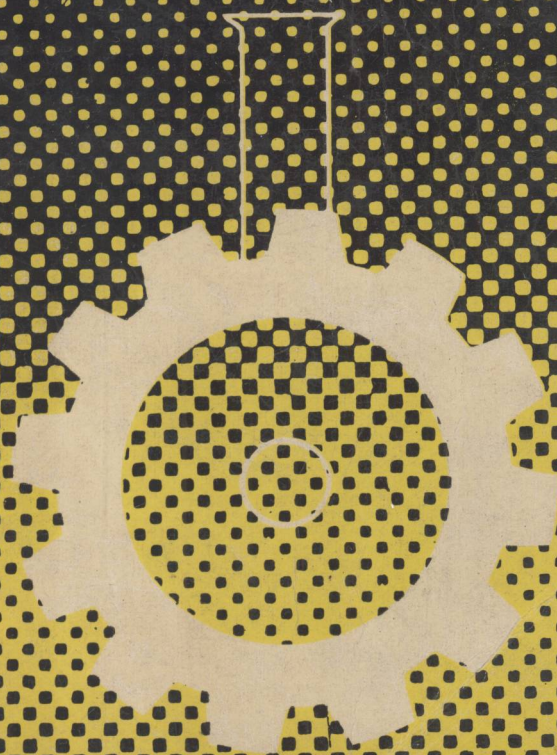


# INDUSTRIAL CHEMISTRY

B.N. CHAKRABARTY



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## PREFACE

The book is intended for use as a textbook for the Honours and Post-Graduate Courses of Indian Universities under the programme 'Writing a Book on Industrial Chemistry' of the University Grants Commission.

The difficulties of preparing a treatise like this are many: first, there are yet no sources in the country for ascertaining the actual practices with statistics and data; second, there is no way of knowing the quantities that are being prepared annually; third, the market condition, and fourth, the absence of commercial publications and research data. A little of each of the above there may be, but information is kept within the manufacturers themselves. In our country, the chemical manufacturers generally follow the standard methods practised in foreign countries, with little or no variation. The author has, therefore, freely consulted the books and journals mentioned in the Bibliography and also other available sources of information. To each of these, the author expresses his deep debt of gratitude. The author's personal experience, first in industries and then as a teacher, also helped him much in his task.

The author expresses his gratitude to the University Grants Commission for permission to prepare the treatise and for financial assistance. His thanks are also due to Dr. A. Roy, Principal, Asansol Girls' College, Asansol, for kindly allowing to prepare the treatise and for other facilities in the College and also to Shri R.N. Chakrabarty for preparing the sketches.

The author expresses his gratefulness to National Book Trust, India, for kindly accepting book for publication under its auspices and for financial assistance towards publication.

The author is also deeply grateful to Prof. Dr. S.C. Shome, Head of the Dept. of Chemistry, Presidency College, Calcutta; Prof. Dr. R.L. Dutta of the Dept. of Chemistry, the University of Burdwan and to Prof. Dr. S. Mukherjee, Head of the Dept. of Chemistry, Kurukshetra University, Kurukshetra (Haryana) for kindly going through the voluminous manuscript, making corrections wherever necessary and offering valuable suggestions for further improvement of the book.

The author would feel grateful if the teachers and the students using the book kindly point out the discrepancies or errors, if any, which might have inadvertently crept in.

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## CHAPTER 1

## WATER

Water is used for industrial and municipal purposes. The largest water requirement is for municipal use but the standard of purity required for this purpose is quite different from that demanded for industrial and commercial use.

In industry more than half the water is used in chemical plants for the purpose of cooling. A large volume of water is also used for the purpose of dilution and making solutions. While for the first purpose the composition of cooling water is of no importance, in the second, the water used should be reasonably pure.

The availability of water, both in quantity and quality, is one of the prime factors in deciding the growth of towns and cities as well as industries. For chemical industries, the available water must be as near as possible to the factory site and should also be soft. Otherwise the manufacturing cost will increase.

