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**PART ONE**

**Principles**



## CHAPTER 1

# Introduction

Analytical chemistry may be defined as the science and art of determining the composition of materials in terms of the elements or compounds which they contain. Historically, the development of analytical methods has followed closely the introduction of new measuring instruments. The first quantitative analyses were gravimetric, made possible by the invention of a precise balance. It was soon found that carefully calibrated glassware makes possible considerable saving of time through the volumetric measurement of gravimetrically standardized solutions. Similar volumetric apparatus also led to the development of methods of measuring gases.

In the closing decades of the nineteenth century, the invention of the spectroscope brought with it an analytical approach which proved to be extremely fruitful. At first, however, it could be applied only qualitatively; gravimetric and volumetric methods remained for many years the only quantitative procedures available for nearly all analyses. Gradually, a few colorimetric and nephelometric methods were introduced, principally for substances for which other techniques were unknown or unreliable. Then electrical measurements were found to be applicable to the detection of end points in titrations. In the years since about 1930, the rapid development of the vacuum-tube amplifier, the photoelectric cell, and other devices has resulted in the establishment of many analytical methods based upon them. Today the analyst must have a working knowledge of a dozen or so instruments which were virtually unknown twenty years ago.

Nearly any physical property characteristic of a particular element or compound can be made the basis of a method for its analysis. Thus the absorption of light by a colored material, the current-carrying capacity of a solution, the power of a gas to conduct heat—each can serve as a tool in the analysis of the material involved. A whole series of related techniques depend upon the varying electrical properties of different elements, as evidenced by their redox potentials. The phenomena of artificially induced radioactivity, so largely explored in connection with the study of atomic energy, have led to several analytical methods of extremely great significance and wide potential applicability.

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It is the purpose of this book to investigate the possibilities of many of these modern instrumental methods of analysis. First, however, it will be worthwhile to summarize some fundamental concepts.

**Qualitative vs. Quantitative Analysis.** A qualitative analysis tells what substances are present in a sample, but only very roughly their amounts. A quantitative determination, on the other hand, gives much more precise information concerning the amount of a specified component of the sample. A few instruments, such as the polarograph and the spectrograph, can give both qualitative and quantitative results at the same time.

**Fundamental and Derived Physical Quantities.** Fundamental physical quantities that can be measured directly are surprisingly few. Most of the measurements which we make in the laboratory consist essentially in the observation of linear or angular displacement, by comparison with some kind of scale. In using the analytical balance, we actually note the angular displacement of a pointer and adjust the weights to bring the displacement to zero. The burette is read by observation of the linear displacement of the meniscus from its initial to its final position. Electrical measurements are made through the angular displacement of meter needles or potentiometer dials, and so on. Many other quantities, such as the intensity of light or of sound, must serve only as null indicators, in the sense that either the quantity or the difference between it and a standard is made zero unless an instrument is available to convert the quantity to a simple displacement. It is the function of the instrument to translate chemical composition into information directly observable by the operator. In nearly all cases, the instrument acts either directly or indirectly as a *comparator*, in that the unknown is evaluated relative to a standard.

Most of the analytical methods to be described rest on sound mathematical theory. Occasionally there is reported an experimental procedure which is purely empirical, with no theoretical background. Such a method may be usable for analytical purposes, but it must be proved valid by extensive study and independent checking of data so that the analyst may have certain knowledge of what he is actually measuring.

**Titration.** Titration is defined as the measurement of an unknown constituent by establishment of the exactly equivalent amount of some standard reagent. Physical measurements are involved in two ways: in the detection of the equivalence point and in the measurement of the quantity of reagent consumed. Usually, and unless otherwise specified, the quantity of reagent is measured volumetrically with a burette. The only important exception is the *coulometric* titration, where the reagent is generated electrolytically on the spot as required, and its quantity determined by electrical measurements.

A number of physical properties can be applied in analysis either with

or without a titration. These include, among others, electrolytic conductivity, potentials of electrodes, and diffusion currents, which will be discussed in succeeding chapters.

