

# Water | Topic Notes

## Water

- **Hard water does not easily form a lather with soap and is caused by the presence of Mg(2+) ions or Ca(2+) ions.**
- **Calcium for teeth and bones, nicer taste and good for brewing and tanning**
- **Produces scum, wastes soaps and blocks pipes, leaves scale on kettles and boilers.**
- Most soaps contain sodium stearate, when soap is added to hard water it forms a grey insoluble compound called scum. This is calcium stearate.
- **$\text{Ca}(2+) + 2\text{C}_{17}\text{H}_{35}\text{COO} \rightarrow (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ca}$**
- Hard water wastes a lot of soap, Modern detergents are now used for washing clothes because they don't contain soap and are not affected by hard water.
- **Temporary hardness** can be removed by boiling water. Temporary hardness arises from rain falling and dissolving carbon dioxide to form a slightly acidic solution of carbonic acid. Limestone or calcium carbonate reacts with this to form calcium hydrogencarbonate. **temporary hardness is really a dilute solution of calcium hydrogencarbonate.** Ca(2+) ions cause hardness here. If water is heated a chemical reaction occurs that removes the Ca(2+) ions from the water.  **$\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 \text{ (insoluble)} + \text{CO}_2 + \text{H}_2\text{O}$**
- The insoluble calcium carbonate is the fur or scale that builds up in kettles and boilers.
- Mg(2+) ions often come from dolomite rock.
- **Permanent hardness cannot be removed by boiling and is caused by the presence of calcium sulfate or magnesium sulfate.**

## Removing permanent hardness:

- **Distillation:** This involves boiling the water and cooling the vapour. All dissolved solids and liquids are removed here but it is not feasible to be carried out on a large scale.
- **Washing soda:** The carbonate ions in the washing soda react with the calcium ions in the water and precipitates them out as calcium carbonate. Commonly used in bath salts to help lather form more easily.
- **Ion Exchange resin:** Man made materials which swap the ions that cause hardness for the ions that don't. Cation exchange resin exchanges the positive ions in the water for Na<sup>+</sup> ions.  
 $\text{Ca}^{2+} + \text{Na}_2\text{R} \rightarrow \text{CaR} + 2\text{Na}^+$ , so the calcium ions remain in the resin. Eventually the resin needs to be regenerated by passing it through a solution of sodium chloride.
- In some cases all ions must be removed - deionized water. This involves passing water through a deionizer with ANION and CATION exchange resin. (mixed bed resin). Anion exchange resin removes the negative ions and replaces them with OH<sup>-</sup> ions. The cation exchange resin replaces positive ions with H<sup>+</sup> ions.

## To determine total hardness in a water sample

- Total hardness = calcium hardness + magnesium hardness
- expressed in terms of mg/l of CaCO<sub>3</sub>
- soft = 0-75 ppm CaCO<sub>3</sub>
- moderately hard = 75 - 150 ppm CaCO<sub>3</sub>
- Hard = 150 - 300 ppm
- Very Hard = 300 < ppm
- the concentration of magnesium and calcium ions is determined using **edta or ethylenediaminetetraacetic acid**.  $\text{H}_2\text{X}^{2-} + \text{Ca}^{2+} \rightarrow \text{CaX}^{2-} + 2\text{H}^+$  it is

represented by **Na<sub>2</sub>H<sub>2</sub>X**, it **wraps itself around** the Ca(2+) and Mg(2+) ions to form a **complex**. Edta and Ca(2+) ions react as 1:1

- Eirchrome Black T is the indicator and goes from wine red to blue telling us the Mg<sup>2+</sup> and Ca<sup>2+</sup> ions have been converted to corresponding edta complexes.
- This is a complexometric titration as the end point can be difficult to detect.
- pH must be at 10 for indicator to work properly, this is done using a buffer solution.

1. Pour 100 cm<sup>3</sup> of the edta solution into a clean dry beaker and 200cm<sup>3</sup> of the hard water sample into another.
2. Rinse out the burette with deionized water and then with some edta, fill then with edta. Remember edta is stored in plastic as it reacts with ions in glass if stored in glass for long periods.
3. Rinse pipette with deionized water and then with the hard water sample.
4. Pipette 50cm<sup>3</sup> of the hard water into the conical flask, add 1cm<sup>3</sup> of pH buffer 10 solution and a small spatula of Eriochrome black T. Colour should be wine red, use white tile and titrate as usual. 1 rough 2 accurate.

