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CHEMICAL ENGINEERING

VOLUME TWO UNIT OPERATIONS

Second Edition

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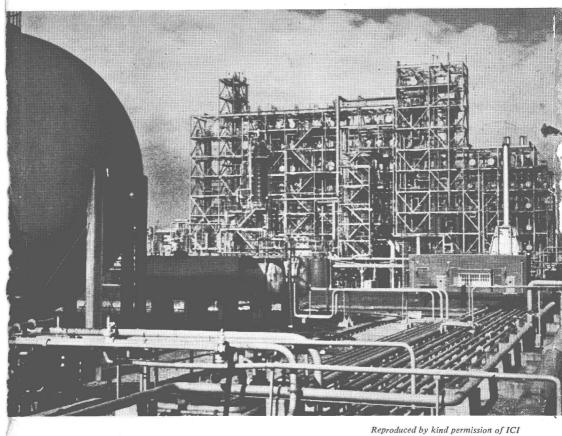
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Polyethylene Plant

Preface to Second Edition

THIS text deals with the physical operations used in the chemical and allied industries. These operations are conveniently designated "unit operations" to indicate that each single operation, such as filtration, is used in a wide range of industries, and frequently under varying conditions of temperature and pressure.

Since the publication of the first edition in 1955 there has been a substantial increase in the relevant technical literature but the majority of developments have originated in research work in government and university laboratories rather than in industrial companies. As a result, correlations based on laboratory data have not always been adequately confirmed on the industrial scale. However, the section on absorption towers contains data obtained on industrial equipment and most of the expressions used in the chapters on distillation and evaporation are based on results from industrial practice.

In carrying out this revision we have made substantial alteration to Chapters 1, 5, 6, 7, 12, 13 and 15 and have taken the opportunity of presenting the volume paged separately from Volume 1. The revision has been possible only as the result of the kind co-operation and help of Professor J. D. Thornton (Chapter 12), Mr. J. Porter (Chapter 13), Mr. K. E. Peet (Chapter 10) and Dr. B. Waldie (Chapter 1) all of the University at Newcastle, and Dr. N. Dombrowski of the University of Leeds (Chapter 15). We want in particular to express our appreciation of the considerable amount of work carried out by Mr. D. G. Peacock of the School of Pharmacy, University of London. He has not only checked through the entire revision but has made numerous additions to many chapters and has overhauled the index.

We should like to thank the companies who have kindly provided illustrations of their equipment and also the many readers of the previous edition who have made useful comments and helpful suggestions.

Chemical engineering is no longer confined to purely physical processes and the unit operations, and a number of important new topics, including reactor design, automatic control of plants, biochemical engineering, and the use of computers for both process design and control of chemical plant will be covered in a forthcoming Volume 3 which is in course of preparation.

Chemical engineering has grown in complexity and stature since the first edition of the text, and we hope that the new edition will prove of value to the new generation of university students as well as forming a helpful reference book for those working in industry.

In presenting this new edition we wish to express our gratitude to Pergamon Press who have taken considerable trouble in coping with the technical details.

J. M. COULSON
J. F. RICHARDSON

Preface to First Edition

In presenting Volume 2 of Chemical Engineering, it has been our intention to cover what we believe to be the more important unit operations used in the chemical and process industries. These unit operations, which are mainly physical in nature, have been classified, as far as possible, according to the underlying mechanism of the transfer operation. In only a few cases is it possible to give design procedures when a chemical reaction takes place in addition to a physical process. This difficulty arises from the fact that, when we try to design such units as absorption towers in which there is a chemical reaction, we are not yet in a position to offer a thoroughly rigorous method of solution. We have not given an account of the transportation of materials in such equipment as belt conveyors or bucket elevators, which we feel lie more distinctly in the field of mechanical engineering.

In presenting a good deal of information in this book, we have been much indebted to facilities made available to us by Professor Newitt, in whose department we have been working for many years. The reader will find a number of gaps, and a number of principles which are as yet not thoroughly developed. Chemical engineering is a field in which there is still much research to be done, and, if this work will in any way stimulate activities in this direction, we shall feel very much rewarded. It is hoped that the form of presentation will be found useful in indicating the kind of information which has been made available by research workers up to the present day. Chemical engineering is in its infancy, and we must not suppose that the approach presented here must necessarily be looked upon as correct in the years to come. One of the advantages of this subject is that its boundaries are not sharply defined.

