

INTRODUCTION

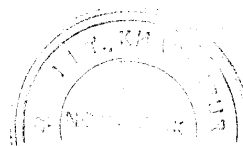
CHAPTER 1

Introduction

It is both pertinent and desirable on the basis of our present knowledge to discuss the principles involved in analytical methods so that they may be placed upon a sound foundation. Such is the object of this chapter. In addition to providing a rationale for existing practices, we hope to point to possible avenues of exploration which could lead to more useful methods of analysis. The aim, in brief, is to present a compact account, based on reactions between silver(I)-gelatin complex and reacting species, which help to understand the choosing the procedures for particular determination and the kinds of conditions under which the reactions were carried out.

1.1 Environmental Pollution

'Pollution' is defined as undesirable change in the environment by the activity of living being and the 'Pollutants' as those components of manmade wastes those contaminate the environment. Recorded history of a man reflects the continual struggle to manage his own natural environment in order to improve the health and well-being. Recently, much attention is being directed towards the environmental sanitation in most parts of the world. Continuous environmental vigilance is necessary to keep the record of toxic substances in the garden of humanity.



Perhaps never in history man has demonstrated such great concern for his total environment as is now being witnessed in many parts of the world. In connection with the development of the chemistry and the ever increasing demands of technology, various metals and toxic substances are being introduced into industries which under production condition can have a toxic effect in the ecosystem. Therefore, there is an urgent and primary need to determine the concentrations of these substances in the atmosphere in order to predict their toxicity and to determine the maximum allowable concentration in the surroundings.

Energy, employment and ecology are the three big factors which influence progress of a country as well as world as a whole. Any imbalance in these parameters results in serious repercussions over progress and economy. Efficient utilisation of resources indigenously available is the only alternative for solving the crisis. The civilised man today consumes enormous quantities of resources. In the process of consumption, he also wastes a lot. Wastes can be classified in two broad categories-material wastes and energy wastes. Material wastes are coming out from industry, mine, agriculture, dairy, slaughter house, leather processing even from domestic houses. Energy loss occurs mainly during the process of generation, distribution and consumption. A discussion on waste not only centres around the need to consider reutilisation but also the problem of their polluting effects which has now become one of the crucial dangers. Very recently,

we have come across the horrifying fact of Union Carbide disaster. Despite being handicapped with various problems environmental concern among governments and industries is beginning to emerge with certain impetus. It may not be possible to control pollution problem or to maintain ecological balance just by enforcing strict laws or by exercising stringent measure but the people should be made conscious by educating them with the problems and consequences - a noble duty of the scientific community. The efforts needed for the environmental management, however, shall have to be undertaken, implemented and enforced honestly.

Classification of Toxic Substances

It is established that there is a relation between toxicity and electronic structure characteristics of the chemical compounds. A few studies have been devoted to the establishment of a relation between the toxicity of the metal ions and the position of the elements in the periodic system. It is observed that in a particular group of the periodic table the toxicity increases with increase in atomic number. But recent literature reveals that aluminium may be deposited in the human brain. Keeping this observation in mind one must say that toxicity of substances and their effects on physiological systems is a very complicated field of research and the chapter has not yet come up to the age.

Therefore, an analysis and assessment of the environmental impact arising out of the developmental project can provide the necessary foundation, guidelines and precautions incorporated in the planning, construction and operation phases of the project, and these should be followed by proper environmental research.

1.2 Colloid Chemistry

In the beginning of the modern period in chemistry, investigators observed that substances ordinarily considered insoluble (gold, arsenic trisulphide, sulphur, aluminium hydroxide, etc.) could sometimes exist in apparently homogeneous solutions. On account of the instability of these solutions, the indirect manner in which they often had to be prepared, and a special branch has been developed in certain other respects. It has gradually become customary to distinguish between these 'pseudo-solutions', and ordinary solutions of sugar, common salt, alcohol, and the like. The pioneering works of Richter, Berzelius, Wohler, Frankenheim, Schneider, Wackenroder, Baudrimont, Selmi, Kuhn, Faraday, Crum, Peande Saint Gilles, and others in preparing and describing the 'pseudo-solutions' were given a certain unity by the classification and lasting nomenclature proposed by Thomas Graham.

