SULFURIC ACID MANUFACTURE

BY

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原书缺页

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company (Reinhold Publishing Corporation, successors) of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years

and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfillment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious

attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

AMERICAN CHEMICAL SOCIETY

BOARD OF EDITORS

PREFACE

In the early 'Twenties I wrote what was perhaps the first American book (of this century at least) on the manufacture of sulfuric acid that treated of technical practice both at home and abroad. This earlier work was a small book, designed expressly for the use of students at one of the larger American correspondence schools, and with that purpose in view it was elementary in scope. Since that time much acid has flowed through the counting box—many improvements in manufacturing practice, some of them almost revolutionary in character, have been introduced—yet during the interval no other American book on the subject has appeared.

The size of the present work, in comparison with the correspondence-school textbook on the one hand and with the three-volume and four-volume sets compiled by authorities in England and in Germany on the other, indicates that it is neither elementary nor exhaustive. The attempt has been made here to produce a book on sulfuric acid manufacture which would be of practical use to the chemical engineer, the technical chemist, the acid manufacturer (actual or potential), the student at college or technical school and the acid consumer, without clogging the text with lengthy descriptions of obsolete processes or of mere proposals that have not been reduced to practice. One object has been to present up-to-date information, in readily accessible form, within the compass of a single volume, so that the work would be of a size adaptable for revision as frequently as advances in the industry may require, such revisions being available, without too great a sacrifice, to all who wish to keep abreast of developments. In order to keep within the limits of a single volume, pertinent matter readily available elsewhere has been omitted, and the temptation to expand the treatment of various topics has been resisted; but in all such cases copious references have been introduced, to supply the reader with information as to sources where the omitted matter may be found.

Foreign books on sulfuric acid manufacture have been pronounced deficient in the space allotted to the consideration of American practice. This book may be criticized abroad on the ground that American practice has been stressed too much. However, it is believed that in the contact processes American practice, during the period 1925 to 1935, has progressed farther than foreign practice, and that there is justification for emphasizing the advances made in the United States.

The preparation of this book, carried on, over a period of years, during brief intervals made or seized amidst the execution of the duties of an active professional life, has been difficult. It is too much to hope

that in this first edition all errors of omission and commission have been found and corrected by the proof-readers. I shall be grateful to all who will take the trouble to call my attention to those errors that escaped us, that they may be avoided in revisions to come. Where opinions are expressed herein, it is natural that some authorities, in certain cases, may find themselves in disagreement. I invite all those holding divergent opinions to communicate with me regarding their views, in order that all such may receive appropriate consideration, for the benefit of future editions. To the same end I invite and shall welcome constructive criticisms and suggestions for the improvement of the work.

Needless to say, a book of this character is not the product of one man alone. I have had the benefit of the advice and help of many friends and co-workers in the sulfuric acid field, and I am indeed glad to have this opportunity to express to all of these my heartfelt thanks for their indispensable assistance. Chief among those to whom I am indebted stands Fred C. Zeisberg, who read and criticized with painstaking care the whole of the manuscript, making many suggestions of great value, and contributing substantially to the text and to the illustrations. I am indebted also to T. R. Harney, D. B. Keyes, R. A. Norton, J. H. Shapleigh and S. F. Spangler for their constructive advice after reading portions of the manuscript. Construction and manufacturing companies rendering substantial assistance include the American Cyanamid Company, the Chemical Construction Corporation, the Mills Packard Construction Company, Ltd., the Silica Gel Corporation, the Tennessee Copper Company and the Texas Gulf Sulphur Company. Among foreign correspondents to whom I am indebted, particular mention should be made of Percy Parrish, Hugo Petersen and Bruno Waeser. For permission to reproduce published material grateful acknowledgment is made to the American Institute of Chemical Engineers, Chemical & Metallurgical Engineering, Gurney & Jackson, Industrial & Engineering Chemistry, the McGraw-Hill Book Company, D. Van Nostrand & Company and John Wiley & Sons, Inc.

But it is manifestly impracticable to enumerate in the Preface all those to whom thanks are due for permission to use material herein incorporated, and other acknowledgments will be found beneath illustrations, tabular matter, etc., throughout the book.

ANDREW M. FAIRLIE

Atlanta, Georgia, U. S. A.
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CONTENTS

NOTE

The measures of capacity, weight, etc. adopted herein are those in common use in the United States. For example:

The gallon is the U. S. gallon of 231 cubic inches. To convert into British (Imperial) gallons, multiply by the fraction $\frac{5}{6}$, or by 0.83267.

The ton is the short (or net) ton of 2,000 pounds. To convert into long tons, multiply by 0.89287, or divide by 1.12. To convert into metric tons, multiply by 0.90718.

Temperatures, unless otherwise designated, are expressed in degrees Centigrade.

SULFURIC ACID MANUFACTURE

Introduction

Sulfuric acid (H_2SO_4), as encountered in the chemical laboratory, is a colorless and odorless liquid of syrupy or oily consistency, whence has been derived the name "oil of vitriol" (O. V.). This liquid is a solution containing 93.19 per cent of sulfuric acid. The specific gravity of this solution is 1.8354. Measured by the Baumé hydrometer it is known as 66° Bé. sulfuric acid.

