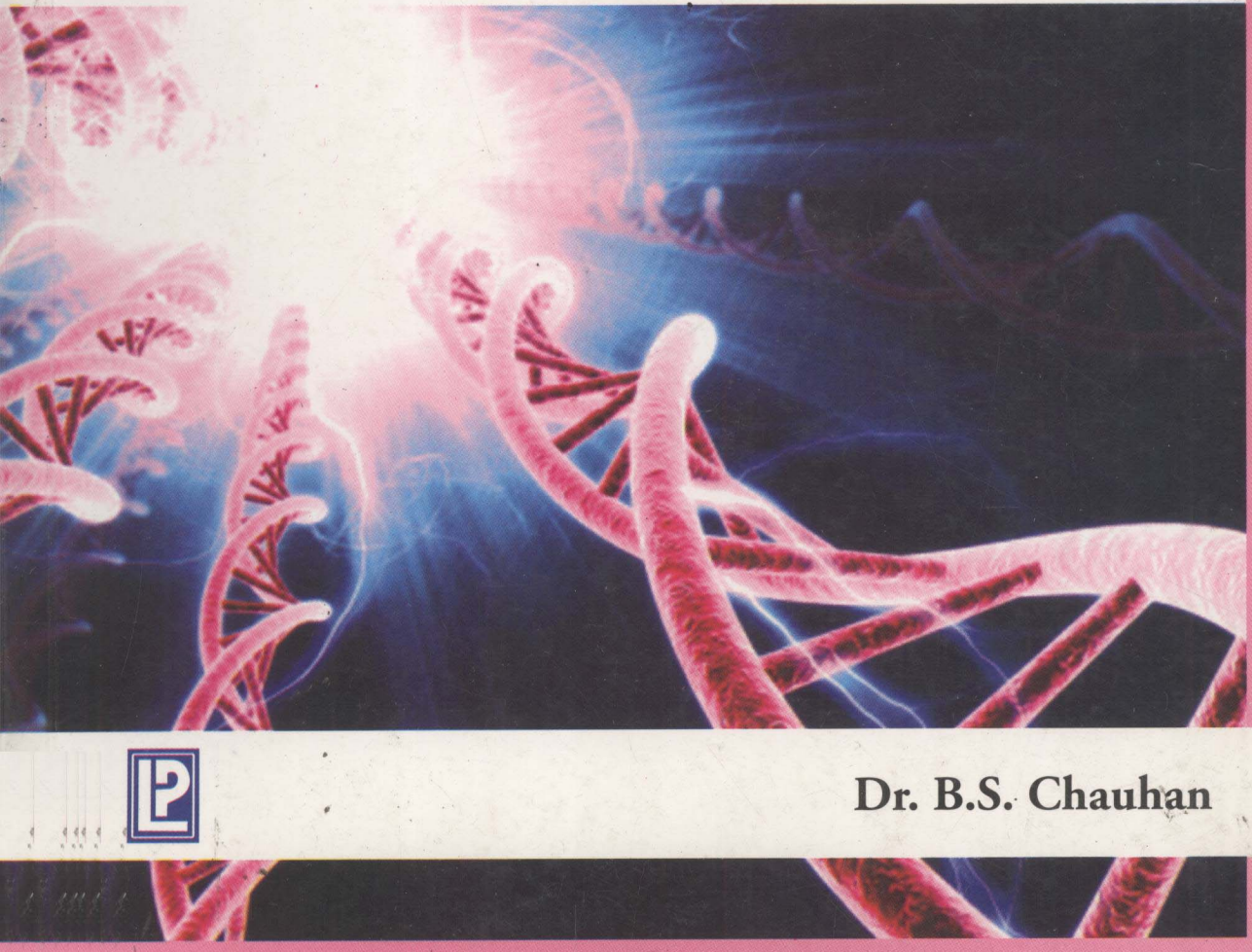
Second Edition

ENGINEERING CHEMISTRY



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Published by :
LAXMI PUBLICATIONS (P) LTD
113, Golden House, Daryaganj,
New Delhi-110002

Phone : 011-43 53 25 00
Fax : 011-43 53 25 28

www.laxmipublications.com
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Price : **Rs. 250.00** *Only.* *Second Edition* : 2008

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Boston
11, Leavitt Street, Hingham,
MA 02043, USA

EEC-0689-250-ENGINEERING CHEMISTRY **C—15432/08/02**
Typeset at : Goswami Associates, Delhi. *Printed at* : Mehra Offset Press, New Delhi.

ENGINEERING CHEMISTRY

To My Parents With
Immense Love and Regard

Preface

This book has been divided into sixteen chapters covering all the disciplines of engineering chemistry such as inorganic, organic, synthetic, physical, applied, industrial, spectroscopic, and environmental chemistry. The book is written with the requirements of engineering students in mind; *i.e.*, every aspect of a topic is dealt with, keeping the focus on engineering science. Key features of the book include a simple and holistic approach with a large number of illustrations and tables.