Calculations:

$$V_{ca} = 50\text{cm}^3$$

$$M_{ca} = X$$

$$N_{ca} = 1$$

$$V_{ed} = \text{titre of } 15.2$$

$$M_{ed} = 0.01$$

$$N_{ed} = 1$$

$$50X = 15.2(0.01)$$

$$X = 0.00304 \text{ moles/L of CaCO}_3$$

$$.003 \times 100 = .3\text{g/l CaCO}_3$$

$0.3 \times 1000\text{mg/l}$  of  $\text{CaCO}_3 = 300\text{mg/l}/300$  p.p.m.  $\text{CaCO}_3$

# Water Treatment

- I. **Screening:** passing water through wire mesh to remove any floating debris like plastic bags, twigs and so on.
- II. **Flocculation:** A flocculating agent is added which is normally Aluminium Sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ). This causes suspended solids to coagulate or stick together to form large particles which settle out in settlement stage. A flocculant is a chemical added to water to coagulate suspended particles.
- III. **Settlement:** The water is passed into settlement tanks, here it flows into the bottom and rises up very slowly so maximum settlement can occur. Over 90% particles are removed here and the water is then collected in channels.
- IV. **Filtration:** The water from settlement tanks is passed through large beds of sand which remove any remaining suspended solids. It is supported by a layer of gravel and these layers are cleaned regularly. The sand acts like a sieve or filter and removes any suspended solids.
- V. **Chlorination:** A small amount of chlorine (0.2-0.5ppm) is added to the water to sterilize it or get rid of any harmful micro organisms. If too much is added it can taste unpleasant so it is regularly monitored by a bacteriological examination of water.
- VI. **Fluoridation:** By law, councils and associations must add small amounts of fluorine to the water, fluorine compounds commonly added are sodium fluoride, hexafluorosilicic acid. The fluoride ion helps reduce dental decay by strengthening teeth enamel.

VII. **pH adjustment:** Some water authorities may need to alter pH before distributing water to homes and factories, pH may be raised by Calcium hydroxide or by sodium carbonate and lowered by CO<sub>2</sub> or dilute sulfuric acid.

**To determine the total suspended solids in a water sample by filtration, the total dissolved solids by evaporation and pH of a sample of water.**

- Fill a 500cm<sup>3</sup> volumetric flask with the water sample.
- Weigh the filter paper and record its mass.
- Filter the known quantity of water through the filter paper. Retain the filtered water for the rest of the experiment.
- Dry the filter paper using a warm oven or desiccator.
- Find new mass of it and by subtraction find the mass of the suspended solids. This will be g/500cm<sup>3</sup>, multiply X2 to get g/1000cm<sup>3</sup> and then by 1,000 to get p.p.m.
- find the mass of a clean dry beaker.

- Use a graduated cylinder to pour  $200\text{cm}^3$  of the filtered water into the beaker.
- Place the beaker on a hot plate and evaporate the water to dryness. Allow to cool and find new mass. Find mass of dissolved solids by subtraction, as above, convert to p.p.m.
  
- Place the electrode of the pH meter in a sample of tap water and read off the pH.

# Water Pollution

- Solubility of O<sub>2</sub> in water is quite low and it depends on the temperature of the water, remember O<sub>2</sub> is a non polar molecule. It is vital for aquatic life. The more hot the water, the less solubility. When organic waste is discharged into a water way organisms use up the oxygen dissolved in water to produce CO<sub>2</sub> and water. Dissolved oxygen level drops. Fish die. If it drops to 0, anaerobic bacteria take over and H<sub>2</sub>S will provide a foul smell of the river.
- **Pollution** is the release of substances into the environment that damage the environment.
- **Biochemical Oxygen Demand is the amount of dissolved oxygen consumed by biological action when a sample of water is kept at 20 degrees in the dark for 5 days.**
- **The B.O.D. is the difference in the 2 dissolved oxygen levels as this is the amount of dissolved oxygen that has been used by biological action during test.**
- mg/L
- NOTE: rate at which micro organisms use up oxygen depends on the temperature of the water, solubility of oxygen in water decreases as temperature of water increases.
- The higher the B.O.D. value the more polluted the water
- May be used to test level of pollution of effluents, however because of low solubility of oxygen in water effluents with **B.O.D. greater than 9mg/L must be diluted by a fixed amount of well oxygenated water. This ensures that dissolved oxygen will**