Sulfuric acid of 100 per cent strength (called "monohydrate," because it contains a single molecule of water for each molecule of sulfur trioxide present) is soluble in water in all proportions with evolution of heat. Acids of different degrees of dilution are useful for different purposes. The more common dilutions range in strength from 32 per cent H_2SO_4 (used in storage batteries) to 98 per cent H_2SO_4 (used in the manufacture of certain organic dyes and in oil refining). In the manufacture of explosives fuming sulfuric acid, a solution of sulfur trioxide in monohydrate sulfuric acid, is used.

Commercial sulfuric acid is sometimes colorless, but it is often slightly pink or yellow, and its color ranges from these pale shades to dark brown, or, occasionally, even black. Sometimes the commercial acid is clear, but frequently it is more or less milky, or opaque, from finely divided solids in suspension. In dilute solution it is highly corrosive and attacks nearly all metals. Platinum and gold are strongly resistant to its corrosive action. Of the common metals, lead is the least attacked by strong or dilute solutions. In general, hot acid is more corrosive than cold. Sulfuric acid rapidly decomposes rubber, textile fabrics, wood and practically all organic substances. Concentrated sulfuric acid has such a strong affinity for water that, in contact with any substance containing hydrogen and oxygen, it decomposes such substance to appropriate these two elements, in the form of water, to itself. For example, a drop of sulfuric acid on a lump of sugar reduces the latter to carbon.

The manufacture of sulfuric acid consists in the oxidation of sulfur dioxide (SO_2) to sulfur trioxide (SO_3), and in the combination of sulfur trioxide with water (H_2O) to form sulfuric acid (H_2SO_4). The sulfur dioxide, a gas, is formed by burning sulfur (brimstone) or some metallic sulfide in oxygen or air. The chemical reactions involved in the oxidation of sulfur dioxide to the trioxide, and in the combination of the trioxide with water, are accomplished by two general groups of processes—the nitration processes, of which the most familiar is that known as the chamber process; and the contact, or catalytic processes.

In the nitration processes nitrogen compounds are used to effect oxidation, and the chemical reactions are complex, involving the formation of intermediate compounds of nitrogen, sulfur, hydrogen and oxygen, and the subsequent decomposition of these by means of water, to produce sulfuric acid, with reproduction of the nitrogen compounds. In the contact processes, on the other hand, the sulfur dioxide is oxidized directly to the trioxide by means of a catalyst.

Hydrometers. One cannot go far in the study of sulfuric acid without a knowledge of hydrometers, which are used for testing the density or strength of acid solutions, up to a strength of 93.19 per cent H_2SO_4. A brief description of the various kinds of hydrometers used in the manufacture of sulfuric acid is given in Appendix I. The hydrometer in common use in England is the Twaddell hydrometer; and in the United States, the Baumé hydrometer, American modulus. A sulfuric acid table adopted by the Manufacturing Chemists' Association of the United States, reproduced in Appendix II, gives, for each degree Baumé from 1° to 66°, the corresponding specific gravity and degree Twaddell, the percentage of H_2SO_4, the weight per cubic foot, the percentage of 66° acid (O. V.), the pounds O. V. in one cubic foot, and the freezing point. Appendix II also gives the allowance for temperature, in making hydrometer readings, the approximate boiling points of various strengths of sulfuric acid solutions and other sulfuric acid tables adopted by the Manufacturing Chemists' Association of the United States.

Nomenclature. Since sulfuric acid can be mixed with water in all proportions, it is necessary, for convenience in marketing, as well as for statistical work, to adopt a few definite strengths as standard strengths. These standard strengths, as adopted in the United States, are enumerated in Table 1.

TABLE 1.—*Standard Strengths of Sulfuric Acid Solutions.*

°Bé.	Specific Gravity	Name	H_2SO_4 Per Cent	SO_3 Per Cent
50	1.5263	Chamber Acid	62.18	50.76
60	1.7059	Glover Acid	77.67	63.40
66	1.8354	Oil of Vitriol (O. V.).....	93.19	76.07
—	1.8391	Monohydrate	100.00	81.63

In works parlance, the name "chamber acid" is given to any strength of acid that may be in the pans of the lead chambers—usually anywhere from 52° to 54° Bé.—and sometimes acid of 60° Bé. strength or stronger, is spoken of as "chamber acid," if produced at a chamber plant. Such uses of the term must be distinguished from its use for statistical or marketing purposes, when 50° Bé. acid is meant.

It is customary, in buying and selling acid made by the chamber process, to calculate the actual weights to the basis of 50°, 60°, or 66° Bé., although the acid itself may be, and usually is, of some intermediate

strength. In computing the production of a chamber plant for any stated period of time, it is usual to measure, and to test by hydrometer and thermometer, the acid contained in all the acid receptacles at the plant, then to calculate the estimated weights of all the different strengths of acid in the various tanks and chambers, to some definite basis, such as 50° Bé., and to report the production as so many short tons of acid calculated to such basis. At some chamber plants, the standard strength used as a basis for reporting production is 60° Bé. At most contact plants, the standard strength used for reporting quantities of acid produced is monohydrate.