**Physical Properties Useful in Analysis.** The following is a list of physical properties which have been found applicable to chemical analysis. This list is not exhaustive, but it certainly includes all those properties which have been extensively investigated, as well as some not yet fully exploited. Most of these are considered in detail in later chapters.

*Extensive Properties*

1. Mass (or weight)
2. Volume (of a liquid or a gas)

*Mechanical Properties*

3. Specific gravity (or density)
4. Surface tension
5. Viscosity
6. Velocity of sound (in a gas)

*Properties Involving Interaction with Radiant Energy*

7. Absorption of radiant energy  
(X-rays, ultraviolet, visible, infrared, microwaves)
8. Turbidity
9. Emission of radiation (following excitation)
10. Raman effect
11. Rotation of the plane of polarized light
12. Refractive index
13. Dispersion
14. Fluorescence and phosphorescence
15. Diffraction of X-rays and electrons
16. Nuclear and electron magnetic resonance

*Electrical Properties*

17. Half-cell potentials
18. Current-voltage characteristics
19. Electrical conductivity
20. Dielectric constant
21. Magnetic susceptibility

*Thermal Properties*

22. Transition temperatures (melting or boiling points, etc.)
23. Heats of reaction (combustion, neutralization, etc.)
24. Thermal conductivity (of a gas)

*Nuclear Properties*

25. Radioactivity

**Methods of Separation Prior to Analysis.** It would be desirable to discover analytical methods which are *specific* for each element or radical

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or class of compounds. Unfortunately, only a few methods are completely specific,\* and it is therefore frequently necessary to perform quantitative separations with the objective either of isolating the desired constituent in a measurable form or of removing interfering substances. Some methods of separation are the following:

1. Precipitation
2. Electrodeposition
3. Formation of complexes
4. Distillation
5. Solvent extraction
6. Partition chromatography
7. Adsorption chromatography
8. Ion exchange
9. Electrophoresis
10. Dialysis

\* An example of an analysis which is specific is the gravimetric or colorimetric determination of nickel with dimethylglyoxime; the only other element to precipitate with this reagent is palladium, and that only at much higher levels of acidity than needed for nickel.



## CHAPTER 2

# Introduction to Optical Methods

A major class of analytical methods is based on the interaction of radiant energy with matter. To introduce these methods, we will summarize briefly some pertinent properties both of radiation and of matter.

**The Nature of Radiant Energy.** An investigation into the properties of radiant energy reveals an essential duality in our understanding of its nature. In some respects its properties are those of a wave, while in others it is apparent that the radiation consists of a series of discrete packets of energy (photons). The photon concept is almost always required in the rigorous treatment of the interactions of radiation with matter, although the wave picture may be used to give approximately correct results when large numbers of low-energy photons are involved.

Radiant energy can be described in terms of a number of properties or parameters: The *frequency*  $\nu$  is the number of oscillations per second described by the electromagnetic wave; the units of frequency are the *hertz* (1 hz = 1 cycle per second) and the *fresnel* (1 f =  $10^{12}$  hz). The *velocity*  $c$  of propagation is very nearly  $3.00 \times 10^{10}$  cm per sec for radiation traveling through a vacuum and usually somewhat less for passage through various transparent substances.

The *wavelength*  $\lambda$  is the distance between adjacent crests of the wave in a beam of radiation. It is given by the ratio of the velocity to the frequency. The units of wavelength are angstroms (A or Å; 1 A =  $10^{-8}$  cm), microns ( $\mu$ ; 1  $\mu$  =  $10^{-6}$  m =  $10^{-4}$  cm), or millimicrons (m $\mu$ ; 1 m $\mu$  =  $10^{-3}$   $\mu$  = 10 A). Another quantity which is convenient in some circumstances is the *wave number*  $\sigma$ , which is the number of waves per centimeter.\*

A beam of radiation consists of energy being propagated from the source through a medium or series of media to a receptor where it is absorbed (except as some of it may be absorbed by the media through which it passes). Since energy per unit of time is power, it is correct to speak of the *radiant power* of the beam, a quantity often loosely referred to as intensity. *Intensity* more correctly refers to the power emitted by the source

\* It is unfortunate that the symbol  $\nu$  is often used both for the frequency and for the wave number, which are distinct concepts. We will consistently use  $\sigma$  for wave number to avoid ambiguity.

