mgs of } CaCO_3$

8. 10³ L water was softened by I.E. method. For regeneration, 150 L of 0.1 N each of HCl and NaOH was needed by respective exhausted resins. Calculate hardness of sample.

Amount of acid or base used to regenerate the resin = hardness of water.

Problems for practice

9. 100000 L of hard water was softened by I.E. method, and the exhausted resins were regenerated by 200 Litres of 0.1 N HCl and NaOH solutions each. Calculate hardness of water sample in ppm.

Ans: Hardness of water = 10 ppm

10. The exhausted Ion exchange resins consumed 250 L of 0.1 N HCl and same of NaOH solutions for regeneration. The resins were used to soften 10⁵ L water. Calculate total hardness of water sample in ppm.

Ans: Hardness of water = 12.5 ppm

13. Two BOD bottles contained each of 5 ml of sewage sample and water diluted with distilled water to 300 ml. One 100 ml portion of the blank consumed 6.4 ml of 0.05 N thiosulphate in the Winkler's method for the determination of dissolved oxygen while 100 ml of the second bottle incubated at 20°C for the five days required 1.6 ml of the same thiosulphate solution. Calculate the BOD content of the sample.

Difference in the volume of thiosulphate solution required for blank and the sample solution = 6.4 - 1.6 = 4.8 ml of 0.05 N thiosulphate solution.

1 Litre of 1N thiosulphate solution = 8 g of oxygen.

4.8 ml of 0.05 N thiosulphate solution =
$$\frac{8 \times 4.8 \times 0.05}{1000} \times \frac{100}{300} = 6.4 \times 10^{-4}$$
 g of oxygen.

∴5 ml of sewage sample = 12.8×10^{-4} g of oxygen.

Now 1000 ml of sewage sample = 12.8×10^{-2} g oxygen.

Problems for practice

14. 10 ml of sewage water sample was taken in to two BOD bottles and then diluted with distilled water to 300 ml. One 100 ml portion of the first bottle incubated at 20°C for the five days required 2.0 ml of 0.05 N thiosulphate solution. While one 100 ml portion of the blank consumed 7.4 ml of 0.05 N thiosulphate in the Winkler's method for the determination of dissolved oxygen. Calculate the BOD content of the sample.

Ans: BOD = 72 ppm

15. A 10 ml of sample of waste water was refluxed with 20 ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 26.2 ml of 0.1 M FAS solution. A blank of 10 ml of distilled water on refluxing with 20 ml of dichromate solution required 36 ml of 0.1 M FAS solution. Calculate the COD value of the waste water.

Difference in the volume of FAS solution required for blank and the sample solution = 36 - 26.2 = 9.8 ml of 0.1 M FAS solution.

1 Litre of 1M FAS solution = 8 g of oxygen.

9.8 ml of 0.1 M FAS solution =
$$\frac{8 \times 9.8 \times 0.1}{1000}$$
 = 7.84 × 10⁻³ g of oxygen.

 \therefore 10 ml of sewage sample = 7.84 X 10⁻³ g of oxygen.

Now 1000 ml of sewage sample = 7.84×10^{-1} g oxygen.

= 784 mg oxygen.

Problems for practice

17. A 5 ml sample of waste water was refluxed with 30 ml of potassium dichromate solution and after refluxing the excess unreacted dichromate required 23 ml of 0.1 M FAS solution. A blank of distilled water ion refluxing with 30 ml of dichromate solution required 36 ml of 0.1 M FAS solution. Calculate the COD value of the waste water. (Dec. 2015, 3 Marks)

Ans: COD = 2080 ppm

18. Calculate the COD of an effluent sample if 25 c.c. of the effluent sample required 8.3 c.c. of 0.001M K₂Cr₂O₇ for oxidation. **(May 2016, 3 Marks)**

Here 1 Litre of 1 M FAS = 8 g of oxygen

∴8.3 ml of 0.001 M FAS =
$$\frac{8 \times 8.3 \times 0.001}{1000}$$

$$=6.64 \times 10^{-5}$$
 g of oxygen for 25 ml of sample.