The technique of separation of dissolved substances by differential diffusion through membranes is known as dialysis



as described by Graham. We have devoted our attention to dialysis technique to find out the amount of silver(I) ion taken up by gelatin. But since the experiment presents a mere qualitative picture we deliberately excluded the electrolysis technique.

Graham distinguished between the inorganic pseudo-solutions mentioned above as well as solutions of proteins, gums, tannin, polysaccharides and the like and ordinary solutions containing small molecules of known composition. The dissolved materials of the former class, displaying a very low rates of diffusion and leaving apparently amorphous solids upon evaporation of the solvent, were called 'colloids' (glue-like) which are in contrast with the other class of substances called the 'crystalloids'. Solutions of colloids were designated as 'sols', or specifically as 'hydrosols', 'alcosols', 'ethersols' etc., depending upon the medium; and the amorphous solids obtainable from sols were referred to as 'gels', or specifically, as 'hydrogels', 'alcogels', etc. The process of dispersing a gel or colloidal solid to form a sol was called 'peptisation'. The spontaneous shrinkage of a gel with the separation of a free liquid phase was termed 'syneresis'. Although Graham recognised that certain substances could form either colloidal or crystalloidal solutions, he often disregarded these and spoke as if the classification of substances into colloids and crystalloids were mutually exclusive.



Unless conditions are favourable, a colloidal solution may be a very transient system. An emulsion of a pure hydrocarbon oil in pure water soon flocculates unless the concentration is exceedingly low. Colloidal particles of pure silver in a mixture of toluene and naphthalene readily agglomerate and settle out. Silver iodide, precipitated from dilute, exactly equivalent solutions quickly flocculates. But if a slight excess of either reactant is present, a relatively stable sol is obtained. A general consideration of the stability of colloidal solutions reveals two important stabilising agencies, viz., solvation and electric double-layers, the former being typical of lyophiles, the latter of lyophobices.

Many agencies are capable of causing the coagulation or flocculation of colloidal solution e.g. variation of temperature, irradiation with electromagnetic or β radiation, addition of tanning agents, nonsolvent liquids and electrolytes.

Usual attempts have been made on the use of silver(I)-gelatin complex and the gelatin stabilised silver sol system to develop procedures to improve the chemistry of trace analysis of several components. Some of these improvements are in fact only the modifications of the classical methods to meet some conditional needs for the development of new analytical techniques.

1.3 Conductometry

The value of the electrical conductance of solution plays a major role in electrochemical processes. It may be used as a basis for rational selection of the composition of an electrolyte. The throwing power of galvanic baths strongly depends on the value of conductance. Data on conductance measurements are used in electrochemistry. Conductometry finds wide application in chemical analysis, production control and scientific research. Conductometry has a number of advantages over chemical methods of analysis since it enables the determination of the content of an individual substance in a solution by simply measuring the conductance of the solution. To do this, it is sufficient to have a conductance-concentration calibration curve. Besides, the solution being analysed undergoes practically no change in the course of conductance measurements, which makes it possible to measure its conductance several times and keep the solution in order to check the results at any time.

Conductometric analysis is one of the most precise technique for determining the solubilities of sparingly soluble substances. The analysis is based on the measurement of the conductance of a liquid phase which is in equilibrium with the corresponding solid substance. Knowing the mobilities of the ions into which a particular sparingly soluble substance dissociates and the conductivity of the solution, one can

calculate its concentration by using the equation

$$C = \frac{x}{z \cdot f \cdot \lambda (\lambda_+^{\circ} + \lambda_-^{\circ})}$$

Since a salt is sparingly soluble, its concentration in solution is very small. Hence the degree of dissociation α and the conductance coefficient f_{λ} may be assumed to be equal to unity, and the ionic mobilities λ_+ and λ_- in a given solution are equal to λ_+° and λ_-° , ionic mobilities at infinite dilution. So if concentration C is known, it is easy to find the solubility of the substance. Conductometry is also employed to determine the equilibrium constants of chemical reactions in solutions, the basicity of acids, etc.

In contrast to ordinary titration techniques, conductometric titration does not require the use of indicator and can be carried out in coloured as well as in very dilute solutions. During titration the course of the reaction is followed and the conductance of the solution is measured after each addition of the titrating agent. The end point of titration coincides with the inflection on the curve obtained by plotting the conductance against the volume of solution added. The change in conductance during conductometric titration is associated with the replacement of some ions by others having different ionic conductance values.