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per unit solid angle in a particular direction. A photoelectric cell gives a response related to the total power incident upon its sensitive surface. A photographic plate, on the other hand, integrates the power over the period of time of the exposure to the beam, and hence its response (silver deposit) is at least approximately proportional to the total incident energy (rather than to power) per unit area. In both photoelectric cells and photographic plates, as well as in the human eye, the response is a more or less complicated function of the wavelength, and this must be taken into consideration in their use. The only detectors which do not share this fault are those which depend on the heating effect of the radiation.

The energy content of each photon in a beam of radiation is dependent on the frequency according to the relation

$$E = h\nu$$

where  $h$  is a fundamental constant (Planck's) =  $6.62 \times 10^{-27}$  erg-seconds.

**Polarization.** A normal beam of radiation can be thought of as a

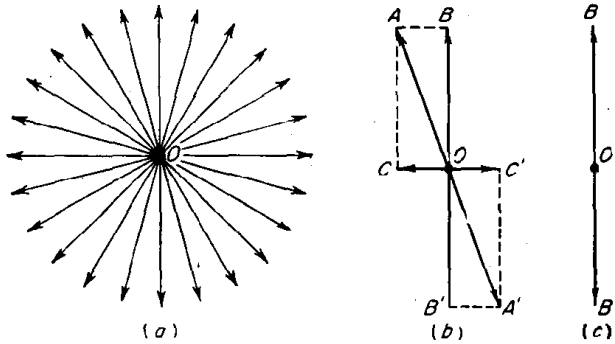


FIG. 2-1. Vibration vectors in ordinary and plane-polarized electromagnetic radiation.

bundle of waves with their vibratory motions distributed over a family of planes all of which include the line of propagation. Figure 2-1a shows a cross section of such a ray which is proceeding in a direction perpendicular to the plane of the paper. If this beam of light is passed through a sheet of Polaroid or a Nicol (calcite) prism, each separate wave of the bundle, for example, that vibrating along the vector **AOA'** (Fig. 2-1b), is resolved into its components **BOB'** and **COC'** in the directions of the  $X$  and  $Y$  axes characteristic of the Polaroid or Nicol. The polarizing material has the property of absorbing one of these component vibrations (say **COC'**) and passing the other (**BOB'**). Thus the emergent beam consists of vibrations in one plane only (Fig. 2-1c) and is said to be *plane-polarized*.

A second Polaroid or Nicol placed in the beam will similarly pass only that component of the light vibrating parallel to its axis; and since the beam is already polarized, that means that in one position essentially all

the radiation will come through, while turning the second polarizer (called the *analyzer*) through a  $90^\circ$  angle will cut the power to zero. This is illustrated in Fig. 2-2. Radiation from a lamp, rendered parallel by a collimating lens, is polarized by Polaroid A,

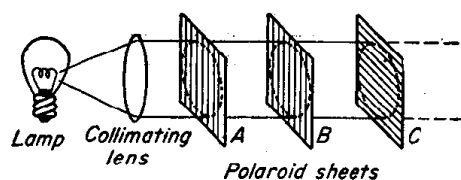


FIG. 2-2. Plane polarization of radiant energy.

which has its axis vertical. Polaroid B, also with a vertical axis, has no further effect on the beam, but C, with its axis oriented horizontally, cuts the light to zero. If C is rotated in its own plane, the power of radiation transmitted varies as the sine of the angle through which it is turned. Two Polaroids or Nicol prisms placed one before the other are said to be *crossed* if their axes are mutually perpendicular, so that no radiation can get through.