Chapter 1, titled *Spectroscopic Methods of Analysis*, describes basic principles of spectroscopic analysis in brief and UV, IR, NMR Mass, and AAS spectroscopy in depth with a number of solved examples. Chapter 2, *Polymer Chemistry*, discusses classification, characteristics and properties, molecular weight, crystallinity, structure and properties of polymers, commercially important polymers and biopolymers. Preparation, properties, and applications of *conducting polymers* have also been described. *Chapter 3* describes general principles involved in organic chemistry, reaction intermediates and types of organic reactions with energy profile diagrams. *Chapter 4* provides complete mechanism and applications of organic name reactions provided in syllabus. *Chapter 5* describes various aspects of stereochemistry. Optical, geometrical and conformational isomerism in organic molecules is explained in a simple manner with energy profile diagrams. *Chapter 6* elaborates on electrochemical principles, galvanic cells, electrode potential, electrochemical series, chemical cells, concentration cells, relation of thermodynamic functions with cell potential and the Nernst equation with a large number of numerical problems and examples. *Chapter 7* deals with concepts of chemical kinetics such as rate of reaction, rate law, order and molecularity of reactions, first and second order rate equation, activation energy, theories of reaction rate, and complex reactions. *Chapter 8* explains Gibbs Phase rule and its applications to water and sulphur systems. *Chapter 9* deals with the theories of corrosion, factors affecting corrosion, types of corrosion, and corrosion control. *Chapter 10* describes water chemistry, explaining water hardness, water softening by zeolite, lime-soda method and ion exchange resins, boiler feed water, waste water treatment, and reverse osmosis. *Chapter 11* discusses classification and calorific value of fuels, coal analysis, liquid and gaseous fuels, and nonconventional energy sources such as solar energy, biomass and biogas. *Chapter 12* describes environmental pollution, different pollutants, air pollution, acid rain, smog, and ozone chemistry. *Chapter 13* explains valence bond theory, molecular orbital theory, metallic bonding, semiconductors, Born-Haber cycle and hydrogen bonding. *Chapter 14* describes the concept of coordination compounds. *Chapter 15* discusses solid state chemistry covering the topics crystal structure, unit cell, space lattice, cubic systems, laws of crystallography, Bragg's Law, graphite and fullerenes.

Chapter 16, titled *Experimental Chemistry,* explains basic principles of volumetric analysis, types of titrations, preparation of solutions, and experiments, including organic analysis. Exhaustive discussion is given at the end of each experiment as well as general discussion questions and answers on volumetry and organic analysis. Complete information regarding laboratory accidents and first aid is provided in the same chapter.

At the end, useful appendices and examination papers are provided.

I hope the book will prove a useful tool for students of undergraduate engineering classes. Critical suggestions from users on material presented are welcomed for the improvement of the book.

—Author

CONTENTS

Chapter 1

SPECTROSCOPIC METHODS OF ANALYSIS

1.1 INTRODUCTION

Molecular spectroscopy is defined as *the study of interaction of electromagnetic radiations with matter.* It provides valuable information regarding molecular structure such as molecular symmetry, bond distances, bond angles; chemical structure such as chemical properties, electronic distribution, bond strength, molecular reactions; and thermodynamic properties.

1.2 ELECTROMAGNETIC SPECTRUM

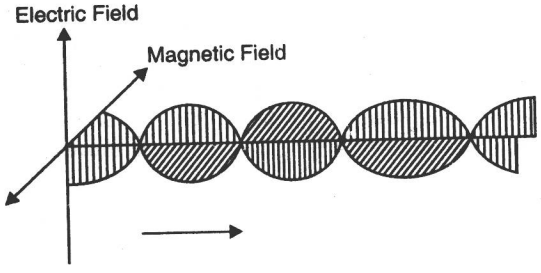

FIGURE 1.1 **Beam of electromagnetic radiation according to wave nature concept.**

An electromagnetic radiation is a form of energy that is transmitted through space at an enormous velocity. Quantum mechanics suggests that electromagnetic radiation has a dual character, *i.e.*, exhibiting wave as well as particle behavior. According to wave nature of radiations, the electromagnetic

wave consists of oscillating electric and magnetic fields. The vectors of electric and magnetic fields are perpendicular to the direction of propagation of radiations (Figure 1.1).

The electromagnetic spectrum extends from the radio wave to the microwave, infrared, visible, and ultraviolet regions. Beyond these are X-ray, gamma ray, and cosmic ray regions shown in Figure 1.2.

