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A TEXT BOOK OF

ENGINEERING CHEMISTRY

FOR

SEMESTER – I & II

FIRST YEAR DEGREE COURSES IN ENGINEERING

Strictly According to New Revised Credit System Syllabus of

Savitribai Phule Pune University, Pune.

(Effective from Academic Year – June 2015)

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PREFACE TO THE NEW ENLARGED SIZE FIFTH EDITION

We are glad and excited to announce that the Fourth Edition of this book received an overwhelming response from the engineering student community, compelling us to release its **Fifth Edition** within a very short period of time.

This thoroughly revised **Fifth Edition** has been **updated** with **additional matter**, many solved problems, including **All University Examination Papers upto May 2018** and Numerous Exercises for practice.

Special care has been taken to maintain high degree of accuracy in the theory and numericals throughout the book.

We take this opportunity to express our sincere thanks to Dineshbhai Furia of Nirali Prakashan, a reputed and pioneer in the field of publication. Our special thanks to Jignesh Furia for their effective cooperation and great care in bringing out this revised edition. We also appreciate the efforts of M. P. Munde and the entire staff of Engineering Books Deptt. of Nirali Prakashan namely Mrs. Deepali Lachake (Co-ordinator) and Mrs. Shilpa Kale for bringing this book to the students in a timely manner.

We sincerely hope that this "**Fifth Edition**" will also be warmly received by all concerned as in the past.

Valuable suggestions from our esteemed readers to improve the book are most welcome and highly appreciated.

Pune **–Authors**

PREFACE TO THE FIRST EDITION

It gives us great pleasure in publishing this text book on **"Engineering Chemistry"** for the Students of First Year Degree Course in Engineering. This book is strictly written According to New Revised Credit System Syllabus of Savitribai Phule Pune University (2015 Pattern).

As per the policy of the University, Engineering Syllabi is revised every five years. Last revision was in the year 2012. New revision is coming little earlier, as university has introduced **Online** system of examination from year 2012.

In New Credit System, there will be two online examinations conducted at the end of first and second month in every semester. The first online (Phase I – 25 Marks) examination will be based on units I and II and the second online (Phase II – 25 Marks) examination will be based on units III and IV. Both the online examinations will be based on Multiple Choice Questions. End Semester Examination (Theory - 50 Marks) will be based on all six units and will be descriptive type and theory course will have 4 credits.

We have given Free Separate book of Multiple Choice Questions (MCQ's) which will be very useful to the students, especially for Online Examinations.

The subject matter is presented in a lucid, fluent and comprehensive manner. All efforts have been taken to present the text matter in Simple & Lucid Language, Illustrative Figures, University Question Papers and Solved Problems with Answers have been added. Also, University Question Papers (New Pattern) have given (Dec. 12 to May 17) at the end of the Book, and it will help student to understand nature of questions that could be asked in the final examination.

We take this opportunity to express our sincere thanks to Shri. Dineshbhai Furia, Shri. Jignesh Furia, Mrs. Nirali Verma and Shri. M. P. Munde and entire team of Nirali Prakashan namely Mrs. Deepali Lachake (Co-ordinator) who really have taken keen interest and untiring efforts in publishing this text.

Finally, we express our gratitude to our family members for their continuous support and encouragement, thanks to all.

We have no doubt that like our earlier texts, student's community will respond favourably to this new venture.

The advice and suggestions of our esteemed readers to improve the text are most welcomed, and will be highly appreciated.

July 2016 **Authors**

Pune.

SYLLABUS

Unit I : Water Technology and Green Chemistry (8 Hrs.)

Water Technology : Impurities in water. Hardness of water and its determination by EDTA method, Alkalinity of water and its determination. Numericals Ill effects of hard water in boilers. Boiler feed water treatment : (1) Internal treatment - Calgon, Colloidal and Phosphate conditioning, (2) External treatment - (a) Zeolite process and its numericals, (b) Ion exchange method. Desalination of brackish water / Purification of water by Reverse osmosis and Electrodialysis. **Green Chemistry :** Definition, Goals of Green Chemistry, Efficiency parameters, Need of Green Chemistry, Major uses - Traditional and Green pathways of synthesis of Adipic acid, Polycarbonate, Indigo dye.