A beam of radiation may possess any degree of polarization from zero (complete symmetry) to 100 per cent (complete polarization). Other types of polarization than plane (elliptical and circular) are also known, but are not important for our present purposes.

The spectrum of radiant energy is conveniently broken down into six regions, as shown in Table 2-1. The limits of these regions are determined by the practical limits of appropriate experimental methods of production and detection of radiations. The figures quoted in the table are not in themselves especially significant, and should only be considered as rough boundaries.

Table 2-1. Regions of the Electromagnetic Spectrum

Designation	Wavelength limits		Frequency limits, hz
	cm	Usual units	
X-rays	$1 \times 10^{-10}$ – $1 \times 10^{-7}$	$10^{-2}$ – $10$ A	$3 \times 10^{20}$ – $3 \times 10^{17}$
Ultraviolet	$1 \times 10^{-7}$ – $4 \times 10^{-5}$	1–400 $m\mu$	$3 \times 10^{17}$ – $8 \times 10^{14}$
Visible light	$4 \times 10^{-5}$ – $8 \times 10^{-5}$	400–800 $m\mu$	$8 \times 10^{14}$ – $4 \times 10^{14}$
Infrared	$8 \times 10^{-5}$ – $3 \times 10^{-2}$	0.8–300 $\mu$	$4 \times 10^{14}$ – $1 \times 10^{12}$
Microwaves	$3 \times 10^{-2}$ –100	0.03–100 cm	$1 \times 10^{12}$ – $3 \times 10^8$
Radio waves	100– $10^5$	1–1000 m	$3 \times 10^8$ – $3 \times 10^5$

**Interactions with Matter: Atomic Spectra.** Electromagnetic radiation originates in the acceleration of electrically charged particles and can be absorbed by the reverse process, contributing its energy to produce such acceleration. Hence an understanding of the interactions between matter and radiation can only be built upon a knowledge of the structure of atoms and molecules, particularly with respect to the possible motions