**Sources of water supply**

In nature water occurs abundantly as: (1) water vapour in the atmosphere, (2) as liquid water in inland waters and the ocean, (3) as ice in polar regions, and (4) as water of hydration in many rocks and minerals in the earth's crust. The original source of all natural water supplies is, however, rain. Rain water, in its passage through the air, dissolves many of the soluble gases present in the atmosphere and in percolating through the various strata of the earth, collects mineral salts and other impurities. These may be either acidic or alkaline. Of the dissolved gases, oxygen and carbon dioxide are the most important. The dissolved minerals include bicarbonates, carbonates, chlorides, sulphates and nitrates of calcium, magnesium, sodium and sometimes iron also. Silica may also be found in places. The water available may also con-



tain suspended matters—both mineral and organic.

The quality of water depends entirely upon its source of supply.

**Rain Water:** Rain water is the purest form of water but to be absolutely pure it should be collected after a heavy shower, because prior to that, the water may contain dissolved gases and also dust. In industrial areas, gases in the atmosphere contaminate rain water, e.g., sulphuric acid. Dissolved carbon dioxide renders water acidic and increases its solvent power. When this acidic water passes through the soil, it reacts with the calcium and magnesium carbonates present in the soil and forms bicarbonates. Pure rain water is soft.

**River Water:** River and canal waters are inland waters fed by rains. These are less pure than rain water as they contain dissolved chemicals. Their composition is subject to considerable variation depending on the areas over which they are flowing and the soluble chemical salts present in the rocks and soil. Dissolved solids in the river water also vary with the rate of flow. The impurities in river water are generally the chlorides, sulphates, carbonates and bicarbonates of calcium, magnesium and iron. The soluble bicarbonates of calcium and magnesium are formed by the action of dissolved carbon dioxide upon insoluble carbonates. The presence of soluble calcium and magnesium salts in river water makes it hard. Besides this, river and canal waters are liable to be contaminated with sewage and sludges of cities by which they flow and also organic matter, ammonia and nitrites.

**Spring and Well Water:** This is percolated rain water which, on reaching the ground, passes through the various strata of the soil, thereby dissolving the soluble salts of the soil. This water is extremely clear as a result of natural filtration through sand beds and strata. The chief difference between spring and well water and river water is that the former contains a much higher percentage of dissolved mineral matter although it is free from organic impurities and ammonia, and often has a palatable taste and in most cases, may be used for drinking. Water from springs and wells is extremely hard.

**Sea Water:** Rivers carry a large volume of water with dissolved impurities into the sea and, as such, the sea contains the



maximum amount of dissolved impurities. The total dissolved impurities in sea water are about 3.6 per cent of which 2.6 per cent is common salt; others are magnesium chloride, magnesium sulphate, calcium sulphate, potassium chloride, magnesium bromide and traces of iodides, silica, etc. The quantity of dissolved salts is very much greater in inland seas. Sea water is saline, hence unsuitable for drinking purposes and is hard. Sea water is also faintly alkaline.

*Surface Water and Ground Water:* As rain falls on the earth, it flows into streams as surface runoff, passes into the air as vapour and goes down into the ground. It is then recovered as surface water or ground water.

The term surface water indicates natural water in rivers, streams, ponds and lakes, although a part of such deposits of water may have percolated more or less through the soil in the course of its flow along the earth's surface. As a result, the water absorbs a part of the materials with which it comes in contact. Surface water, therefore, indicates the chemical constitution and physical conditions of the area in question.

The water obtained from springs and wells in a given locality may be very different from the local surface water. Ground water also indicates the local geological strata and contains a greater percentage of dissolved salts. Ground water is more nearly constant in composition. Some of the ground water may be hot and may contain dissolved gases. It is sometimes used for medicinal baths. Ground water may be different in taste and chemical character—acid, alkaline, bitter, hepatic, ferruginous, iodinous or siliceous.