Unit II : Electro Analytical Techniques (8 Hrs.)

Introduction : Types of reference electrode (Calomel electrode), Indicator electrode (Glass electrode), Ion selective electrode, Half cell reaction and complete cell reaction. **Conductometry :** Introduction, Kohlrausch's law, Conductivity cell, Measurement of conductance, Applications - Conductometric titrations, Acid-base titrations, Precipitation titrations. **pH Metry :** Preparation of Buffers, Standardization of pH metry, Mixture of acids versus strong base titration, Differential plots. **Potentiometry :** Introduction, Potentiometric titrations - Differential plots, Applications - Redox titrations Fe/Ce titration. **UV/Visible spectroscopy :** Interaction of radiation with matter, Beer Lambert's law, Chromophore and Auxochrome, Types of electronic transitions. Instrumentation and Principle - Block diagram of Single and Double Beam Spectrophotometer. Applications of UV-Visible spectroscopy.

Unit III : Synthetic Organic Polymers (8 Hrs.)

Introduction, Functionality of Monomer, Polymerization-Free radical mechanism and Step growth polymerization. Concept and significance of - Average molecular weight, Crystallinity in polymers, T_m and T_g. Thermoplastic and Thermosetting polymers. Compounding of plastics. Techniques of polymerization. Preparation, Properties and Engineering applications of : Polyethylene (LDPE and HDPE) and Epoxy resin, Elastomers - Natural rubber - Processing and Vulcanization by Sulphur. Synthetic rubbers - SBR. **Speciality polymers :** Engineering thermoplastics - Polycarbonate, Biodegradable polymers – Poly (hydroxybutyrate-hydroxyvalarate), Conducting polymers - Polyacetylene, Electroluminescent polymers - Polyphenylene vinylene, Liquid crystalline polymers - Kevlar, Polymer composites - Fibre Reinforced Plastic (FRP).

Unit IV : Fuels and Combustion (8 Hrs.)

Fossil fuels : Definition, Calorific values, Determination - Bomb calorimeter, Boy's gas calorimeter, Numericals. **Solids fuel :** Coal - Proximate and Ultimate analysis. Numericals. **Liquid fuels :** Petroleum - Composition and refining. Octane number of petrol, Cetane number of Diesel, Power alcohol, Biodiesel. **Gaseous fuel :** Composition, Properties and Applications of NG, CNG, LPG. **Combustion :** Chemical reactions, Calculations for air required. Numericals. **Fuel cells :** Definition, Advantages and limitations, Phosphoric acid fuel cell, Polymer electrolyte membrane fuel cell.

Unit V : Chemistry of Hydrogen and Carbon (8 Hrs.)

Chemistry of Hydrogen : The elements - isotopes-importance. Methods of preparation : (1) Laboratory-from aqueous acid and alkali. (2) Industrial-steam reforming of methane and coke, Electrolysis of water. (3) From solar energy (water splitting). Storage-chemical (sodium alanates), Physical (carbon materials), Difficulties in storage and transportation. Compounds of hydrogen, Methods of preparation and applications : (a) Molecular hydrides - Hydrocarbons, Silane, Germane, Ammonia. (b) Saline hydrides - LiH, NaH. Applications of hydrogen, Hydrogen as a future fuel. **Chemistry of Carbon :** Position in the periodic table, Occurrence, Isotopes. Allotropes (crystalline and amorphous) - Occurrence, Structure based on bonding and applications in detail.

Unit VI : Corrosion Science (8 Hrs.)

Introduction. Types of corrosion - Dry corrosion - Mechanism, Pilling-Bedworth rule. Wet corrosion - Mechanism. Factors influencing corrosion - Nature of metal, Nature of environment. Methods of corrosion control : Pourbaix diagram, Cathodic and anodic protection, Use of inhibitors, Protective coatings : Surface preparation : (a) Metallic coatings : Types of coatings, Methods of applications (hot dipping, cladding, electroplating and cementation), Electro less coatings, (b) Non-metallic coatings : Chemical conversion coatings, Powder coatings.