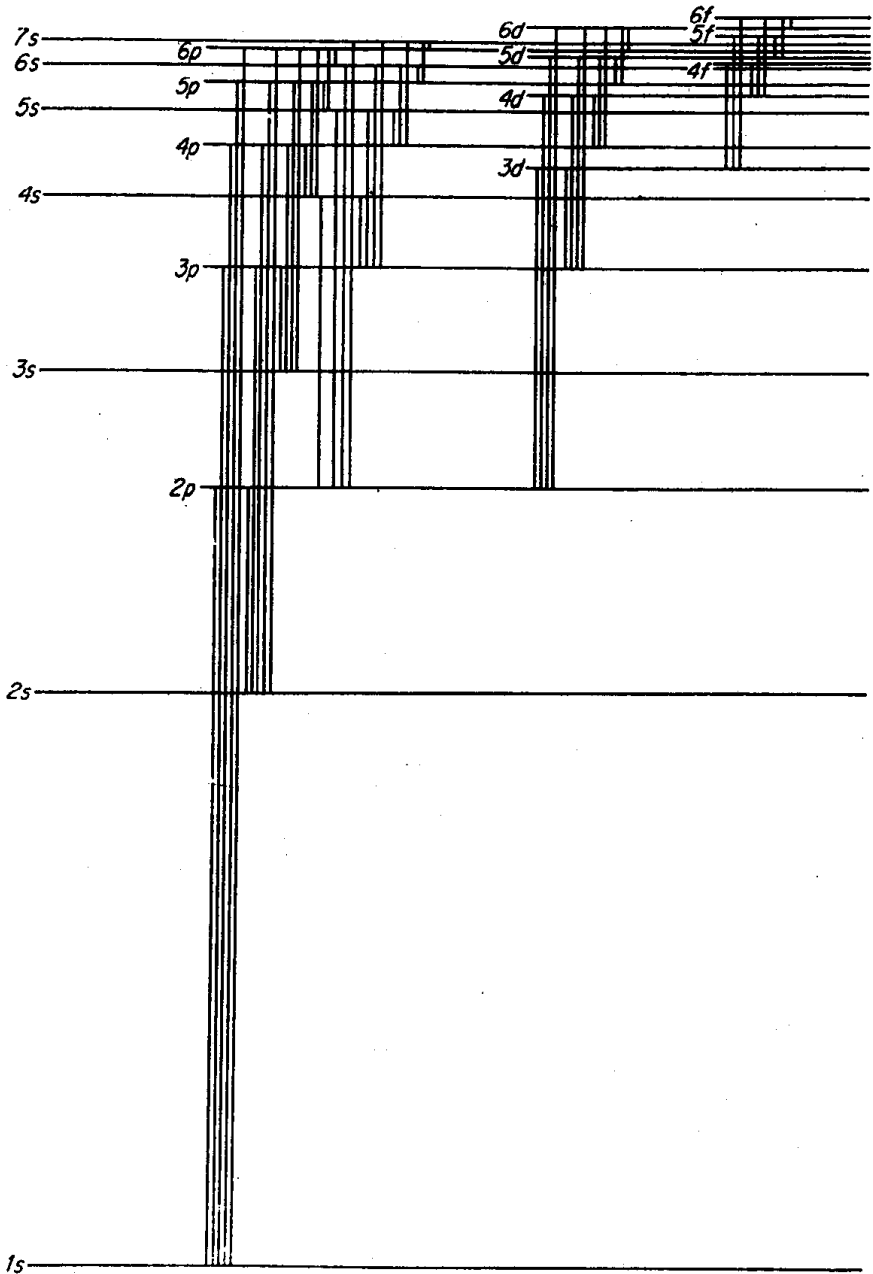


FIG. 2-3. Atomic energy levels, schematic.

involved. Figures 2-3 and 2-4 show typical energy-level diagrams for an atom and a molecule, respectively.

Consider first the energy levels (orbitals) of an atom (Fig. 2-3). The vertical lines in this figure indicate permitted electronic transitions between the various levels. In a normal (*i.e.*, unexcited) atom, the electrons occupy as many orbitals as needed, starting with the lowest (1s) and pro-

ceeding upward according to the well-known quantum rules. Sodium, for example, has 11 electrons, designated  $1s^2, 2s^2, 2p^6, 3s^1$ . The  $3s$  electron is the least strongly held and hence can easily be pushed upward from the  $3s$  to the  $3p$  level, which is an example of electronic excitation. This can be accomplished by providing energy in any one of a number of forms. The excited electron has a strong tendency to return to its normal state, the  $3s$  level, and in doing so emits a quantum of radiation (a photon). This emitted photon possesses a very definite and uniform amount of energy,

