HANDBOOK OF LABORATORY DISTILLATION

by **Erich Krell**

HANDBOOK
of
LABORATORY DISTILLAT

ERICH KRELL
Deutsche Akademie der Wissenschaften zu Berlin
Institut für physikalische Stofftrennung, Leipzig

Edited by
E. C. LUMB
Research Chemist, Shell Research Ltd.
Thornton Research Centre, Chester

Translated from the Second German Edition by
C. C. VERVER
formerly of the Koninklijke / Shell Laboratorium, Amsterdam

ELSEVIER PUBLISHING COMPANY
AMSTERDAM – LONDON – NEW YORK
1963

Original Title
HANDBUCH DER LABORATORIUMSDESTILLATION
published by
VEB DEUTSCHER VERLAG DER WISSENSCHAFTEN, BERLIN

SOLE DISTRIBUTORS FOR THE UNITED STATES AND CANADA
AMERICAN ELSEVIER PUBLISHING COMPANY, INC.
52 VANDERBILT AVENUE, NEW YORK 17, N.Y.

SOLE DISTRIBUTORS FOR GREAT BRITAIN
ELSEVIER PUBLISHING COMPANY LIMITED
12B, RIPPLESIDE COMMERCIAL ESTATE
RIPPLE ROAD, BARKING, ESSEX

LIBRARY OF CONGRESS CATALOG CARD NUMBER 63-9918

WITH 440 ILLUSTRATIONS AND 77 TABLES

From the Foreword to the Second German Edition

The first edition of the book was sold out in a relatively short time. It was exported to twenty-five countries; translations into English, Russian and Polish are in preparation.

Numerous favourable reviews in German and foreign scientific publications have stressed the urgent need for such a compilating work on laboratory distillation. The form of the book has found wide approval both in theoretical and practical circles.

On this account the author has retained its fundamental scheme of arrangement, corresponding to the order of the steps involved in a separation by distillation. The subject-matter has, however, been expanded appreciably and brought up to date by the inclusion of research data published since 1955. The number of references to literature has been increased, so that they may also be consulted in connection with very special problems. The methods of calculation have purposely been chosen from the standpoint that, in the laboratory, only the simpler forms of calculation have any sense, since the required result is usually obtained more speedily by experiment than by lengthy computations including a number of assumptions.

Section 5.14 on the separation of stable isotopes by countercurrent distillation has been re-written. At the request of several readers an "Example of the Calculation of Distillation Conditions" has been included as an Appendix.

I believe that the book, in its present form, is more complete and satisfactory than the first edition. In effecting the alterations, I received valuable suggestions from Prof. Dr. ULLRICH VON WEBER of Rostock, Dr. H. RÖCK of Trostberg (Obb.), Dr. H. SCHUBERTH of Leipzig and Dr. H. STAGE of Niehl, Cologne, to whom I again express my sincere thanks.

It is to be hoped that this second edition will also contribute to the further development of laboratory distillation and that, in laboratories, in industry, in technical schools and universities, it will serve as a textbook and as a guide in the solution of problems of separation by distillation.

E. K.

Foreword to the first Edition

This book has been written with the object of giving an account of the subject of laboratory distillation, including recent views and developments. The literature has been reviewed up to the year 1955 and in so far as available, publications of 1956, 1957 and later have also been considered. The author has adopted the course of dealing only with generally accepted facts; there are still numerous problems in simple and countercurrent distillation which have not yet been completely clarified and in which there exist differences of opinion among various investigators. Distinct trends in development have nevertheless been mentioned, in order to give an incentive for further work. Owing to the large mass of material, a critical selection has been necessary. The writer has in principle avoided the inclusion of abstruse methods of calculation, seldom used in practice, since they only complicate the subjectmatter; on the other hand, an attempt has been made to introduce the mathematical deductions and formulae required in laboratory work in a readily understandable form. Readers with a mathematical turn of mind and those interested in particular problems will find extensive references to literature for further study.