CONTENTS

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UNIT I

WATER TECHNOLOGY AND GREEN CHEMISTRY

WATER TECHNOLOGY

1.1 INTRODUCTION

Water is essential for survival of life on the earth. Life has originated and evolved in water. Water acts as a solvent and medium for all living body reactions. Water is also essential for development of human civilization. All the ancient civilizations developed on the banks of rivers.

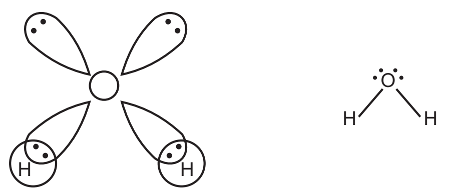
The industrial revolution in Europe started with the invention of the steam engine by James Watt. The steam is generated from water. Water is an important component of the infrastructure essential for industrial development. Water plays a significant role in industries such as textile, paper, food processing, etc. in addition to that of agriculture.

Although water is abundant on the earth's surface, only a very small quantity (4-5%) of water is useful. The significant portion of water (≈ 96%) is present in the seas and oceans which is salty and hence cannot be used directly either for drinking or for industrial purpose. The remaining small quantity which is present in the lakes, rivers and as underground water.

The focus in the present chapter will be on chemical analysis of water, its requirement in the industry, hardness of water and water softening methods.

1.2 STRUCTURE OF WATER

- Water is a covalent compound represented by H_2O or H–O–H. It contains two O–H bonds. The structure of water can be explained on the basis of hybridization of atomic orbitals of oxygen.
- The atomic number of oxygen is 8 and the electronic configuration can be written as $1s^2$, $2s^2$, $2p_x^2$, $2p_y^1$, $2p_z^1$. The outermost 2s and 2p orbitals undergo sp^3 hybridization. The partially vacant $2p_y$ and $2p_z$ orbitals overlap with partially filled 1s orbitals of hydrogen. For these two orbitals, two hydrogen atoms are required and hence H_2O is formed.
- The structure of water molecule can be drawn as



(a) (b)

Fig. 1.1: Structure of sp^3 hybridized H_2O molecule

- The bond angle H–O–H is found to be 104.5°. It is 'V' shaped molecule. The shape is due to the repulsion between two lone pairs of electrons (present in 2s and $2p_x$) and the hydrogen bonded electrons.
- Another important aspect of O–H bond in water molecule is its polar nature. It is known that, the electronegativity of oxygen is more than that of hydrogen. Due to this, oxygen atom attracts (pulls) bonded electrons towards itself and hence electron cloud is oriented on oxygen resulting in the partial negative charge on oxygen and partial positive charge on the hydrogen as shown in Fig. 1.2.
- Due to this, there is a charge separation. This is as if a dipole is formed. Hence, water molecule can be regarded as a combination of two dipoles. This dipole formation gives dipole moment to water.

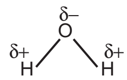


Fig. 1.2: Partially polarized O–H bonds in water

- The polar nature of O–H bonds in H_2O has imparted many unique properties to water.

1.3 PHYSICAL PROPERTIES OF WATER

Due to the structure and polar nature, water has the following physical properties:

- Bond length (O–H) = 98 pm
- Bond energy = 0.47 MJ/mole
- Latent heat = 2.4 kJ/mole
- Bond angle = 104.5°
- Dielectric constant = 78.6 at 25°C
- Dipole moment = 1.8 Debye

1.3.1 Dielectric Constant of Water

- The dielectric constant gives an idea about the ease with which water can separate the anions and cations in ionic compounds when dissolved.

  i.e. $$D.C. = \frac{W_m}{W_v}$$

  where, D.C. = Dielectric constant

  W_v = Work required to separate the charges in vacuum

  W_m = Work required to separate the charges in medium
- Experimentally, the dielectric constant of water is found to be 78.6 at room temperature.

- This means that if the ionic compounds (in which the charges i.e. ions are well separated) are dissolved in water, then the ions will be separated 78.6 times faster than that of in vacuum or, in other words, it can be stated that the amount of work required for water to separate ionic charges is 78.6 times less than that required by vacuum at the given temperature.
- Hence because of the high dielectric constant of water, the ionic substances are easily soluble in water.