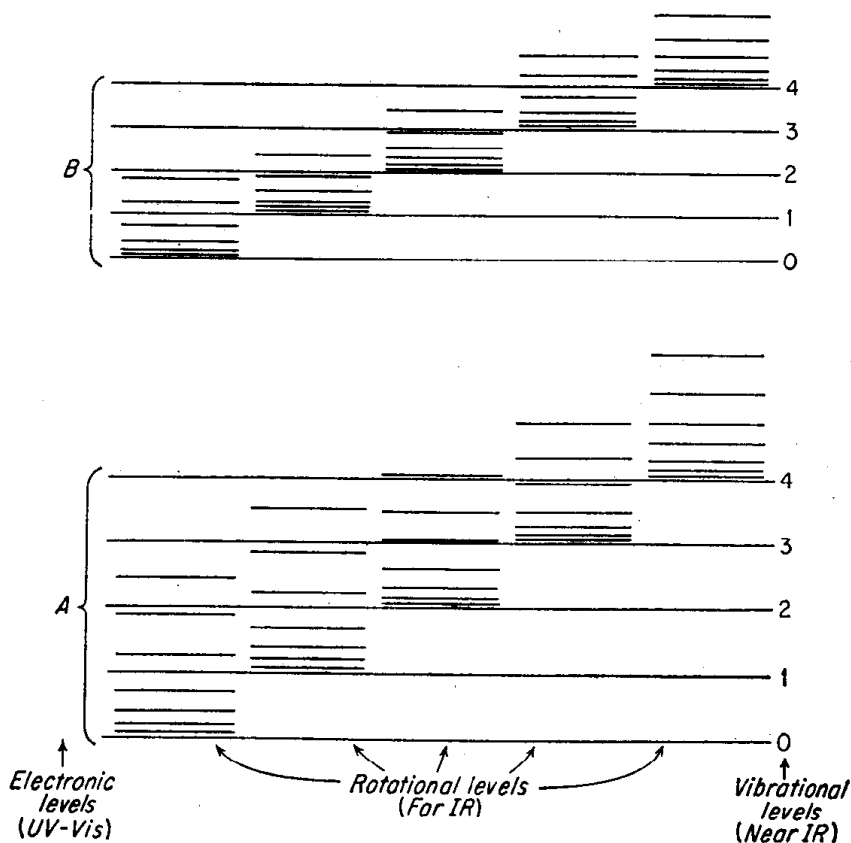


FIG. 2-4. Molecular energy levels, schematic.

dictated by the spacing of the energy levels. In the present example, it constitutes the familiar yellow light characteristic of flames or lamps containing sodium in the vaporized state. This simple case, where the outer electron is raised by one energy level, then returns, is known as *resonance radiation*. If the electron is given more than enough energy to produce resonance, it may become more highly excited, raised to some level higher than  $3p$ , say  $4p$ . Then it may not drop back to  $3s$  by a single process but may pause at intermediate levels, like a ball bouncing down steps. This situation no longer fits the definition of resonance radiation but is more

complex. With a highly potent source of energy, many electrons (not only the outermost) in any element can be excited to varying degrees, and the resulting radiation may contain as many as several thousand discrete and reproducible wavelengths. This is the basis of the analytical method of *emission spectroscopy*.

If the source of excitation is extremely energetic, an inner electron can be torn loose from its atom. An electron from a higher level will then drop in to fill the vacancy. Since the energy change corresponding to this transition is much greater than in the case of excited outer electrons, the photons radiated will be of much greater frequency and correspondingly shorter wavelength. This describes the emission of *X-rays* from atoms subjected to bombardment by a beam of fast-moving electrons.

**Molecular Spectra.** In a typical molecule, as contrasted with an atom, a few energy levels might show relations such as those depicted in Fig. 2-4. The major divisions, labeled *A* and *B*, are separated by a considerable energy space; they are known as *electronic levels*, as transitions from one to another of these levels involve changes in the energy of one or more electrons in the molecule. The sublevels numbered 0, 1, 2, 3, . . . within each electronic level are called *vibrational levels*, as they correspond to differences in the energy of the molecule as a whole due to interatomic vibrations of one sort or another. The sub-sublevels related to each vibrational level correlate with rotation of atoms or groups of atoms within the molecule and so are called *rotational levels*.

Transitions within molecules are not usually observed as emission spectra (except in the phenomenon of fluorescence) but rather by their selective *absorption* of radiation passing through them. Transitions between electronic levels are found in the ultraviolet and visible regions; those between vibrational levels (within the same electronic level), in the near infrared (approximately 1 to 15  $\mu$ ); and those between neighboring rotational levels, in the far infrared and microwave regions. Of course, electronic transitions may involve jumps from and to various sublevels, so that ultraviolet absorption spectra may under suitable conditions show "fine structure," owing to the various vibrational and rotational sublevels.

In general, different substances differ in the details of their energy-level patterns and therefore show different absorption spectra throughout the ultraviolet, visible, and infrared ranges. The analytical significance of such spectra will occupy the next two chapters.