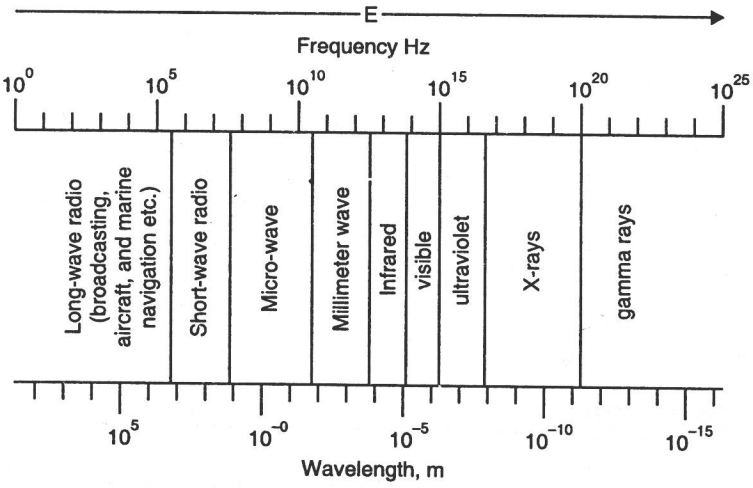

***FIGURE 1.2* Various regions of the electromagnetic spectrum.**

TABLE 1.1 Some Components of the Electromagnetic Spectrum

Type of Spectra	Wavelength	Energy in kcal/mol	Effect on the Molecule
1. Ultraviolet	200–400 nm	143–82	Changes in electronic energy levels within the molecule.
2. Visible	400–800 nm	82–36	Changes in electronic energy levels within the molecule.
3. Infrared	2–16 μm	14.3–1.8	Changes in vibrational and rotational movements of the molecule.
4. Nuclear magnetic resonance			Induces changes in the magnetic energy levels of certain nuclei.

The wavelengths of visible light range from 400 nm (violet) to 800 nm (red). The *visible region* however, is a very small part of the entire electromagnetic spectrum. Wavelengths slightly shorter than those of the visible fall into *ultraviolet region*, while slightly longer wavelengths fall into *infrared region*. Some components of the electromagnetic spectrum are listed in Table 1.1 along with their wavelength, the energy associated with them, and the type of effect they are capable of producing in a molecule.

Common symbols used in spectroscopy are given in Table 1.2.

TABLE 1.2 Symbols Used in Spectroscopy

Symbol	Definition
ν	Frequency in Hz cycles per second.
λ	Wavelength.
μm	Micrometre, same as micron (μ), 10^{-6} m.
Å	Angstrom, 10^{-10} m or 10^{-12} cm.
cm^{-1}	Wave number, frequency in reciprocal or $1/\lambda$.

1.3 LAMBERT-BEER OR BEER'S LAW

Lambert's law states that, *when a monochromatic light is passed through a solution, the decrease in the intensity of light with the thickness of the solution is directly proportional to the intensity of incident light.*

$$I_t = I_o e^{-kx} \tag{1.1}$$

where, I_t = intensity of the transmitted light

I_o = intensity of the incident light

x = thickness of the medium or the length of the solution

k = absorption coefficient

Beer's law an extension of Lambert's law states that, *when a monochromatic light is passed through a solution, the decrease in the intensity of light with the thickness of the solution is directly proportional to intensity of incident light as well as the concentration of the solution.*

$$I = I_o e^{-\varepsilon cx} \tag{1.2}$$

where, ε = Molar absorption coefficient

c = concentration of solution

The equation (1.2) may be written

$$\frac{I}{I_o} = e^{-\varepsilon cx}$$

$$\log \frac{I}{I_o} = -\varepsilon cx$$

where, $\frac{I}{I_o}$ is called *transmittance*, T and, $-\log \frac{I}{I_o} = -\log T$ and is called *absorbance.*

$$-\log \frac{I}{I_o} = -\log T = A$$

$$\therefore \quad A = \varepsilon c x \tag{1.3}$$

$$\varepsilon = \frac{A}{cx}$$

where, ε = molar absorbing coefficient

c = molar concentration

x = path length in centimeters

The magnitude of the molar absorption coefficient is directly related to the probability of a particular transition.

$$\varepsilon_{max} = 0.87 \times 10^{20} \text{ P.a.}$$

P = Transition probability with values ranging from 0 to 1.

a = Target area of the absorbing system.

Generally transitions with ε_{max} value more than 10^4 are called *allowed transitions* and ε_{max} value less than 10^4 are called *forbidden transitions.*

The instrument used for absorption measurement is composed of various instruments. For example, colorimeters or spectrometers are constructed according to the following general scheme (Figure 1.3).