The book is intended primarily for physicists, chemists and engineers engaged in chemical industry and in research or development centres, whose work includes distillation on a laboratory or semi-technical scale. It will, however, also be useful to chemical technologists and laboratory assistants as a source of answers to many questions in the field of practical distillation and separating processes. It is hoped that it will prove a guide to better and more economical methods of operation for all who have to carry out distillation in the laboratory.

The writer wishes to express his special gratitude to Prof. Dr. Ing. E. Leibnitz for his kind co-operation in the book, for his valuable encouragement and constant support. Many of the data included were obtained while the author was in charge of the distillation laboratory in the Institut für Verfahrenstechnik der Organischen Chemie. Further he wishes to thank all colleagues who have contributed to the solution of distillation problems by discussion, especially those of the German Standards Association, Section for Laboratory Apparatus, for their assistance in questions of standardization. He is also grateful to the various manufacturers of laboratory apparatus who have provided him with prospectuses and illustrations.

ERICH KRELL

Institut für physikalische Stofftrennung, Leipzig
Deutsche Akademie der Wissenschaften zu Berlin.

Contents

Chapter 1

Introduction

Although simple and countercurrent (rectified) distillation are among the most important physical separating methods employed in chemical industry, and hence also in research and works laboratories, it is often found that the apparatus used for this purpose in the laboratory has a low efficiency by present-day standards. Furthermore, calculations on the process are seldom made; instead, the work is as a rule based entirely on experience and empirical data.

In this field, nevertheless, a large amount of research work has been carried out during the last thirty years. To-day we have available modern components, high-vacuum and completely automatic equipment; methods of calculation have been developed, whilst laboratory separations now range from micro-distillations with less than 1 gram of charge to continuous operations with a throughput of up to 5 litres per hour, from the distillation of liquified gases at low temperatures to that of tars at high temperatures and from separations at normal pressures to so-called molecular distillations at pressures below 10^{-4} mm of mercury. Selective procedures have been perfected, and it is now possible to separate mixtures formerly considered inseparable by appropriately influencing the vapour pressure relationship.

The classical text-book of Young[1] provides an excellent review of theory and practice, including that of industrial installations, but is now out of date in many respects, particularly as regards methods of calculation and apparatus. The work written by Badger and McCabe[2] in 1931 already contains the graphical method of computation of McCabe and Thiele[3] and excels in clarity of presentation. They are, however, mainly concerned with large-scale operations and fall short in their treatment of the special problems of laboratory distillation. A great impetus to research in the latter field was given by the work of Jantzen and his students. In a Dechema monograph[4] published in 1932 he gave a detailed description of the fundamental requirements for columns (previously presented in 1923[5]); these are still largely valid to-day. The later book of Kirschbaum[6] has a mainly industrial

orientation; this also applies to that of Robinson and Gilliland[7], which, apart from the theory, deals with difficult separations of multi-component mixtures and with azeotropic and extractive distillation. Perry's Chemical Engineer's Handbook[8] contains a chapter on distillation with numerous examples, tables and nomograms for calculating industrial installations; laboratory distillation is, however, but briefly discussed. Furthermore, all these books presuppose a knowledge of the basic theory and a measure of practical experience. The entire distillation literature of the world for the years 1941 to 1945 and 1946 to 1952 was summarized in short references by A. and E. Rose[9]; the first group contains 1000 investigations, the second 5000. In the publication "*Fortschritte der Verfahrenstechnik*", Stage[10] gave a revue of the developments during 1952–1957. Besides the numerous references to literature which this contains, the lists of vapour pressure and phase equilibrium data are particularly valuable. Walsh[11] annually gives a critical summary of literature in "*Unit Operations Reviews*". Not until the appearance of the works of Carney[12], Ewers[13] and of Rose et al.[14] have the special requirements of laboratory distillation been systematically treated. Short books based on fundamental principles have been published by Zuiderweg[15] and by Coulson and Herington[16].