**be present throughout the 5 day test and a measurable amount of oxygen at least 2 p.p.m. will be left after the 5 days.**

- Fill bottle under the surface of the water to prevent atmospheric oxygen being trapped and thus giving an artificially high level of oxygen.
- Fill COMPLETELY to ensure there is no air trapped between water and screw cap.
- Place the second bottle in the dark immediately to prevent photosynthesis.
- **Eutrophication is the enrichment of water with nutrients which leads to the excessive growth of algae.**
- These include the enrichment of water with plant nutrients, especially nitrate ions ( $\text{NO}_3^-$ ) and Phosphate ions ( $\text{PO}_4^{3-}$ ). As these levels rise many plants and floating algae explode in population. These algae are short lived and when they decay a heavy oxygen demand is placed on water. It is a green scum and many life forms are killed as a result of the drop in dissolved oxygen levels.
- Natural eutrophication - in lakes caused by gradual increase in nitrogen and phosphorous levels caused by sediments building up in the lake.
- Artificial eutrophication - sudden increase in nutrients caused by artificial fertilisers being washed into rivers and lakes or by domestic sewage or waste from intensive farming.
- **Water pollution is also caused by release of toxic metal ions** such as cadmium, lead and mercury ions. These are heavy metals or cumulative poisons that build up in the body upon continuous exposure. Caused by industrial effluents or dumping of

batteries with these metals. (Minamata Bay Japan - mercury poisoning , mercury salts damage intestine and kidneys - birth defects and death).

- These ions are removed by precipitation e.g.  $\text{Pb}^{2+} + 2\text{Cl}^- \rightarrow \text{PbCl}_2$

## To measure the amount of dissolved oxygen in a sample of water by means of a redox titration

- This is done by the Winkler method. Collect a sample of water in a bottle and take the precautions outlined previously.
- Small quantities of Manganese sulfate solution  $\text{MnSO}_4$  and alkaline potassium iodide solution - a mixture of  $\text{NaOH}$  and  $\text{KI}$  are added to the water.
- The  $\text{Mn}^{2+}$  ions and  $\text{OH}^-$  ions from the alkali react together to form manganese (II) hydroxide which is a white precipitate.
- The white precipitate then reacts with the dissolved oxygen in the water to form a brown precipitate of manganese (III) hydroxide.
- Winkler method is NOT used for chlorinated water - chlorine is an oxidizing agent
- A small amount of sulfuric acid is added to supply  $\text{H}^+$  ions so that the iodide ions from  $\text{KI}$  react with manganese (III) hydroxide to liberate iodine. The brown precipitate dissolves and the red/brown iodine color now appears.
- The amount of iodine liberated is determined by titrating it against standard sodium thiosulfate.
- Submerge bottle completely in water to be analysed and add  $1\text{cm}^3$  with a dropper of manganese (II) sulfate solution. **Make sure the end of the dropper is under the surface of the solution.**

- Repeat with another dropper adding  $1\text{cm}^3$  of alkaline potassium iodide solutions.  
Both are denser and sink to the bottom and form a brown precipitate of Manganese (II) hydroxide.
- Stopper and shake vigorously until there is a 5cm depth of clear liquid below stopper.
- Use a graduated dropper to carefully add  $1\text{cm}^3$  concentrated sulfuric acid.
- Shake bottle to redissolve precipitate - red/brown.
- Fill burette with the sodium thiosulfate and titrate until pale yellow, then add starch indicator which is blue/black and titrate until colorless.

- **Calculations:**

**$100\text{cm}^3$  water samples, iodine liberated was titrated against 0.02M thiosulfate  
average titre was 5.7**

**2I<sub>2</sub> reacts with 4 moles of thiosulfate**

$$V_o = 100$$

$$M_o = ?$$

$$N_o = 1$$

$$V_r = 5.7$$

$$M_r = 0.02$$

$$N_r = 4$$

$$100X = 0.0285$$

$$X = 0.000285 \text{ moles per litre}$$

rmm of O<sub>2</sub> is 32g - we are treating water as a solution of oxygen

$$0.000285 \times 32 = 0.00912\text{g/L} \times 1000 = 9.12 \text{ p.p.m.}$$

Remember for **B.O.D.**, **take away the amount of dissolved oxygen at beginning of 5 day period from that at the end of 5 day period and multiply by the dilution factor of the water sample.**

