

**PHYSICAL AND  
CHEMICAL METHODS  
OF SEPARATION**

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**EUGENE W. BERG**

# physical and chemical methods of separation

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Physical and Chemical Methods of Separation

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## *Preface*

This book has been written to serve as the textbook for a course in separation techniques to be taught at the advanced undergraduate and beginning graduate level in chemistry. It can serve also as an introductory work and guide to the literature for practicing chemists who are unfamiliar with some of the more recent innovations in the field of separations. And last, but not least, I hope that this book will stimulate others to offer a formal course in separation techniques which will supplement the present offerings of their department in advanced analytical chemistry.

The formal presentation of separation methods in the chemistry curricula at both the undergraduate and graduate levels has been a hit-or-miss affair for some time. Generally, individual methods have been discussed only in relation to some other problem. Some separation topics are considered in quantitative analysis, others in physical chemistry, still others in courses in inorganic or organic chemistry, but they are usually treated inadequately and are of little use to the student in formulating ideas as to their general applicability. The demands placed on separation technology by modern research are entirely too great for us to continue with this lackadaisical approach. The beginning researcher must be made aware of some of the most potent tools available to him, namely, modern separation techniques.

Probably much of the reluctance in offering an advanced course on separation methods is traceable to the absence of a textbook in the field. The task of surveying the literature and sorting out the desired information for a number of separation methods is an onerous one. There is a voluminous literature on separation methods which is scattered through a variety of sources, such as encyclopedias, monographs, and treatises on organic, analytical, and physical chemistry and biochemistry, not to mention the reviews and specific research articles appearing in the old and current chemical literature. I undertook the job of assimilating this mass of material so as to be able to present a concise and informative survey of separation techniques to my students.

My objective has been to prepare the advanced student to recognize the inherent limitations of a particular method and the type of system to which the method would be applicable. To this end, no attempt has

been made to treat each topic exhaustively or to give a complete survey of the pertinent literature. The physical principles which govern the behavior of a given method and pinpoint the important system variables are cited with a minimum of mathematical detail. Only a cursory knowledge of physical chemistry and thermodynamics is required by the student. Experimental details are avoided by giving schematic diagrams of the needed equipment with brief descriptions of the technique. Only that experimental detail is given which is necessary for an understanding of the method. A few specific examples of separations achieved by each technique are briefly discussed to emphasize the potentials of the method. Standard references, monographs, and important general sources to special topics are tabulated in a selected bibliography at the end of each chapter. In addition, there are the many necessary references in the text to specific research papers and reviews.

A course in separation techniques based on the content of this book has been offered at Louisiana State University since 1952 as a complement to our advanced course in instrumental analysis and the usual undergraduate offerings in analytical chemistry. The results have been gratifying. A void in the students' training has been partially filled. Now the beginning graduate student who must embark simultaneously upon a career of research and advanced study can at least be aware of the potentialities of modern separation methods.

I am grateful to my friends and colleagues who have discussed the preparation of this book with me and encouraged me to complete the task. Their thoughts and suggestions have been invaluable in the preparation of the manuscript. Much credit for any acclaim accorded this text must go to Drs. Philip W. West and Buddhadev Sen for their fine contributions to the text material and to Dr. Gilbert H. Ayres who made a painstaking review of the entire manuscript. Special thanks must go to Dr. Hulen B. Williams, Dean A. R. Choppin, and Louisiana State University for providing an academic atmosphere conducive to scholarly work. I hope that their faith in me has been justified.

My deepest appreciation is extended to my wife for her constant encouragement, for typing rough copy and final manuscript, and for untold hours spent reading proof, while maintaining a pleasant home atmosphere. I shall never know how she accomplished it.