### Characteristic properties of water

Water freezes at  $0^{\circ}\text{C}$  and boils at  $100^{\circ}\text{C}$  at NTP. This is in sharp contrast to the melting and boiling points of its higher analogues, hydrogen sulphide, hydrogen selenide and hydrogen telluride. Moreover, the latter are bad smelling gases at ordinary temperature and pressure. Water also exhibits many other abnormal properties. Compared with hydrogen sulphide, it has a higher surface tension and a higher dielectric constant. Liquid water shows a maximum density at  $4^{\circ}\text{C}$ , unlike all other substances, whereas ice is less dense than water. The specific

heat as well as latent heat of fusion and evaporation of water is all abnormally high. All these facts are explained by attributing to water molecules the tendency to associate, giving rise to polymers of the type  $(H_2O)_n$ , as a result of hydrogen bonding.

Pure water is virtually a non-conductor of electricity. On heating to a very high temperature water molecules are dissociated into the elements. The formation of water from hydrogen and oxygen is an exothermic reaction:



Pure water takes part in a variety of chemical reactions. Pure water at room temperature acts on alkaline metals violently and on alkaline earth metals rapidly with evolution of hydrogen. Magnesium and aluminium amalgams are rapidly attacked. Magnesium, iron, zinc and carbon react with water at high temperature. Iron and lead are also attacked by water in the presence of air. Hard water has less reaction on lead than pure and soft water, as the sulphates and bicarbonates present in hard water form a coating of sulphates and carbonates of lead upon the metal which protect it from further action. Hence, soft water should not be supplied for drinking purposes through lead pipes. A solution containing traces of lead is poisonous to the human system.

Water acts as a catalyst for many physical and chemical changes. Perfectly dry hydrogen and oxygen do not react. Although pure water is a non-conductor, water shows a slight dissociation.



At  $25^\circ C$ , the ionic product of water is  $1 \times 10^{-14}$ . Water is an excellent electrolytic solvent, particularly for ionic compounds.

### Water for industry

The quality and quantity of available water are important in the location of a chemical plant. Both, surface and ground water should be considered. Supply of water must be adequate throughout the year and this supply should not disturb the municipal water supply of the area.

Over half the water used in chemical plants is for cooling.

The composition for cooling water is of no great importance—its function is to carry away heat by warming or by evaporation.

A considerable volume of water is used in chemical plants for solutions and dilution. Reasonably pure water is necessary for the purpose.

The most important factors deciding the location of a chemical industry are: raw materials, power, water and transport. But as regards water, every industry has its own special requirements and sometimes that which is suitable for one is fatal to another. It is, therefore, necessary to bear in mind the uses to which a given water will be put and its suitability based on the results of chemical analysis and sometimes decided by bacteriological examination. The principal requisites of water for certain important industries are:

(1) Boiler feed water—should be as soft as possible and should not contain much nitrate or organic matter so as to avoid incrustations or corrosion of the boiler plates.

(2) Water for spirit distilleries—should be pure and cool and should contain few micro organisms and a little sodium chloride and magnesium chloride.

(3) Water for paper mills—the presence of iron is injurious and any excess of lime and magnesia decomposes the resin soaps.

(4) Water for sugar factories—if water rich in sulphates and alkaline carbonates and especially in nitrates is used, crystallisation becomes more difficult, molasses are more abundantly obtained and the sugar becomes deliquescent on exposure. Water rich in micro organisms partially decomposes the sugar.

(5) Water for breweries—must contain lesser quantities of lime and magnesia.

(6) Water for dyeing—should be limpid, free from iron and should possess little hardness.

(7) Water for cooking—should contain little hardness, otherwise the vegetables do not cook easily.

(8) Water for laundries—must be soft.