In view of the enormous development in laboratory distillation during the last fifteen years and the extensive specialization in this field it seemed desirable that an introduction to laboratory distillation technique should appear, not assuming any previous knowledge in this field, but nevertheless containing the methods for determining vapour pressures and equilibrium curves and giving a detailed description of continuous and selective separating processes, together with a chapter on measuring and control devices. This review has the object of removing many erroneous notions about the factors affecting the process of separation and of giving a comprehensive account of the performance of simple and difficult distillations.

The chapter entitled "A review of the history of laboratory distillation" at once introduces the general ideas, whilst chapter 3 clarifies concepts and defines the units of measurement and the symbols. After the physical theory of separation and the properties of the mixtures to be separated have been discussed, the general and selective separating processes used in various cases are dealt with from several points of view (chapters 4 to 6). The apparatus required, together with all auxiliary equipment such as measuring and control apparatus, is described in chapters 7 and 8. Finally chapter 9

details points to be considered in fitting out a distillation laboratory and preparing the apparatus.

It was considered particularly important to deal with the procedures followed in laboratory distillation from the aspect of semi-technical and commercial-scale distillations, since the former are often the forerunners of the latter. Formerly it happened all too often that distillation methods were developed in the laboratory without any consideration of development; the result was that serious difficulties frequently occurred in scaling up the laboratory experiments to the full dimensions. If, however, the experiments are properly designed at the outset for technical interpretation, much expense and time can often be saved and the data obtained can be employed in technical calculations without appreciable correction. This does not, of course, exclude the need for using conditions in certain cases, say in analytical distillation, that would be entirely uneconomic in industrial operation. Only with a knowledge of the fundamentals of the separating process is it possible to decide on the optimum conditions for every problem. It is the purpose of the present book to provide this knowledge.

Two tables of data are given as appendices. For convenience in use, the nomograms have been collected in a separate booklet which will be found inside the back cover. The references to the literature are listed at the end of each chapter, while the illustrations, tables and equations have been numbered consecutively, throughout the book.

REFERENCES

1 S. YOUNG, *Distillation Principles and Practice*, Macmillan, London, 1922.
2 W. L. BADGER and W. L. MCCABE, *Elements of Chemical Engineering*, McGraw-Hill, New York and London, 1911.
3 W. L. MCCABE and E. W. THIELE, *Ind. Eng. Chem.*, 17 (1925) 605.
4 E. JANTZEN, *Dechema Monograph.*, Vol. 5 (1932) No. 48.
5 E. JANTZEN, *Angew. Chem.*, 36 (1923) 592.
6 E. KIRSCHBAUM, *Distillation and Rectification*, Chemical Publishing Co. Inc., New York, 1948.
7 C. S. ROBINSON and E. R. GILLILAND, *Elements of Fractional Distillation*, McGraw-Hill, New York, 1950.
8 J. H. PERRY, *Chemical Engineers Handbook*, McGraw-Hill, 3rd. Ed., 1953.
9 A. and E. ROSE, *Distillation Literature Index and Abstracts, 1941–1945, 1946–1952*, Applied Science Laboratories, State College, Pennsylvania, 1953.
10 *Advances in Process Technology, 1952/3, 1954/5 and 1956/7*, published by the Scientific and Engineering Division of Farbenfabriken Bayer A. G., Leverkusen, Verlag Chemie, Weinheim, 1954, 1956 and 1958.

11 T. J. WALSH, *Ind. Eng. Chem.*, 48 (1956) 492–495; 49 (1957) 503–506; 50 (1958) 453–457; 51 (1959) 370–372; 52 (1960) 277–279; 53 (1961) 248–250.
12 TH. P. CARNEY, *Laboratory Fractional Distillation*, Macmillan, New York, 1949.
13 M. J. ROSENGART (translated from Russian by EWERS) *Die Technik der Destillation und Rektifikation im Laboratorium*, VEB Verlag Technik, Berlin, 1954.
14 A. and E. ROSE *et al.*, *Technique of Organic Chemistry*, Volume IV "*Distillation*", Interscience Publishers, New York, 1951.
15 F. J. ZUIDERWEG, *Manual of Batch Distillation*, Interscience Publishers, New York, 1957.
16 E. A. COULSON and E. F. G. HERINGTON, *Laboratory Distillation Practice*, George Newnes, London, 1958.