*Eugene W. Berg*

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## CHAPTER 1

### INTRODUCTION

**1.1. The Scope and Aims of Separation Methods.** Analytical chemistry is the chemistry of the identification and separation of substances—the resolution of substances into their component parts and their subsequent determination. In relatively recent years the development of instrumental methods of analysis and newer techniques not involving instrumentation has sometimes unwittingly relegated the actual separations of substances to a minor position in analytical work. Rather than separate substances prior to a determination, one now resorts to masking of interfering substances through complexation; controlling conditions such as pH, electrode potentials, etc., so carefully as to eliminate the reaction of possible interferences; or measuring some specific physical property that is characteristic of the material being analyzed. Unfortunately, we have not yet become ingenious enough to do away with separations prior to many qualitative and quantitative analyses; try as we may, it is still necessary to remove interfering substances. Separations are always a must when we consider the purification and isolation of substances.

Modern research has imposed very exacting requirements on separation procedures. Consider only a few accomplishments: the reduction of impurities in germanium to  $10^9$  atoms per mole, the separation of the rare-earth metals and complex mixtures of amino acids, the isolation and identification of some 10 to 40 atoms of a transuranium element, the separation of the various isotopes of an element and the various isomers of a complicated compound, the isolation and determination of some 20 hydrocarbons from milligram-sized samples. These are fabulous accomplishments which emphasize the importance of separation techniques to modern technology. Other more challenging separation problems are constantly arising to take the place of those solved.

Adsorption, chromatography, ion exchange, flotation, extraction, dialysis, zone melting, etc., must become as familiar tools in the hands of the researcher as the more conventional techniques of precipitation,

fractional crystallization, and distillation. Simple awareness of the many techniques employed in separations is not enough. Several methods may be suitable for the resolution of a mixture, but only one method may be the best. The objective researcher can no longer confine himself to the conventional procedures. Indeed, the outstanding accomplishments of recent years have stressed the need for the successive application of different techniques that depend upon widely different chemical or physical properties of the sample molecules.

Ingenuous combinations of techniques and processes and selections of methods most applicable for a given system require a thorough knowledge of the practical limitations inherent in each method. The choice of separation tool is usually governed by the size of sample available, the simplicity and selectivity of the method, the degree of resolution required, and the general applicability of the procedure. An objective researcher would not necessarily expect to solve a difficult separation problem by using only one technique.

**1.2. Classification of Separation Methods.** It is virtually impossible to arrange such a variety of separation methods as are treated here in a completely logical order that will be satisfying to everyone. Any classification of these methods by basic principles is likely to be a tenuous one, which can be somewhat misleading in the practical presentation of the material.

One possible approach, though, would be to group all the methods utilizing columns (distillation, solvent extraction, chromatography, ion exchange, and ion exclusion) in sequence. In all these methods the height equivalent of a theoretical plate (HETP) is a fundamental tie with sample holdup, throughput, and separation efficiency. Unfortunately, the HETP concept is not a practical means of relating all column operations; it does not provide a mechanistic picture of the phase-distribution process.

A second approach would be to group all the differential-migration methods (solvent extraction, chromatography, ion exchange, ion exclusion, dialysis, and zone melting) in sequence. All differential-migration methods of achieving separations depend on the different components of a mixture migrating through some medium at their individual characteristic rates. Inherent in this idea is the concept of a driving force to produce the migration, either selectively or nonselectively, and a retarding force which can act on the migrating particles either selectively or nonselectively.<sup>1</sup> Driving forces can be any single force or combination of forces acting on a particle that cause it to migrate. The following group of factors is usually effective as a unidirectional force within a system and causes the net migration of particles to proceed in a single general direction. Other forces acting within the system may cause migrations

to occur, but frequently they are of such a nature as to redistribute the particles rather than lead toward a unidirectional flow.

## DRIVING FORCES\*

<i>Force</i>	<i>Particles affected</i>
Mechanical.....	Microscopic to macroscopic
Gravity.....	Microscopic to macroscopic
Centrifugal.....	Colloid to macroscopic
Magnetic.....	Magnetic or charged ions
Electrostatic.....	Magnetic or charged colloids
Concentration gradients.....	Ions, molecules, colloids
Flow of liquids.....	Ions, molecules, colloids, microscopic, macroscopic
Flow of gases.....	Ions, molecules, colloids, microscopic, macroscopic

\* From H. H. Strain, T. R. Sato, and J. Engelke, *Anal. Chem.*, **26**, 91 (1954).