Besides the special requirement as regards the quality of water of every chemical industry, there is the problem of water to be used for drinking purposes. There should be arrangements in every establishment for the re-use of as much as possible of the

used and discarded water. Even if there may be some initial expenditures on this account, it is worthwhile considering the problem of the acute shortage of water almost everywhere.

### Hard and soft water

Water is classed as hard or soft, depending upon its behaviour towards soap solution.

Water that easily forms a lather of films and froths when agitated with a soap solution is known as soft water.

Water that reacts with soap solution to form a white scum only without producing a lather easily, is said to be hard water. Hard water does not, therefore, yield a lather easily until a considerable amount of soap has been used up.

The hardness of water is due to the presence of dissolved salts of metals (except the salts of alkali metals such as sodium or potassium), notably those of calcium, magnesium and iron, in water.

Besides the presence of bicarbonates of calcium and magnesium (which cause carbonate or temporary hardness) and sulphates and chlorides of calcium and magnesium (which cause permanent hardness) water may also contain varying amounts of sodium salts, silica, iron, alumina and manganese. Other impurities present in water may be the suspended impurities which cause turbidity, organic matter dissolved gases and colouring matter. The dissolved gases may be carbon dioxide, oxygen, nitrogen and hydrogen sulphide (in sulphurous waters).

As a matter of interest the constituents of sea water will give an idea of the chemical elements present. The major elements present, besides oxygen and nitrogen, are chlorine, sodium, magnesium, sulphur, calcium, potassium; minor elements present are bromine, carbon, strontium, boron and the trace elements are iodine, copper, lithium, silver and gold.

The difficulties involved in removing all these impurities are obvious. While calcium, magnesium and iron are removed by water-conditioning, silica is removed with difficulty by ferric coagulation. Presence of soluble sodium salts do not harm boiler-feed water. Alumina and manganese are seldom removed; if required, manganese is removed by aeration followed by filtration or filtration through manganese-zeolite.

From sea water, potassium and bromine are removed as potassium bromide, sodium and iodine as sodium bromide; sulphur, carbon and chlorine separate as sulphates, carbonates and chlorides of calcium, manganese and iron respectively. Boron, lithium and copper are difficult to separate—these are allowed to remain as such in industry. Picking of gold particles from river water in basins is an age-old process.

The best form of pure water is of course distilled water. Distillation keeps back all types of impurities.

### Temporary and permanent hardness

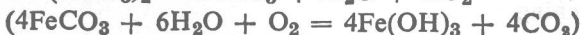
For convenience, hard water is classified as temporary and permanent.

*Temporary Hardness:* is due to the presence of soluble bicarbonates of calcium, magnesium and iron in water.

*Permanent Hardness:* it is caused by the presence of the chlorides and sulphates of calcium and magnesium in the water as chlorides and sulphates.

*Removal of Temporary hardness:* Temporary hardness can be removed by:

(a) Boiling: When the soluble bicarbonates are converted into insoluble carbonates which are precipitated and  $\text{CO}_2$  is evolved.



While  $\text{CaCO}_3$  and  $\text{MgCO}_3$  form white powdery precipitate, iron is precipitated as slimy brown precipitate of  $\text{Fe}(\text{OH})_3$ . Magnesium bicarbonate hardness is not fully removed by boiling, as  $\text{MgCO}_3$  is appreciably soluble in water compared to  $\text{CaCO}_3$ .

(b) Clark's process: Temporary hard water is softened for industrial purposes by adding the calculated quantity of slaked lime which precipitates the insoluble carbonates.



The  $\text{MgCO}_3$ , which is appreciably soluble, then reacts with further quantity of  $\text{Ca}(\text{OH})_2$  to form insoluble  $\text{Mg}(\text{OH})_2$ .

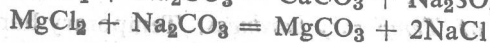
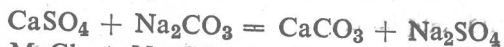


$\text{Mg(OH)}_2$  is sparingly soluble and hence removed.