**Fluorescence.** Some materials are capable of becoming electronically excited by irradiation with high-energy photons. The radiant emission produced thereby may be of the same wavelength, in which case it may be difficult to observe and will not be of much use for analytical purposes. Of greater importance is the case where the emitted radiation has less energy than the exciting radiation and hence a longer wavelength; this

phenomenon is known as *fluorescence*. This can occur when the electron is raised by more than one energy level: the absorbed energy is then emitted not all in one quantum but in a series of steps, each with less energy than that of a quantum of the exciting radiation. Many organic and a few inorganic compounds, when irradiated with ultraviolet, fluoresce in the visible spectrum. Fluorescence is even more important in the X-ray field, where irradiation of a sample with high-energy X-rays is a most convenient method of exciting X-ray spectra in somewhat lower-frequency regions.

**Raman Spectra.** A phenomenon which bears some relation to fluorescence is the *Raman effect*. Here also radiation is absorbed by a substance and reemitted, usually with a longer wavelength. The difference is that in the present case the emergent radiation is less energetic than that absorbed, because energy has been extracted by the molecule to raise it to a higher vibrational or rotational level. Since these levels are subject to quantum rules, the energy change in the Raman effect is also quantized, and discrete wavelength shifts are observed. Occasionally there is a Raman shift toward higher energies. This effect arises with molecules which are so easily excited that a relatively large proportion of the molecules already possess rotational or vibrational energy in excess of their ground states. The excess energy can be lost to the radiant energy in the reverse of the more common process. The lines so produced in the spectrum are known as *anti-Stokes* lines in contrast with the *Stokes* lines, which are of longer wavelength than the exciting source.

**Dispersion.** The *index of refraction* is another important optical property of matter. It is defined as the ratio of the velocity of radiation in a vacuum to that in the substance considered. The variation of the refractive index of a substance with wavelength is called its *dispersion*. The dispersion of a substance throughout the electromagnetic spectrum is intimately related to the degree to which radiation is absorbed. In regions of high transparency, the refractive index decreases with increasing wavelength (not linearly); in regions of high absorbance, the index is usually difficult to measure precisely, but must show a rather abrupt rise with increasing wavelength. Figure 2-5 shows schematically the absorption spectrum and the dispersion curve\* of a substance such as glass, which is transparent to visible radiations. The shape of the dispersion curve in regions of transparency is an important property, particularly of solids, because it is largely this curve which dictates the design of the lenses and prisms which are incorporated into optical instruments.

\* The existence of indices of refraction less than unity in certain portions of this curve indicates the possibilities of velocities of radiation greater than the *in vacuo* value. This would appear to violate relativity theory, but actually does not, because of a difference in the definition of velocity which need not concern us here. This point is discussed on p. 477 of the work by Jenkins and White.<sup>1</sup>