Finally, we should like to thank the following friends for valuable comments and suggestions: Mr. G. H. Anderson, Mr. R. W. Corben, Mr. W. J. De Coursey, Dr. M. Guter, Dr. L. L. Katan, Dr. R. Lessing, Dr. D. J. Rasbash, Dr. H. Sawistowski, Dr. W. Smith, Mr. D. Train, Mr. M. E. O'K. Trowbridge, Mr. F. E. Warner and Dr. W. N. Zaki.

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Introduction

THE understanding of the design and construction of chemical plant is frequently regarded as the essence of chemical engineering. Starting from the original conception of the process by the chemist, it is necessary to understand the chemical, physical and many of the engineering features in order to develop the laboratory process on an industrial scale. In this volume, we shall be mainly concerned with the physical nature of the processes that take place in industrial units, and, in particular, with determining the factors that influence the rate of transfer of material. The basic principles of these operations, namely fluid dynamics, and heat and mass transfer, have been discussed in Volume 1, and it is the application of these principles that forms the main part of this volume.

Throughout what are conveniently regarded as the process industries, there are many physical operations that are common to a number of the individual industries, and, as explained in Volume 1, these are regarded as unit operations. Thus, the separation of solids from a suspension by filtration, the separation of liquids by distillation, or the removal of water by evaporation and drying are typical operations of this kind. The problem of designing a distillation unit for the fermentation industry, the petroleum industry or the organic chemical industry is, in principle, the same, and it is mainly in the details of construction that the differences will occur. The concentration of solutions by evaporation is again a typical operation that is basically similar in the handling of sugar, or salt, or fruit juices, though there will be differences in the most suitable arrangement. This form of classification has been used here, but we have grouped the operations according to the mechanism of the transfer operation, so that the diffusion processes of distillation, absorption and liquid-liquid extraction are taken in successive chapters, and the operations involving solids in fluids are considered together. In examining many of these unit operations, we shall find that the rate of heat transfer or the nature of the fluid flow is the governing feature. The transportation of a solid or a fluid stream is another instance of the importance of understanding fluid dynamics.

One of the difficult problems of design is that of maintaining conditions of similarity between laboratory units and the larger industrial plants. Thus, if a mixture is to be maintained at a certain temperature during the course of an exothermic reaction, then on the laboratory scale there is rarely any real difficulty in maintaining isothermal conditions. On the other hand, in a large reactor the ratio of the external surface to the volume—which is inversely proportional to the linear dimension of the unit—is in most cases of a different order, and the problem of removing the heat of reaction becomes

a major item in design. Some of the general problems associated with scaling up are considered in Chapter 18 on mixing, and particular features occur in many chapters. Again, the introduction and removal of the reactants may present difficult problems on the large scale, especially if they contain corrosive liquids or abrasive solids. The general tendency with industrial units is to provide a continuous process, frequently involving a series of stages. Thus, exothermic reactions may be carried out in a series of reactors with interstage cooling between them.

The planning of a process plant will involve the determining of the most economic method, and later the most economic arrangement of the unit operations used in the process. This amounts to designing a chemical process to provide the best combination of capital and operating costs. We have not in this volume considered the question of costs in any great detail, but we have aimed at indicating the conditions under which various types of units will operate in the most economical manner. Without a thorough knowledge of the physical principles involved in the various operations, it will not be possible to select the most suitable one for a given process. This aspect of the design can be considered by taking one or two simple illustrations of separation processes. The particles in a solid-solid system may be separated, first according to size, and secondly according to the material. Generally, sieving is the most satisfactory method of classifying relatively coarse materials according to size; but the method is impracticable for very fine particles and a form of settling process is generally used. In the first of these processes, we are directly utilising the size of the particle as the basis for the separation, and, in the second, we are dependent on the variation with size of the behaviour of particles in a fluid. A mixed material can also be separated into its components by means of settling methods, because the shape and density of particles also affect their behaviour in a fluid. Other methods of separation depend on differences in surface properties (froth flotation), magnetic properties (magnetic separation), and on differences in solubility in a solvent (leaching). For the separation of miscible liquids, the three commonly used methods are:

- 1. Distillation depends on difference in volatility.
- 2. Liquid-liquid extraction—depends on difference in solubility in a liquid solvent.
- 3. Refrigeration depends on differences in melting point.