Slaked lime must be added in extremely calculated quantities, as any excess of  $\text{Ca(OH)}_2$  present in the softened water would again cause hardness. The mixing of lime and water is done in large settling tanks. After the precipitates have settled down, the clear soft water is pumped to reservoirs for distribution.

**Removal of Permanent Hardness:** Permanent hardness of water is caused by the presence of the chlorides and sulphates of calcium and magnesium in the water. While temporary hardness can be removed by boiling or adding lime, permanent hardness cannot be removed by those processes since such methods do not precipitate the calcium or magnesium of hard water.

Permanently hard water is softened by the addition of  $\text{Na}_2\text{CO}_3$  to water, when insoluble  $\text{CaCO}_3$  and  $\text{MgCO}_3$  precipitate. The insoluble carbonates can then be removed by filtering through a filter press.



It must be noted that along with the chlorides and sulphates of calcium and magnesium (permanent hardness), there are also present the bicarbonates in some quantities (temporary hardness) —hence method or methods capable of removing both types of hardness is adopted.

### Water softening

Boiler feed water, specially that for use in high pressure steam boilers, should be as soft as possible to avoid formation of boiler-scale and corrosion of boiler-tubes.

Laundries require soft water of zero hardness to prevent precipitation of calcium and magnesium soaps on textiles.

Paper mills require soft water, as the calcium and magnesium would otherwise precipitate the resin soaps which are used in sizing the paper. Water for paper mills should also be free from iron which stains the paper.

The water to be used for dyeing must be soft and free from iron to avoid formation of insoluble lakes of undesirable shades on the fabric. As a rule water for industrial use must be soft.

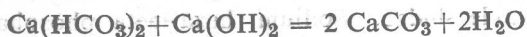


Modern methods to soften hard water are the following: (1) Lime-soda treatment; (2) Phosphate conditioning; (3) Base-exchange or Permutit process, and (4) Deionisation of water.

### 1. Lime-soda treatment

This procedure removes both permanent and temporary hardness. Hard water is treated with slaked lime and soda ash when the calcium and magnesium are precipitated as  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$ .

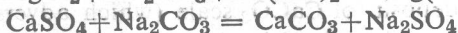
Typical reactions are:



Then, since the  $\text{MgCO}_3$  is fairly soluble (100 ppm), it reacts with excess of lime, precipitating  $\text{Mg(OH)}_2$ :



For non-carbonate hardness, i.e., hardness due to the presence of calcium and magnesium salts, the chemical reactions are:



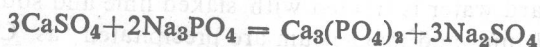
The precipitates are removed by filtration, small amount of  $\text{Al}_2(\text{SO}_4)_3$  or  $\text{NaAlO}_2$  are usually added to help the precipitate formation. The requirement of lime and soda ash is calculated by the analysis of raw water.

It is evident that for carbonate hardness, one mole of calcium bicarbonate requires one mole of lime; while for each mole of magnesium bicarbonate two moles of lime are required. For non-carbonate hardness also, the magnesium salt requires more chemicals (one mole each of soda ash and lime, while the calcium salts need only one mole of soda ash).

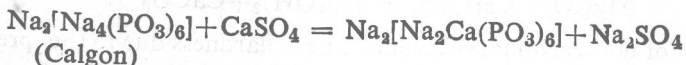
Coagulation and precipitation are greatly facilitated by heating. The hot lime-soda process, (by using hot water), is invariably used for boiler feed water. The effluent from the hot process is reasonably soft and has a hardness of about 20-25 ppm only. The effluent gets a further treatment with phosphate in order to soften it completely for use as a boiler feed water. For feeding high pressure steam boilers, the effluent from the hot lime-soda process is demineralised by ion-exchange resins.

## 2. Phosphate conditioning

Various phosphates, e.g., mono- and di-sodium phosphates are added to boiler water to precipitate the calcium ions as easily removable calcium phosphate sludges, instead of a hard crust or scale.



