RATE-CONTROLLED SEPARATIONS

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PREFACE

Separations have always been very important in chemical engineering. This importance has recently escalated with the imminent emergence of new industries in biotechnology and high-performance materials. Separations will continue to remain important in bulk chemical manufacturing, petroleum processing, and the other standard areas of chemical engineering interest.

The development of new industries requiring the expertise of chemical engineers leads to problems and opportunities for chemical engineering education. Chemical engineering students need to be prepared for both the "known future" and the "unknown future." The known future includes the use of standard chemical engineering separation methods such as distillation and absorption which will remain important for many years. The unknown future involves the use of many relatively new separation methods such as adsorption, chromatography, electrophoresis, membrane separations.

A major question for chemical engineering education is what to teach. In the area of separations my personal answer has been to require undergraduates to study classical separations including distillation, adsorption and extraction. Then an elective course on newer methods which require a mass transfer analysis should be made available to seniors and graduate students. I would not mind if this second course were required of graduate students; certainly, that would be preferable to an additional distillation course.

My first book, *Equilibrium-Staged Separations*, was my response for the required undergraduate course. This book is my response to both the proposed second course, and to practicing chemical engineers who missed this material when they were in school.

This book, *Rate-Controlled Separations*, includes separation processes which require a rate analysis for complete understanding. This includes most of the newer separation methods. The style of this book is similar to the style of *Equilibrium-Staged Separations* and problem solving is emphasized throughout. However, a higher level of mathematical analysis is required, and an understanding of mass transfer is assumed.

The plan for this book is to start with crystallization which is essentially equilibrium based. Sorption separations which can be (but seldom are) operated as equilibrium staged systems are discussed next. Then membrane separations which are inherently rate processes are discussed. Finally, a progress report on selection and sequencing of separations is presented.

This book has been used in an elective course for seniors and graduate students at Purdue over a period of several years. My experience has been that the students have no great difficulty with crystallization even though this is their first exposure to population balances. The students find that the chapters on sorption separations are more difficult; possibly because of the inherent batch nature of these processes. The average and better seniors and all of the graduate students have been able to work their way through these difficulties. The membrane methods seem to pose no unusual difficulty for the students.

Many people have helped me with the writing of this book. My students have been most helpful in helping me develop clear methods to explain the separation methods. My teaching assistants (when I had this luxury), Sung-Sup Suh and Narasimhan Sundaram, have been very helpful in solving problems and finding errors. Professors Linda Wang and David Graves used parts of this book in their courses. Their comments were very helpful and have been incorporated into the text. Mr. Steve Leeper was very helpful in providing references on membrane separations. Dr. Scott Rudge did a very thorough review of Chapter 11, and he helped me appear to be reasonably knowledgeable in the area of electrophoresis. Professors Lowell B. Koppel and William R. Schowalter taught me my undergraduate and graduate courses in separations and awakened my interest in the field. Professor C. Judson King's book convinced me there were interesting research problems in separations. Professor L.B. Rogers who was in Chemistry at Purdue gave me my introduction to chromatography when I audited his course. My interest in problem solving was sparked by Professors Richard Noble and Donald Woods.

The keyboarding of this book was done by Mrs. Karen Parsons and Ms. Jan Gray. Their cheerfulness in the face of endless revisions is appreciated. Ms. Barbara Hildebrandt patiently drew and redrew the figures.

Finally, my wife Dot has supported me when I thought I would never finish, and my children Charles and Jennifer have provided light to my life.

Phillip C. Wankat

CONTENTS

PART I. CRYSTALLIZATION

PART II. SORPTION AND CHROMATOGRAPHY

PART III. MEMBRANES

PART IV. SELECTION AND SEQUENCING

Chapter 1

INTRODUCTION

This textbook considers separation processes where mass transfer rates need to be included for a complete analysis. Included in the book are crystallization, adsorption, chromatography, ion exchange, electrophoresis and membrane separations. We will start with equilibrium-based separation processes and gradually switch to rate processes. This will be done by starting with crystallization and finishing with membrane separations.

1.1. PART I: CRYSTALLIZATION

Crystallization is a complex, multifaceted subject. On one level of sophistication, crystallization can be considered entirely as an equilibrium stage separation process. This is done in Chapter 2 which could be included in a book on equilibrium staged separations. The coverage in Chapter 2 is concerned with crystallization from solution. Crystallization is done from a solution containing a solvent such as water or alcohol. This is the most common type of industrial crystallization. It is used for production of a large variety of inorganic salts and organic compounds. Usually, only a single equilibrium stage is required. The equilibrium diagrams discussed in Chapter 2 are similar to the enthalpy-composition diagrams used for distillation and the triangular diagrams used for extraction. Thus the principles will often be familiar although the diagrams may be more complex. In ternary systems such as two salts plus water, a single equilibrium stage operating at one temperature can produce a single pure salt plus a solution containing both salts. Fractional crystallization can be used to produce both salts as pure products. Fractional crystallization usually uses two equilibrium stages operating at different temperatures. These cycles are explained using triangular equilibrium diagrams.

When temperature has a large effect, a large amount of crystals can be obtained by *cooling* the solution. When temperature has a small effect cooling will have little effect. Crystallization then requires removal of solvent by *evaporation* or changing the solubility by adding another component (salting out). When there is a moderate temperature effect, both cooling and evaporation are used in a *vacuum* crystallizer. The equipment types used for these processes will be explained in Chapters 2 and 4.

The product from a crystallization is often sold as a solid (e.g. table salt or sugar). The size distribution and the shape of the crystals is very important in customer acceptance of the product. (It is annoying to buy a bag of sugar which is a single solid lump). The *crystal size distribution (CSD)* and the crystal shapes are *not* determined by equilibrium. Thus, if we stop at Chapter 2 we will miss a very important part of crystallization. To determine crystal size distributions, nucleation and growth rates are studied in Chapter 3.

Chapter 4 develops *population balances* (a count of the number of crystals in a given size range) and from this crystal size distributions are generated. The population balance is used first to develop the crystal size distribution for a simple case. From this several other distributions are calculated. Use of experimentally determined crystal size distributions to determine nucleation and growth rates is explored, and the effects of equipment variations on CSD are determined.

The second major type of crystallization is *melt crystallization.* In melt crystallization no solvent is present. Instead, the solid is melted and then slowly crystallized to purify it. This method is used for purification of organic chemicals, pharmaceuticals, and in the semi-conductor industry. Although many of the principles of melt crystallization are similar to crystallization from solution using cooling, the equipment is often very different. Some of the methods which will be discussed in Chapter 5 are normal freezing, zone melting, and counter-current column crystallizers.

The chapters on crystallization assume familiarity with equilibrium stage concepts and mass transfer. No prior knowledge of crystallization is required. The structure of the information is shown in Figure 1-1. This figure shows the