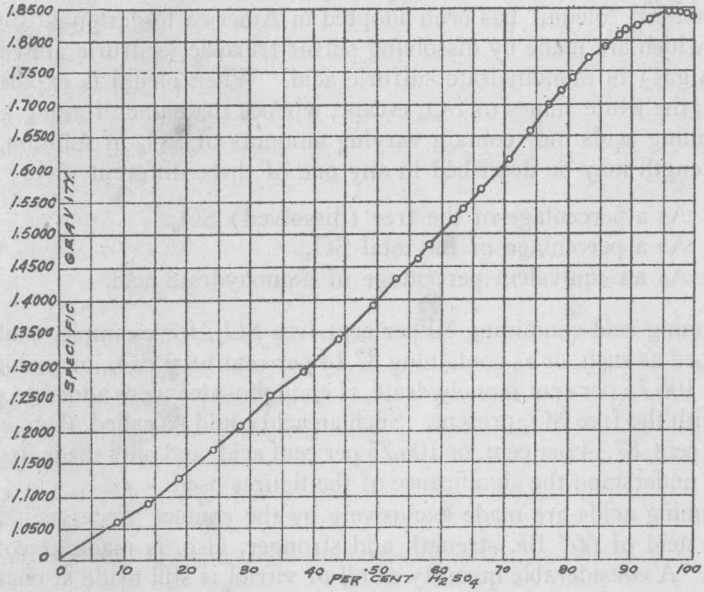

FIGURE 1.—Curve showing Relation between Specific Gravity and H_2SO_4 Percentage of Sulfuric Acid Solutions.

It is often desirable to convert weights of sulfuric acid from one standard strength to another, and for this purpose the table given in Appendix IV has been compiled.

Sulfuric acid solutions display a reliable relation between specific gravity and percentage H_2SO_4 from zero to, but not beyond, 93.19 per cent H_2SO_4, as is clearly shown by the curve in Figure 1, which indicates, for example, the same specific gravity for 95 per cent acid as for 100 per cent. Hence for acid solutions stronger than oil of vitriol the hydrometer does not serve as a testing means. Such solutions must have the acidity determined by chemical analysis, and they are described as of so many per cent sulfuric acid or so many per cent monohydrate (H_2SO_4).

The term "oil of vitriol," used in the United States to designate acid of 66° Bé. strength, has no such definitely restricted meaning in Europe. In England, "oil of vitriol" is often used as a synonym for the term, "sulfuric acid," and the English speak of "123° Tw. oil of vitriol," for example, just as an American uses the phrase "55° Bé. sulfuric acid."

In continental Europe, because the modulus used there in the manufacture of Baumé hydrometers is different from that adopted in the United States, the entire Baumé scale is different, and the American oil of vitriol (66° Bé., 1.8354 sp. gr.) is only 65.7° Bé. according to the German scale. Even fuming acid, in Germany, is referred to as "Nordhausen oil of vitriol," frequently abbreviated to "oleum."

The term "oleum" has been adopted in America to designate fuming acids, which are made by dissolving sulfur trioxide (sulfuric anhydride, SO_3, a gas) in monohydrate sulfuric acid. When oleum is exposed to the air, the white fumes of SO_3 escape, whence the name "fuming acid."

Fuming acids may contain varying amounts of SO_3 in solution, and the strength may be described in any one of three different ways:

1. As a percentage of the free (dissolved) SO_3.
2. As a percentage of the total SO_3.
3. As an equivalent percentage of monohydrate acid.

Fuming acid containing 30 per cent free SO_3, for example, could be described as such, or as containing 87.14 per cent total SO_3, or as equivalent to 106.75 per cent monohydrate, if enough water were added to combine with the free SO_3 present. Such an acid could be called, then, either 30 per cent, 87.14 per cent, or 106.75 per cent acid, and only the instructed would understand the significance of the figures used.

Fuming acids are made exclusively by the contact processes. Most of the acid of 66° Bé. strength and stronger, also, is made at contact plants. A considerable quantity of oil of vitriol is still made at chamber plants by concentrating Glover acid to 66° Bé. in a fuel-fired concentrator. Chamber acid can be concentrated by means of heat to as high as 97.5 per cent H_2SO_4, but this practice is not economical.* Strengths above 94 per cent H_2SO_4 are not made from chamber plant acid except under exceptional circumstances, such as existed during the World War of 1914-1918. The bulk of the acid of 60° Bé. and weaker strengths is made at nitration-process plants. It is obvious, however, that the weaker acids can be produced by diluting contact-plant acid of high concentrations, when it is expedient to do so.

The names thus far defined or explained have been names designating different strengths of sulfuric acid. There are other names which indicate, more or less definitely, the degree of purity of the respective kinds of acid or the uses to which the acids are applied.

*It is claimed that concentrations up to 97 per cent H_2SO_4 can be economically produced by the Simonson-Mantius vacuum process.