1.3.2 Hydrogen Bonding in Water

- Hydrogen bonding is generally observed in the compounds which contain atoms with difference in the electronegativities. Water contains hydrogen and oxygen with significant differences in electronegativities, hence hydrogen bonding is observed in water.
- In water, there is a intermolecular hydrogen bonding i.e. hydrogen atoms in one molecule form a weak hydrogen bond with oxygen atom of other molecules resulting in the cluster of water molecules as shown in Fig. 1.3.

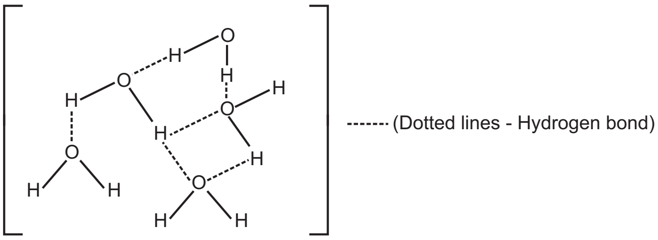


Fig. 1.3: Hydrogen bonding in water molecules

- In the case of ice, each H_2O molecule is hydrogen bonded with four other H_2O molecules resulting in the rigid tetrahedral structure.
- Due to structure, polar nature, hydrogen bonding, water has unique properties. The important one is the physical state, it is a stable solvent in the common temperature range (0 – 100°C) i.e. liquid, it is solid below 0°C and can be used as solid coolent and it is a steam (gaseous state) above 100°C which can be used for many industrial applications involving steam engines and boilers.

1.4 IMPURITIES IN WATER [May 09, Dec. 10]

- Water condensed from the steam or rain water does not contain any impurity, hence can be regarded as the purest form of water. For industrial applications, this form of water is not available readily. The water available for industrial applications always contains some impurities.
- Pure water is colourless, odourless and tasteless but because of the presence of impurities, colour, odour and taste are imparted to water. The impurities present impart hardness to water. The commonly occurring impurities due to which water becomes hard are discussed in the following sections.

1.4.1 Suspended Matter

- When water is flowing in the river or present in the lake, then it appears turbid due to the presence of fine impurities visible to eyes. Such suspended impurities in water are called as suspended matter. Such suspended matter can be removed from water by simple filtration using suitable assembly.
- The commonly occurring suspended impurities are clay particles, precipitates of iron hydroxides, calcium carbonates, bicarbonates and silicates. These impurities are of inorganic type.
- In addition to this, water may contain organic impurities such as from decay of living matter (animals and plants), pesticides, etc.
- Underground water contains almost negligible suspended matter impurities due to the filtering action of soil and rocks during the time it reaches the underground level.
- When suspended matter particle size exceeds 1 μm, then they are called colloidal impurities.

1.4.2 Biological Impurities

When water is flowing in the rivers or dammed in lakes and dams, then the biological impurities, which include many micro-organisms, fungi grow in the water because of dissolved oxygen. Commonly occurring biological impurities are bacteria (aerobic and anaerobic), fungi, viruses, many pathogens, parasites, water hyacinth etc. Under favourable conditions, these impurities grow in concentration with time.

1.4.3 Dissloved Impurities

- Rain drops while coming down to the earth's surface, get impure due to dissolution of the gases such as O_2, SO_2, NH_3, H_2S, CO_2 etc. present in the atmosphere.
- If water from these sources is directly used for industrial applications, then there is a possibility that it will cause many problems to the materials (storage tanks, boilers etc.) that it is in contact with.
- Underground and surface water when they come in contact with soil, rocks, asbestos then inorganic cations such as Ca^{++}, Mg^{++}, Fe^{++}, Mn^{++}, Al^{3+}, Na^+, K^+ and anions such as Cl^-, NO_3^-, HCO_3^-, SO_4^{--} are present in the water.
- In speciality industries such as sugar and fermentation, pesticides, agrochemicals, fertilizers the effluent water contains dissolved organic compounds such as sugars, alcohols, carboxylic acids, aldehydes and ketones.
- Hence dissolved gaseous, inorganic and organic impurities are present in water and in order to remove these impurities, various physical and chemical methods such as filtration, boiling, chemical treatment, oxidation have to be employed.