Trisodium phosphate (T.S.P.) has a distinct alkaline reaction, and precipitates magnesium ions as the hydroxide which is also a readily removable sludge. Sodium hexa-meta phosphate or Calgon is also used for water softening, but instead of precipitating the ions causing hardness, namely Ca, Mg, Fe ions, etc., it forms complexes with them and thereby prevents the formation of scale or insoluble soaps, e.g.



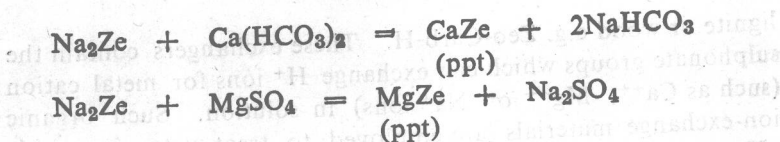
The addition of 1-2 ppm of Calgon to water for softening operations prevents an after-deposit of  $\text{CaCO}_3$  scale (which adversely affects the heat transfer and fluid flow) in pipes. This is known as the threshold treatment of water, and is important in water pipes in heat exchangers and also in laundering.

## 3. The base-exchange or Permutit Process

This is the modern and most effective method of removing both temporary and permanent hardness of water. The Permutit is the trade name for artificially prepared sodium aluminium silicate allied to the natural mineral zeolite. The permutit is precipitated as a gel by mixing solutions of sodium silicate and sodium aluminate.

The base exchange material permutit may be formulated as  $\text{Na}_2\text{Ze}$  where Ze is the zeolite radical, often formulated as  $\text{Al}_2\text{H}_4\text{Si}_3\text{O}_{12}$ .

In the permutit process, the hard water is allowed to percolate through a bed of grounds of permutite, when the calcium and magnesium salts in the water react with the permutit forming insoluble calcium and magnesium aluminium silicates which are retained in the filter bed. The issuing water, free from Ca and Mg, is soft.



The  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ions in hard water are thus exchanged for an equivalent amount of sodium ions in the permutit and the hard water gets softened. Permutit process furnishes water of practically zero hardness.

After use for some time, when the permutit gets exhausted and loses its activity, it is regenerated by treatment with a 10 per cent solution of common salt. The  $\text{NaCl}$  displaces the calcium and magnesium from the exhausted permutit and replaces these by sodium, so that the bed is regenerated and ready for use again.



Very hard water is first given a lime treatment for partial softening, and then followed up with the permutit treatment.

#### 4. Demineralisation and deionisation of water

**Hydrogen Cation Exchangers:** The methods generally used for softening water scarcely alter its mineral content, since sodium ions are added in amounts equivalent to the calcium or magnesium ions removed. But by using new types of ion-exchange materials, it is possible to obtain demineralised or deionised water without recourse to distillation.

The hydrogen cation exchangers are either synthetic organic resins, e.g. sulphonated polystyrene resins, sulphonated phenol-formaldehyde resins or such materials as sulphonated coal,

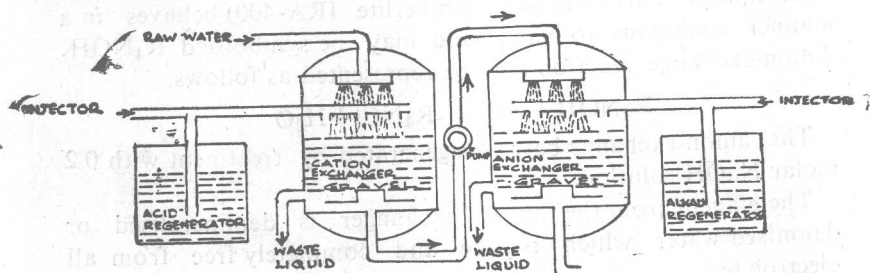


Fig. 1. Demineralisation of water