This problem of selecting the most appropriate operation will be further complicated by such factors as the concentration of liquid which gives rise to crystals. Thus, in the separation of a mixture or ortho-, meta-, and paramononitrotoluenes, the decision must be made as to whether it is better to carry out the separation by distillation followed by crystallisation, or in the reverse order. The same kind of consideration will arise when we are concentrating a solution of a solid; we must decide whether to stop the evaporation process when a certain concentration of solid has been reached and then to proceed with filtration followed by drying, or whether to continue the

concentration by evaporation to such an extent that we can leave out the filtration stage and go straight on to drying.

In many operations, for instance in a distillation column, it is necessary to understand the fluid dynamics of the unit, as well as the heat and mass transfer relationships. These factors are frequently interdependent in a complex manner, and it is essential to consider the individual contributions of each of the mechanisms. Again, in a chemical reaction the final rate of the process may be governed by a heat transfer process or by the chemical kinetics, and it is essential to decide which is the controlling factor.

Some indication of the method of using the information on unit operations can be obtained by considering the example of a sulphuric acid plant. First it is necessary to select the process and the raw materials which are to be used. It will be supposed that the process involves burning sulphur to sulphur dioxide, followed by oxidation to sulphur trioxide by what is known as the contact process, and that it is proposed to employ rock sulphur, oxygen from the atmosphere, and water. Alternative sources of sulphur include iron pyrites and spent oxide from gas works, but, although these are considerably cheaper than rock sulphur, it is necessary to install additional equipment for cleaning the gas. Secondly, we must study the kinetics of the chemical reactions. Here we are concerned basically with the following three reactions:

- (i) $S + O_2 = SO_2$ ($\Delta H = -70,920$ lb-cal/lb-mol at 25°C).
- (ii) $2SO_2 + O_2 = 2SO_3$ ($\Delta H = -47,500$ lb-cal/lb-mol at 420° C).
- (iii) $SO_3 + H_2O = H_2SO_4$ ($\Delta H = -32,000 \text{ lb-cal/lb-mol at } 100^{\circ}C$).

The overall reaction is therefore

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4$$
.

Each of the reactions is exothermic, and the successful and economic operation of the plant depends on the removal and subsequent utilisation of the heats of reaction. The first reaction is a simple gas-phase combustion which goes virtually to completion under adiabatic conditions, and it is not necessary therefore to remove heat in the combustion chamber itself. The second reaction does not proceed sufficiently rapidly except in the presence of a catalyst, generally vanadium pentoxide dispersed on a filler, and it becomes self-supporting at temperatures above about 400°C. Because the reaction is strongly exothermic, the equilibrium point is adversely affected by rise in temperature, and, because this effect is very marked, the reaction should be carried out as nearly as possible under isothermal conditions. The reaction rate is high in the presence of the catalyst, and the reaction can be regarded as proceeding to completion at each stage. The composition of the final gas can be calculated as a function of temperature, and therefore the composition of the equilibrium mixture at each adiabatic stage can be determined because all the heat of reaction appears in the products. The temperature of the outlet gases from each successive reactor will be lower,

and therefore the SO_3 content will rise. The third reaction involves absorption of SO_3 in water and an immediate chemical reaction to produce H_2SO_4 . As this reaction is exothermic, there would be a considerable rise in temperature and mist formation if it were carried out in this way. In practice, the heat capacity of the liquid phase is increased by absorbing the SO_3 in 98% H_2SO_4 rather than in water.

It can be seen from these considerations that a thorough understanding of the physical processes taking place in the individual units of chemical plant is an essential requirement in the training of a chemical engineer. It is only by understanding the mechanisms, and then the method of constructing the equipment, that it will be possible to obtain a complete picture,

including the cost of the operation.

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