1.5 NEED FOR CHEMICAL ANALYSIS OF WATER

- Water which contains excessive impurities cannot be used either for drinking or for industrial applications.
- At the same time water in its purest form is not available readily and economically.
- The acceptable levels of impurities in drinking water are fixed by international standardizing agencies such as World Health Organization (WHO), Indian Council of Medical Research (ICMR) etc.
- If the concentrations of impurities present in the water are above the level stated by these agencies, then the water cannot be used for drinking purpose.
- Similarly, acceptable impurity levels in the water that can be used for industrial purpose are also fixed and water sample that contains more impurities than the acceptable level cannot be used.
- In order to determine the suitability of water for drinking or industrial purpose, the given water sample has to be analysed for its impurity levels. Hence, chemical analysis of water is an essential parameter in water resource management.
- Once using chemical analysis, if type and the concentration of impurity in the given water sample is determined then the method that can be used to remove the impurities can be selected.

1.6 CHEMICAL ANALYSIS OF WATER [Dec. 07, 08]

- Chemical analysis of water is qualitative and quantitative determination of impurities present in water.
- The impurities present in water with higher concentrations are generally carbonate and bicarbonate salts of monovalent and divalent cations such as K^+, Na^+, Ca^{2+}, Mg^{2+} etc. in the dissolved form in addition to that of chloride.
- In chemical analysis of water, the important parameters are:
  - Hardness of water.
  - Chloride content in water.
  - Alkalinity.
- These parameters will be studied in the following section.

1.6.1 Hardness of Water

- When soap is dissolved in distilled water or rain water that does not contain any impurities, then lather (foam) is formed. This water is called as **soft water**.
- If water contains certain impurities and if soap is dissolved in such water, then lather is not formed instead scum (curd like insoluble impurities) is formed. This type of water is called as **hard water**.
- The soluble salt impurities present in water impart hardness to water.
- If carbonate, bicarbonate, sulphate, nitrate and chloride salts of bivalent cations such as Mg^{++}, Fe^{2+}, Mn^{2+}, Ca^{2+} are present in water, then the hardness of water is high as compared to that due to presence of salts of monovalent cations such as K^+ and Na^+.
- Hard water is not suitable for industrial applications.
- The hardness of water is of two types:

(a) Temporary Hardness/Carbonate Hardness:

- Temporary hardness is also called as **carbonate hardness**. If hardness of water is due to presence of carbonate and bicarbonate salts such as $CaCO_3$, $MgCO_3$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, etc., then it is called temporary or carbonate hardness.
- This type of hardness can be removed easily by simply boiling the water. During boiling the carbonates and bicarbonates are converted into the form (generally hydroxide) that is insoluble in water.
- The insoluble precipitate formed can be removed by simple filtration method.

$$Mg(HCO_3) \xrightarrow[100°C]{\Delta} Mg(OH)_2 \downarrow + 2\,CO_2 \uparrow$$

$$MgCO_3 + H_2O \xrightarrow[100°C]{\Delta} Mg(OH)_2 \downarrow + CO_2 \uparrow$$

$$Ca(HCO_3) \xrightarrow[100°C]{\Delta} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$$

- Since the hardness can be removed by simply boiling and filtering the water, it is called as **temporary hardness**.

(b) Permanent Hardness:

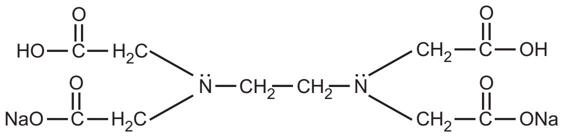
- Permanent hardness to water is caused by presence of dissolved salts of metals other than carbonates or bicarbonates.
- These salts are generally chlorides, sulphates and nitrates.
- The commonly occurring salts that cause the permanent hardness to water are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $FeCl_2$, $CuCl_2$, etc.
- This type of hardness cannot be removed simply by boiling but needs special chemical treatments.
- Total hardness of water is due to temporary as well as permanent hardness and hence can be calculated by adding them.

i.e.