1. **Light source.** In the infrared region, the source of heat radiations is Nernst glower or globar. In the Nernst glower, the filament consists of a mixture of oxides of the cerium and thorium, which are kept at high temperature (~ 1500°C) electrically. For more rarely studied regions (25 to 1000 μ), sources like the Welsbach lamp (a quartz-jacketed mercury arc), strongly heated glass, etc. have been used. However, the radiation is not monochromatic, and for use in spectrographs it must be followed by some dispersing element.

   In the visible-UV region, the usual sources are incandescent lamps or many types of discharge tubes such as hydrogen discharge lamps, deuterium lamps, and mercury arc. In Raman spectrometer, the source is mercury arc.

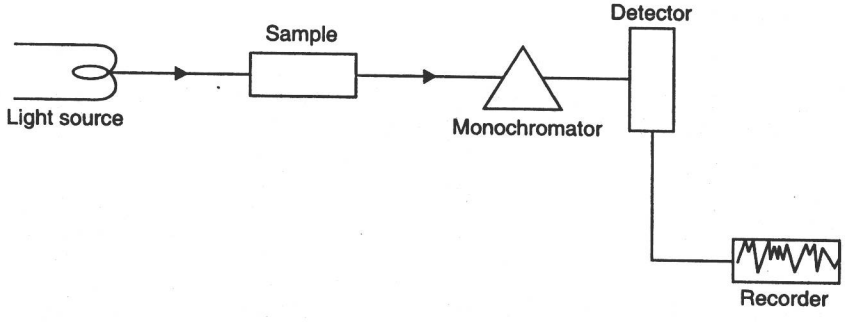

FIGURE 1.3 **A simple sketch of absorption measurement instruments.**

2. **The sample container.** The sample is placed in the sample container. The windows of the sample must be chemically resistant to the sample. In the visible-ultraviolet regions,

glass or quartz windows are used. In the infrared region, NaCl and KBr windows are used. For the study of aqueous solutions, AgCl windows are necessary. The length of the sample container is 0.91 mm to 01 mm for solid and liquid samples. Gas samples are usually contained in cells 5 cm to 10 cm long.

3. **The monochromator.** Except for microwave spectroscopy, some element is necessary by means of which the radiations can be separated in space according to wavelength, after it has passed the sample. This part of the spectrometer is known as monochromator. Its principal part is a dispersing element, *viz*, a prism or grating. Sometimes filters transparent over limited wavelength ranges can be used in combination with gratings.
4. **The detector.** In all spectrometers, the emitted radiations from the sample must be analyzed with regard to radiation intensity as a function. The radiation energy is measured by transforming it to some other forms of energy, usually electrical energy. The "transformer" is called the detector.

   In the microwave region, the detector is a crystal rectifier. At the higher frequencies in the infrared region, thermocouples are used. In the visible and the ultraviolet region the photocells are used.
5. **Spectrum recording.** When there is no sample present, the detector output will be constant over the range of frequencies covered by the instrument. However, when the radiations are passed through a sample, having just two possible energy levels E_1 and E_2, the detector output will show a sudden fall at frequency given by $\nu = [(E_2 - E_1)/h]$. It means some energy at this frequency will be absorbed by the sample and it no longer reaches the detector. The resulting trace on chart paper records the detector output on the percentage of the energy absorbed by the sample on the light (I). The spectrum has been scanned between the beginning and ending frequencies. Such a spectrum is referred to as 'frequency domain', which indicates record of detector output against frequency.

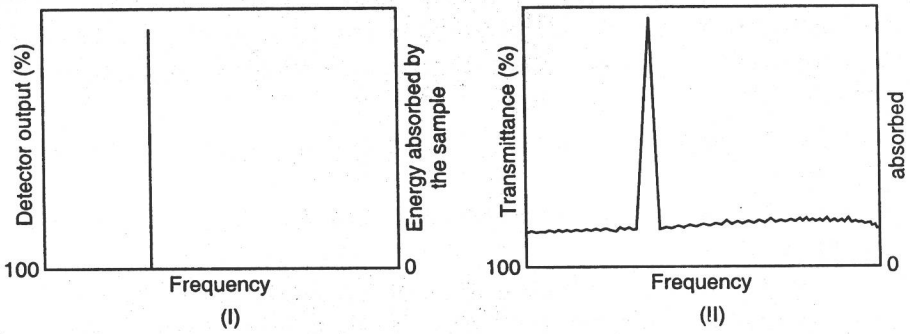

FIGURE 1.4

It is evident from the record (II) that the ideal situation represented in (I) is seldom attained. Thus, the base line is seldom horizontal (as represented in ideal situation). The reasons for this are:

- It is impossible to make the slits infinitely narrow. Therefore, a range of frequencies rather than a single frequency reaches the detector.
- Energy transitions in atoms or molecules are not absolutely sharp but always occur over a range of frequencies.