Similarly, any force or combination of forces that tend to resist the migration of particles is designated as a resistive force. The common resistive forces are listed here.

## RESISTIVE FORCES\*

<i>Force</i>	<i>Particles affected</i>
Viscosity.....	Ions to macroscopic
Density.....	Molecules, colloids, macroscopic
Hydrostatic and density gradients.....	Molecules, colloids, macroscopic
Adsorption.....	Ions, molecules, colloids
Permeability.....	Ions, molecules, colloids, macroscopic

\* From H. H. Strain, T. R. Sato, and J. Engelke, *Anal. Chem.*, **26**, 91 (1954).

No restriction is placed on the type of migration medium employed or the character of the migrating particles. Intrinsic differences in the migration media and the size, weight, charge, and ionic or nonionic character of the migrating particle only enhance the selectivity of the driving or resistive forces and lead to more selective separation procedures.

Although there are numerous and varied possibilities for combining driving and retarding forces with various migration media and solutes, there is much that is common to all differential-migration separations. The basic requirements for efficiency in diffusion processes are the same regardless of how the migration is produced. Sample resolutions will depend on the dimensions of the initial zone and the arrangement or position of the constituent particles, the difference in migration rates of individual components, and the distance traversed by the migrating particles. These fundamental concepts should be kept in mind when differential-migration separations are considered because system variables are usually altered in order to enhance or suppress one of the above factors.

Regardless of the great similarity among various differential-migration methods, sequences of methods based upon differential-migration rates are unrealistic because as the migration medium, driving forces, and

resistive forces are changed in progressing from one method to the next, there is little physical resemblance among the separation techniques. For example, the principles of differential-migration separations can be applied easily to both chromatography and dialysis but the physical manner by which separations are achieved with the two techniques is totally unlike.

Classification and arrangement of methods by either the column principle or the differential-migration-rate principle leave precipitation, coprecipitation, adsorption, flotation, and biological methods unclassified.

In view of these expressed difficulties (and many not expressed) the author fully anticipates considerable criticism of the arrangement of topics in this book. I believe, though, that the arrangement is a logical one for showing the similarity between methods *and* underlying principles and that it is particularly effective for introducing the topic to a person with a broad chemical background. A brief justification for the arrangement decided upon follows.

Distillation introduces the column concept, the HETP, and the phase diagram. Extraction follows naturally as a distribution of solutes between two liquid phases as opposed to the gas-liquid distribution in distillation. Adsorption chromatography follows extraction and introduces the concept of solid-liquid distribution and the differential-migration concept. Partition chromatography is a pseudoextraction method, but the principles of operation are exactly the same as for adsorption chromatography, so it logically follows adsorption chromatography. Gas chromatography extends the chromatographic principle to a solid-gas distribution. However, lest the student lose sight of the fact that chromatography is a column operation which can be treated by the HETP concept, the theory of gas chromatography is developed on both the HETP and differential-migration concept.

Paper chromatography supplants the solid adsorbent used in adsorption chromatography with cellulose and is the most reasonable precursor in the series for electrochromatography and ring-oven methods, both of which employ cellulose sheets for the migration medium. The principles of zone melting are not greatly different from those used in the ring-oven method, and zone melting fits into the series well at this point.

Ion exchange comes as a somewhat abrupt change in the sequence because it introduces an entirely new mechanism for the establishment of equilibrium in column operations, but with the change in thought a new principle, dialysis, is introduced which acts as the connecting link in the discussion of ion exchange, ion exclusion, dialysis, and electrodialysis.

A real discontinuity appears in the sequence of methods with the introduction of precipitation, but again, as with ion exchange, a new

sequence is established with a common underlying principle. Precipitation leads naturally into a discussion of coprecipitation and adsorption. Adsorption in turn leads to flotation methods. The features common to each of these methods are the phenomena which occur at solid-liquid interfaces. There is indeed a remarkable similarity among precipitation (the formation of crystals in solution), coprecipitation, adsorption, and flotation.