Total hardness = Temporary hardness + Permanent hardness

1.6.2 Experimental Method to Determine Total Hardness of Water

- The most commonly used experimental method to determine the total hardness of water is the complexometry using ethylene diamine tetra acetic acid (EDTA) as a complexing agent.
- This is a volumetric method of analysis using Eriochrome black-T (EBT) dye as an indicator. Sometimes chalcones can also be used as indicators under suitable conditions.
- The commercially available form of EDTA is its disodium salt and its structure is as:



Disodium salt of EDTA

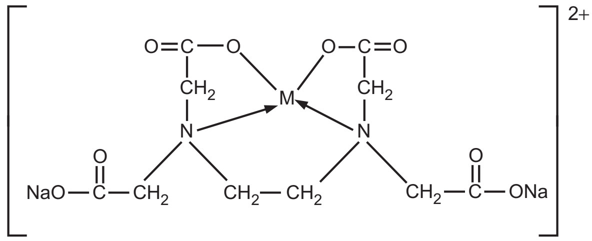
- It is well known that EDTA forms a stoichiometric 1: 1 complex with monovalent and divalent cations. Hence, if suitable reaction conditions are maintained, this complexometric reaction can be used to determine the metal ion concentration in water responsible for causing hardness.
- This complexometric reaction takes place at pH = 10, hence suitable basic buffer solution (NH_4OH + NH_4Cl) must be used to maintain constant pH throughout the reaction/titration.
- Initially during the titration, the indicator (EBT) is added to water sample whose hardness is to be determined along with the buffer solution. The indicator reacts with metal ions in water to give wine red complex. This reaction can be written as:

$$\underset{\text{Metal ions in water}}{M^{2+} + EBT} \xrightarrow{pH\ =\ 10} \underset{\text{Wine red}}{M - EBT}$$

- Then this wine red solution is titrated with standardized EDTA. This leads to formation of M-EDTA (metal-EDTA) complex because M-EDTA complex is more stable than M-EBT complex i.e. EBT in the complex is displaced by EDTA.
- Once M-EDTA complex is formed, then the reaction mixture contains EBT (displaced) which gives blue colour to the solution. This reaction can be written as:

$$\underset{\text{Wine red}}{\text{M-EBT} + \text{EDTA}} \xrightarrow{pH\ =\ 10} \underset{\text{Colourless}}{\text{M-EDTA}} + \underset{\text{Blue}}{\text{EBT}}$$

- A sharp colour change from wine red to blue can be taken as the end point of the reaction and using the concentration and volume of EDTA required to achieve the end point, the concentration of metal ions causing hardness to water can be calculated.
- The structure of M-EDTA complex can be written as:



Experimental Procedure:

- The experiment can be performed in two parts:

  Part I: Standardization of EDTA:

  - Prepare accurately 0.01 M $ZnCl_2$ solution and approximate 0.01 M EDTA solution.
  - Fill the burette upto the mark with EDTA solution.
  - In a conical flask, pipette out 25 ml of $ZnCl_2$ solution. Add 10 ml of pH = 10 buffer and 2 ml of EBT indicator. The colour of reaction mixture becomes wine red.
  - Titrate this reaction mixture with EDTA solution from burette till colour changes to blue.
  - Record the burette reading at the end point.
  - Calculate concentration of EDTA using following equality.

  $$\boxed{1\ M\ 1000\ ml\ ZnCl_2 \equiv 1\ M\ EDTA}$$

  Alternatively, the standardization of EDTA can also be done using standard hard water.

Part II: Total Hardness of Water:

- Fill the burette with standardized EDTA.
- Pipette out 25 ml of the given water sample in a conical flask and repeat the procedure as mentioned above to get the constant burette reading at the end point.
- Calculate the hardness of water using following equality:

	1 M 1000 ml EDTA $\equiv$ 1 M $CaCO_3$ eq. hardness
i.e.	1 M 1000 ml EDTA $\equiv$ 100 g $CaCO_3$ eq. hardness

(Molecular weight of $CaCO_3$ = 100)

- Express the obtained hardness in terms of parts per million (ppm).
- If the water sample is taken without boiling and then filtered then the hardness obtained by EDTA method is total hardness.
- Then take the same sample, boil and filter and then if again EDTA method is performed on this sample, then the permanent hardness is obtained.
- Then using total and permanent hardness, the temporary hardness can be calculated.