Chapter 2

A Review of The History of Laboratory Distillation

(From early times to 1920)

Not only is it interesting to study the development of a chemical operation through the centuries from a historical point of view, but it is often found that valuable pointers for research are obtained from parallels between old and present-day methods. As an introduction to a special field of chemical technology, such as distillation, a historical review gives the reader an appreciation of how the human mind has always sought for new ways of achieving better processes and more efficient apparatus with the facilities available at the time.

The present review has been written, not with the object of providing complete historical details or etymological derivations, but rather of giving a clear account of the steps by which laboratory methods and apparatus (not omitting those for semi-technical use) have developed to their present forms.

Distillation is an art that was practised long before the Christian era by the ancient Egyptians and was cultivated and protected as secret science by temple priests. It also appears to have been carried out in early times in India, Persia and China. Schelenz is of the opinion that the discovery of distillation must be ascribed to the Persians, who employed the art for the preparation of rose water. Another view is that the principle of distillation found its origin in the carbonization of wood, since descending distillation is referred to in the "Ebers papyrus" of about 1500 B.C., so that the process would be almost 3500 years old. It should be noted in this connection that the word distillation was at that time a collective term for all separating processes then known; the word may be translated as "separation drop by drop" and in alchemistic speech denoted the separation of more or less subtle (or "fine") elements from each other. The concept of distillation also covered operations such as filtration, crystallization, extraction and the expression of oil. We shall here deal only with the history of distillation in the present meaning of the term: the separation of bodies by evaporation and condensation of the vapour. In this connection it should be observed that by

the foregoing definition descending distillation is a true distillative operation.

The earliest uses of distillation were the preparation of rose oil and other ethereal oils, distilled water for sailors (Aristoteles mentions how fresh water can be made from salt water) and a large number of alchemical mixtures and draughts. Fig. 1 shows a so-called alembic (helmet) on a furnace, surrounded by the magic inscriptions which in early ages played such a large part in the process of distillation. The illustration is taken from a treatise on the preparation of gold, dating from the second century A.D., by the Egyptian woman alchemist Cleopatra. A typical apparatus of this period is shown in

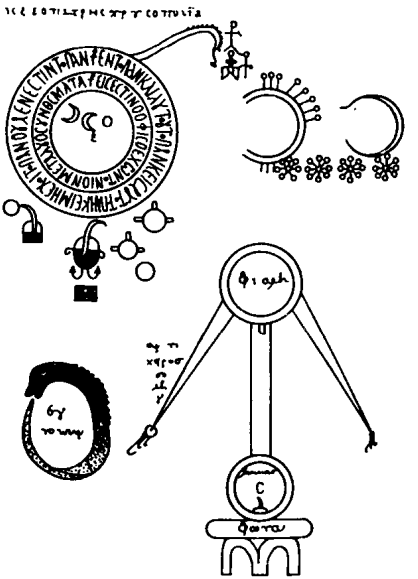


Fig. 1. Alembic on furnace, surrounded by magic signs. From a treatise on the making of gold by the Egyptian alchemist Cleopatra (2nd century A.D.).

the next figure (2a). It is a glass still on a sand or water bath, an arrangement still in use to-day, as demonstrated by the adjoining illustration of a mercury still (2b). The four separate parts–the heating bath, the still (curcurbita), the head (alembic) and the receiver (receptacula)–have remained in use as components to this day. It is interesting to note that the collar for collecting the distillate is also still found in a number of modern forms of equipment. The material employed for the apparatus in antiquity was chiefly glass, a ceramic compound or copper.