Biological methods are an entity which must stand alone.

Masking and complexation are considered last because they offer an alternate approach to the determination of substances without their prior separation.

A brief description of the various separation methods treated in this text is given in the following paragraphs to familiarize the reader with the fundamental principles and general analytical importance of each method. The more detailed description of each method is then presented in the text.

**1.3. Distillation.** In its simplest case distillation is the volatilization of a liquid by the application of heat and the subsequent condensation of the vapor back to the liquid state. Every liquid has a tendency to vaporize and reach an equilibrium characterized by vaporization and condensation proceeding at equal rates. The pressure of the vapor above the liquid at equilibrium is characteristic of the liquid and is referred to as the *vapor pressure* of the liquid. Vapor pressure increases with an increase in temperature, and the volatility of a liquid has been shown to be roughly proportional to the vapor pressure and inversely proportional to the boiling point of the liquid.

These fundamental concepts of distillation have been appreciated for many years, and this knowledge has made it possible for researchers to develop more versatile distillation techniques and processes. The resolving power of modern distillation columns is remarkable. Multiple-component systems can be readily resolved when only minor differences of vapor pressure exist among the components. Fractions usually approach a high degree of purity except in the case of azeotropic mixtures.

Some closely related phenomena, simple volatilization and sublimation, can be considered along with distillation as a method of separation. Volatilization implies only the conversion of a solid or liquid into the gaseous state, whereas sublimation is the direct vaporization of a solid and the subsequent condensation of the vapor back to the solid state without passing through the intermediate liquid form.

Each process is dependent on the vapor pressure of either solids or liquids being great enough to effect a change in the physical state of the substance, but a simple change in physical state is not enough to effect a resolution. For resolutions to be complete, there also must be a mass

transfer of at least one of the sample components. The versatility of volatilization techniques is based on the ease with which a mass transfer can be effected when the substance is in the gaseous state.

Each of these processes has found its greatest application in the field of organic chemistry. Volumes have been written describing distillation principles for organic separations; therefore, scant attention will be given separations in this area. Emphasis will be placed on the utility of vaporization and sublimation techniques for the separation of inorganics and metal organic coordination complexes.

**1.4. Solvent Extraction.** Solvent extraction as applied to solids is the selective dissolution of the soluble portion of a solid with an appropriate solvent. Such processes have been utilized for centuries by laymen and depend only on an appreciable difference in the solubility of the various solid substances involved. Formerly, leaching was used extensively to obtain lye from wood ashes and to recover salt from the debris of the smokehouse floor. Present commercial processes are numerous and include such varied procedures as extracting oil from fish and plant seeds, sugar from sugar beets, and precious metals from ores.

Liquid-liquid extraction is a physical partitioning process dependent on the favorable distribution of a given solute between two immiscible solvents. The distribution of a component between the two immiscible phases follows (in the ideal case) the distribution law when the system is at equilibrium.

$$\frac{C_1}{C_2} = K \quad \text{distribution law}$$

$C_1$  and  $C_2$  represent the concentration of the solute in the respective phases, and  $K$  is the distribution constant or partition coefficient. Frequently the distribution deviates considerably from this law owing to the association or dissociation of the solute in one or both phases, but a rigorous treatment of the distribution law can result in a correction for this anomalous behavior. At this point it becomes difficult to designate extraction as a physical method or chemical method because of these complicating factors. The solute particles may actually undergo a change in structure or composition as they change phases.

Gases can also be extracted from the gaseous phase into a liquid phase. The partitioning phenomenon here also follows the distribution law, but it is more common to express it as Henry's law:

$$\frac{m}{p} = K$$

where  $p$  is the partial pressure of the gaseous component in the atmosphere above the liquid and  $m$  is the concentration of the gas in the liquid phase.