∴ Oxygen required for 1000 ml of waste sample = 2.656×10^{-3} *g* of oxygen. = 2.656 ppm of oxygen.

1. A sample of polymer has 4 molecules with molecular weights of 3 X 10⁵, 2 X 10⁵, 6 X 10⁵ and 8 X 10⁵. Calculate the number average molecular weight.

$$\overline{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{M}_n = \frac{\left(1 \times 3 \times 10^5\right) + \left(1 \times 2 \times 10^5\right) + \left(1 \times 6 \times 10^5\right) + \left(1 \times 8 \times 10^5\right)}{(1 + 1 + 1 + 1)}$$

$$\overline{M}_n = \frac{\left(19 \times 10^5\right)}{(4)}$$

$$= 475000$$

4. A polymer sample consists of 10 chains with the following molecular weights. Calculate number-average and weight average molecular weights of the sample.

Number of polymer (N _i)	5	3	2
Molecular weight of each polymer (M _i)	50000	30000	20000

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\bar{M}_n = \frac{(5 \times 50000) + (3 \times 30000) + (2 \times 20000)}{(5 + 3 + 2)}$$

$$\bar{M}_n = \frac{(380000)}{(10)}$$

$$= 38000$$

4. A polymer sample consists of 10 chains with the following molecular weights. Calculate number-average and weight average molecular weights of the sample.

Number of polymer (N _i)	5	3	2
Molecular weight of each polymer (M _i)	50000	30000	20000

$$\begin{split} \overline{M}_W &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \cdots}{N_1 M_1 + N_2 M_2 + N_3 M_3 + \cdots} = \frac{\sum N_i M_i^2}{\sum N_i M_i} \\ \overline{M}_n &= \frac{(5 \times (50000)^2) + (3 \times (30000)^2) + (2 \times (20000)^2)}{(5 \times 50000) + (3 \times 30000) + (2 \times 20000)} \\ \overline{M}_n &= \frac{1.6 \times 10^{10}}{(380000)} \\ &= 42105.26 \end{split}$$

5. A polymer sample contains 30%, 20%, 10% and 40% molecules with molecular weights of 28000, 26000, 32000, 30000 respectively. Calculate the number-average and weight average molecular weight of polymer sample.

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \cdots}{N_1 + N_2 + N_3 + \cdots} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\bar{M}_n = \frac{(30 \times 28000) + (20 \times 26000) + (10 \times 32000) + (40 \times 30000)}{(30 + 20 + 10 + 40)}$$

$$\bar{M}_n = \frac{(2880000)}{(100)}$$

5. A polymer sample contains 30%, 20%, 10% and 40% molecules with molecular weights of 28000, 26000, 32000, 30000 respectively. Calculate the number-average and weight average molecular weight of polymer sample.

$$\overline{M}_{w} = \frac{N_{1}M_{1}^{2} + N_{2}M_{2}^{2} + N_{3}M_{3}^{2} + \cdots}{N_{1}M_{1} + N_{2}M_{2} + N_{3}M_{3} + \cdots} = \frac{\sum N_{i}M_{i}^{2}}{\sum N_{i}M_{i}}$$

$$\overline{M}_n = \frac{(30 \times (28000)^2) + (20 \times (26000)^2) + (10 \times (32000)^2) + (40 \times (30000)^2)}{(30 \times 28000) + (20 \times 26000) + (10 \times 32000) + (40 \times 30000)}$$

$$\overline{M}_n = \frac{(83280000000)}{(2880000)}$$

Phase Rule

1. An alloy of tin and lead contains 73% tin. Find the mass of eutectic that contains 64% of tin.

73% tin is present in alloy means 730g of tin and 270g of lead are present in 1kg alloy.

Eutectic contains 64% tin means 640g of tin and 360g of lead is present in 1kg of eutectic.

Therefore mass of tin present in eutectic = $\frac{640 \times 270}{360} = 480 \ g$

Total mass of eutectic in an alloy = 480g + 270g = 750g