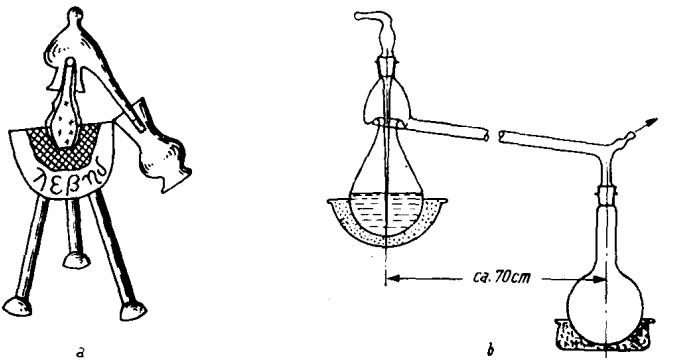


Fig. 2a. Glass distillation apparatus with sand or water bath (2nd century A.D.).
Fig. 2b. Vacuum still for mercury with collecting collar for the distillate (20th century).

From about 1300 A.D. onwards the methods of distillation may be divided into two basic types:
per ascendum = "rising distillation", *per descendum* = "descending distillation."
The descending procedure (Fig. 3a) sank into oblivion after about 1800, although it is the best method for certain types of separation. We find the principle again in a water still of the year 1952, where it is chosen to ensure an economical use of heat (See Fig. 3b).

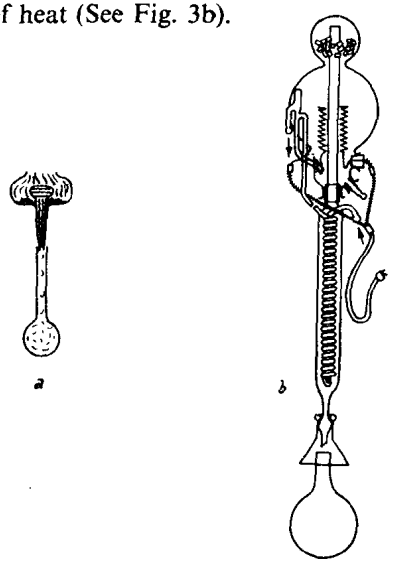


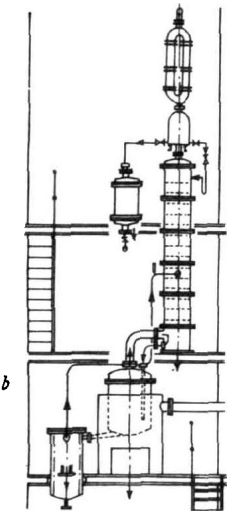
Fig. 3a. Dry distillation of bark and herbs "*per descendum*" (1300 A.D.).
Fig. 3b. Water still of Blome according to the "*per descendum*" principle (20th century).

Reference p. 16

Soon after the invention of printing a series of very graphic descriptions of distillation were published, showing the state of development at the end of the middle ages. The most important of these were the following:
1483, Schrick: Verzeichnis der ausgeprannten Wässer (Account of the burnt-out waters);
1500, Brunswig: Das Buch der rechten Kunst zu destillieren die eintzige Ding (Book of the true art of distilling the sole things);
1507, Brunswig: Das Buch der wahren Kunst zu destillieren (Book of the true art of distilling);
1528, Ulstad: Coelum philosophorum (The philosopher's heaven);
1536, Ryff: Neu gross Destillierbuch wohl begründeter künstlicher Destillation (New large distilling book of well-founded artificial distillation).

After the 16th century a large variety of methods of heating the stills is observed. Heating is carried out by air bath, water bath, sand or ash bath and also with the aid of wax candles. The furnaces are provided with fuel hoppers, in order to permit of working without interruption. Very strange systems of heating are also encountered, such as those utilizing the heat of fermentation of bread dough or pressed-out fruit. In hot climates heat was occasionally obtained from burning mirrors and it is of interest to find that

a



b

Fig. 4a. Separate heating furnace for wooden distilling apparatus, with condensing coil (17th century).
Fig. 4b. Separate boiler for continuous industrial plant (20th century).