## Sewage Treatment:

- I. **Primary Sewage Treatment:** Mechanical process, the sewage flows through steel bars to remove any floating debris like twigs, leaves, plastics etc... These could interfere with the equipment in the plant. Then it is passed through grit channels where items like pebble and grit settle and are removed periodically. Suspended particles settle out of the sewage when the flow of the liquid stops. Sewage then flows into large settling tanks where it stays for a few hours and the solids or suspended particles settle out at the bottom. These are removed at regular intervals to be disposed of on land or sea. Then the supernatant liquid is passed onto secondary treatment.
- II. **Secondary Treatment:** Biological process where by the levels of suspended and dissolved organic material is reduced.

**Activated Sludge Process** - Sewage is pumped into a large aeration tank where it provides nutrients for growing micro organisms called activated sludge. They digest the sewage and the liquid in the aeration tank is kept aerated by a mechanical rotor that continuously churns liquid and sludge with the air. Sometimes compressed air is bubbled through the tank. **Prevents concentration of dissolved oxygen dropping too low.**

From here the sewage flows into settling tanks. Some is recycled back into aeration tanks to come into contact with fresh sewage. The sludge removed is rich in nutrients and may be used as a fertilizer or stored in sealed tanks for anaerobic bacteria to

convert it to methane - used as fuel. Micro organisms are continually decomposing organic waste into compounds like CO<sub>2</sub>, nitrates and so on. After secondary treatment 95% of the B.O.D. from original sewage is removed. Effluent may be discharged into nearby waterway, however may still contain compounds of nitrogen and phosphorus. These are removed in tertiary treatment. Older system instead of ASP was to spray sewage over circular beds of rock so it percolates down the rock and leaves a layer or slime of micro organisms on rock.

III. **Tertiary Treatment:** Involves the removal of nitrogen and phosphorus compounds from effluents.

- Nitrates are from organic materials in sewage and phosphates are from house hold detergents.
- Phosphates are removed via precipitation e.g. adding aluminium sulfate - aluminium phosphate precipitates or by adding iron (III) chloride to precipitate it as iron(III)phosphate.
- Nitrogenous compounds are difficult and expensive to remove, may be present via ammonia, nitrites, nitrates or organic compounds containing nitrogen. Remember nitrates and phosphates cause eutrophication.

## **Instrumental analysis of water:**

- **pH meters**

- **Atomic Absorption Spectrometry** - each element has its own unique atomic absorption spectrum, it detects and measures concentrations of heavy metals in water.
- **Colorimetry** - White light is passed through a colored solution and the color of the solution is then compared with the color of solutions of known concentrations of that substance.

### **Estimate concentration of free chlorine in swimming pool water using a comparator/Hatch test kit**

- Chlorine is added to swimming pool water to prevent water borne diseases. It reacts with water to form hypochlorous acid and hydrochloric acid.
- Hydrochlorous acid is weak and dissociates in water to form hypochlorite ions and  $H^+$  ions.
- Chlorine that exists in water as hypochlorite ion and hypochlorous acid is free chlorine.
- If level of free chlorine is too low bacteria may survive in water and infect swimmers.
- If it is too high compounds like  $NCl_3$  will be formed and irritate swimmers' eyes.
- Must be kept from 1-5 p.p.m.
- DPD measures amount of chlorine present in swimming pool. Reacts with chlorinated water to give a pink colored solution, the more pink the more chlorine.
- The intensity of the pink color is compared to a colored disc with different shades of pink, this is calibrated using solutions of known quantities of chlorine.

- Take one color viewing tube and fill with 5cm<sup>3</sup> deionized water. This will be just below the frosted part of glass in the tube. Place the stopper in it. This is a reference tube and indicates to us how much light will be absorbed by that depth of water.
- open black comparator box and place tube with clear water in top left hand opening.
- Place 5 cm<sup>3</sup> of swimming pool water into the other viewing tube and open sachet of chlorine free DPD and add contents to swimming pool water. Swirl gently to dissolve and note the pink color. Place in right opening.
- Remove disc, place in comparator box, close comparator lid and hold the box up to a source of white light. Rotate disc until colors in each opening match. Immediately read color



lue of chlorine given for that

- When done rinse with deionized water and return disc to envelope to prevent color fading.