Conductometric titration depends very strongly on the difference in the mobilities of the associated and appearing ions, and the greater this difference the higher is the sensitivity. In carrying out conductometric titrations one should take into account not only the degree of completeness of the principal reaction which is of great importance but also the mobilities of ions which do not participate directly in the reaction.

Another feature distinguishing the conductometric titration from the ordinary procedure is that it does not yield a single point but the full curve for the entire process of titration. On the basis of this curve one can get an idea of the course of the reaction and some properties of the substances obtained.

The electrical conductance of a solution depends on all the components present and is therefore an integral property of the system. Conductometry is successfully utilised for the control of precipitate washout, regeneration of ion-exchange resins, water purification and for many other technological processes.

So-called high-frequency conductometry has been gaining an ever increasing application. In this method alternating currents of frequencies of the order of several millions of hertz is used. With these frequencies the electrodes may be

removed from the solution and placed outside the cell. This eliminates many difficulties involved in ordinary conductometry, viz., the catalytic effect of electrodes on the reactions taking place in solutions, the change of electrode surfaces during the measurements. Hence there is the necessity of using electrodes made of noble metals, etc.

The conductometric method cannot, however, be employed for the determination of a single ionic species against the background of other electrolytes.

We have achieved the control selectivity in the reaction of gelatin stabilised silver sol with inorganic cyanides and peroxides which are discussed in relation to simple conductometric measurements.

1.4 Ultraviolet Spectra of Proteins

We feel unable to add anything significant and would therefore like to resume the old custom which many previous presidents have followed of presenting in somewhat general terms a topic closely connected with the present investigation. We present important spectral informations to become more deeply aware of the fundamentals of protein molecules.

Most proteins are colourless in the visible region of the spectrum, however, they exhibit absorption in the near ultraviolet region. These spectroscopic absorptions afford information

relevant to the composition of these complex molecules, as well as the conformation or three dimensional structure of the molecules in solution.

The simplest way of accounting for the absorption spectrum of a protein may be considered as the sum of the spectra of its components. More the complex is the protein more is the complexity in the absorption spectra of protein. The ultraviolet spectra of proteins were reviewed by Beaven and Holiday (1952), and by Doty and Geiduschek (1953). The review of Dannendery (1951) was also be noted. In this present chapter, most of the attention is made on the developments in the past decade.

The ultraviolet spectra above 2500 \AA is simple and most easily accessible to experimentation. The region between $2500-2100 \text{ \AA}$ is less promising because of its greater complexity. Lastly, the region below 2100 \AA stands for the exciting peptide bond and its conformation. Study of the fluorescence and fluorescence-polarisation of proteins appear to constitute one of the most sensitive new approaches to protein study. The absorbing components of proteins are the amino acids. The $\pi - \pi^*$ transitions in proteins represent the absorption due to aromatic amino acids.

Ham and platt showed that the peptide bond exhibits an

absorption peak at 1850 \AA° . The study of absorption due to peptide bond falls in the range $1450\text{-}2400 \text{ \AA}^{\circ}$ while studying in solid films. It was also shown that the absorption due to amide group takes place in the region 1900 \AA° which includes components associated with electronic coupling in the crystalline state. Absorption in the region 1600 \AA° stands for Rydberg transition, finally the weak absorption around 2200 \AA° is given the assignment $n - \pi^*$ transition. Since the spectrum of the amide groups shows electronic resonance coupling in the crystal, one could guess that the presence of orderly arrays of amide groups in proteins might also be reflected in the spectrum. The splitting of bands is observed in proteins due to different helical conformation authenticated by the study of dichroism.

The absorptivity of peptides, in the range, $2000\text{-}2100 \text{ \AA}^{\circ}$, decreases in strongly acidic solution, this reflects protonation of peptide bonds. Ionisation constants calculated from spectral measurements were in good agreement with independently determined values. Gelatin, on the other hand, showed no significant absorptivity change as a function of acid concentration. Moreover, the spectral change with protein solutions is shown to be reversible. No adequate interpretation of these observations is apparent.

Much has already been accomplished in the study of the ultraviolet spectra of proteins and related substances. It is also clear that much useful work are yet to be done.