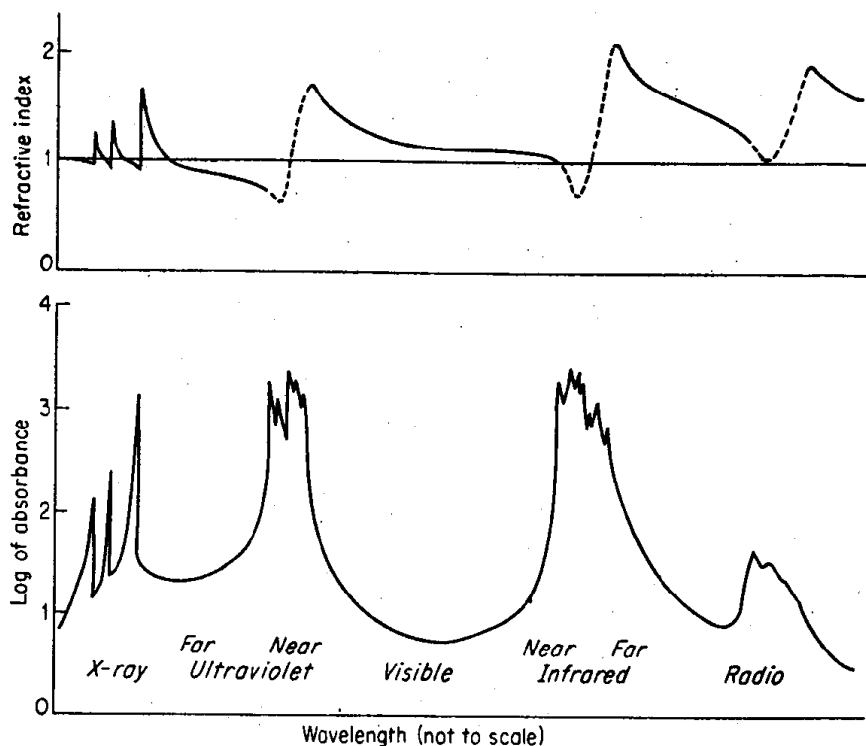


FIG. 2-5. Refractive index and absorbance as functions of wavelength over the whole electromagnetic spectrum. Schematic; for a hypothetical substance. (Upper section, after Jenkins and White<sup>1</sup>)

**Optical Activity.** Another optical property of analytical significance is the so-called *optical activity*, the ability exhibited by some crystals and solutions to rotate the plane of polarized light which is passed through them. The variation of this property with wavelength is known as *rotatory dispersion* and is related to regions of absorption in much the same manner as the refractive dispersion discussed previously.

A number of transparent crystalline materials, including calcite and quartz, show a phenomenon known as *double refraction*, which is evidenced by the fact that a beam of light passing into the crystal is split into two beams of equal power which diverge from each other at a small angle. The two beams are found to be plane-polarized at right angles to each other. This effect is of great value in the identification and study of crystals; it is also important in that it permits design of a number of optical instruments and components useful in the measurement of polarized light. One example is the Nicol prism.

#### REFERENCE

1. F. A. Jenkins and H. E. White, "Fundamentals of Optics," 3d ed., McGraw-Hill Book Company, Inc., New York, 1957.



## CHAPTER 3

# The Absorption of Radiation: Ultraviolet and Visible

If a beam of white light is allowed to pass through a glass container filled with liquid, the emergent radiation will be less powerful than that entering. The diminution in power may be approximately equal over the whole wavelength range, or it may be of different extent for different colors. The loss is due in part to reflections at the glass-air and glass-liquid surfaces (small arrows, Fig. 3-1) and in part to scattering by any suspended particles present; but it is primarily accounted for by the *absorption* of radiant energy by the liquid. In experiments with clear solutions, scattering may be reduced to a vanishingly small amount by ordinary care and cleanliness. In the study of colloidal suspensions, the scattered fraction may itself be important as an analytical tool.

The extent to which energy is absorbed by the liquid in the vessel of Fig. 3-1 is generally greater for some of the colors making up the white light than for others, with the result that the emergent beam is colored. Table 3-1 gives the colors of radiation of successive wavelength ranges, together with their complementary colors. These ranges are approximate only, as different observers give widely varying figures. The apparent color of the solution is always the complement of the color which is absorbed. Thus a solution which absorbs in the blue region (450 to 480  $m\mu$ ) will appear yellow; one which absorbs green will appear purple, etc.

In referring to color, we are of course restricting the discussion to the visible region of the spectrum, but, as will appear, many of the concepts and analytical methods will carry over with no change in principle into both the ultraviolet and infrared ranges.

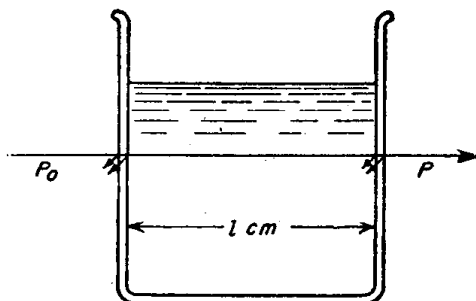


FIG. 3-1. The passage of radiation through a solution contained in a transparent vessel.