

CASEIN AND ITS
INDUSTRIAL
APPLICATIONS

SUTERMEISTER
AND
BROWNE

CASEIN

and Its Industrial Applications

By

Edwin Sutermeister

and

Frederick L. Browne



American Chemical Society
Monograph Series

SECOND EDITION

BOOK DEPARTMENT
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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 co-operation with the American Chemical Society and 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 society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with 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 by 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*, Moissan's *Traité de Chimie Minérale Générale*, Friend's and Mellor's *Textbooks of Inorganic Chemistry* and Heilbron's *Dictionary of Organic Compounds*, it often takes a great deal of time to coördinate the knowledge on a given

topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a 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 enable such men to form closer contact with work 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, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature 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 is made of those papers which are most important.

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Introduction

Preparation of the first edition of this book, which appeared in 1927, was undertaken because it was felt that there was no satisfactory work on the subject and that a volume of this sort was therefore needed. At that time casein was already long established in the coated paper industry in the United States, had recently come into wide use in water-resistant glues for woodworking and in insecticide sprays, was in the pioneering stages of development in plastics, and was being used to a minor extent in a number of other industries, such as textile printing, leather dressing, and manufacture of washable calcimine. Domestic production of casein was increasing steadily and was improving in quality, largely as a result of technical advances in methods of production by batch methods; but more than half the casein consumed was imported.

Since this book first appeared, conspicuous progress has been made in both production and utilization of casein. Further improvements in batch processes of production and in drying equipment and development of continuous processes under careful technical control have made domestic casein uniformly high in quality. Domestic production has increased very greatly while importation has fallen to less than 10 per cent of the total amount of casein consumed. Although no striking new developments have occurred in the use of casein in paper coatings, glues, insecticide sprays, textile printing, leather dressing, foods and pharmaceuticals, there have been at least three spectacular new technological achievements. Casein plastic, through improvements in processing, has become firmly established in the button business. Casein paste paint, an entirely new product, has appeared and won an important place in the paint industry, while the older powder paints have also been improved and grown in volume. A new synthetic textile fiber resembling wool has been invented and has found commercial application in Europe and Japan, though its place in American economy remains to be demonstrated.

On the theoretical side there have been many important developments in both the organic and physical chemistry of casein, some of which, such as the demonstration of the heterogeneity of casein, render the subject even more abstruse than it formerly seemed to be. That, however, is more of an excuse than a reason for the characteristically empirical approach to the technology of casein, which grows more by invention than by research. Perhaps the growth of the farm chemurgic movement will soon provide the stimulus for more effective technologic research in this field. At any rate technical understanding of the industrial uses

of casein is still in an elementary stage of development, offering abundant opportunities for interesting and possibly fruitful study.

In view of the marked changes that have taken place in the past decade it is felt that a new edition of this book is needed. Although there is some rearrangement of chapters, the general plan and scope of the book remain unaltered. Nearly all the chapters have been thoroughly revised or completely rewritten, as far as practicable by the original authors. With each chapter more extensive citations to the literature, particularly to the patent literature, are included.

The junior editor, who is chiefly responsible for assembling and coordinating the manuscripts for this edition, is grateful to Mr. Sutermeister for the free hand allowed him in guiding the revision and to the collaborators for their whole-hearted co-operation and kindly indulgence of his whims. To the publishers, collaborators, and readers who have patiently endured a long delay in completing his task he sincerely apologizes and in extenuation points out that the task was accepted at a time when he had good reason to expect a period of freedom from other occupations that turned out instead to be a period of exceedingly urgent demand upon his time.

U. S. Forest Products Laboratory
Madison, Wisconsin
October 19, 1938

F. L. BROWNE

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Chapter I

Casein in Milk and Its Isolation

FREDERICK L. BROWNE

The casein of commerce is a by-product of the dairy industry, and is usually prepared from skim milk, less often from buttermilk. Consideration of casein, therefore, begins logically with the manner in which it occurs in milk, its relation to the other constituents of milk, the general principles of its isolation, and the changes it undergoes during isolation. For reasons that will appear, a description of the laboratory methods of isolating casein is desirable before discussing the organic and physical chemistry of casein (Chapters 2 and 3). Commercial methods of manufacturing casein are described in Chapter 4.

Practical knowledge of casein in the form of curd and cheese dates back before the dawn of written history. Casein was recognized as a constituent of milk, together with butter fat, lactose a little extractive substance, salt, and water, by Scheele in 1780.¹¹⁸ For many years casein was regarded as a chemical individual remarkable among proteins for ease of isolation in a reasonably pure state. More recent investigations, discussed in Chapter 3, prove that casein, after it has been separated from milk, is not a homogeneous substance. The product may be separated into fractions that differ seriously in many important properties; and yet when the fractions are recombined a product apparently identical with the original casein is obtained. There may be a homogeneous protein in milk that gives rise to casein after material alteration resulting from the treatments necessary for its separation, as is known to be the case with some proteins, or there may be a mixture of proteins in milk that separates as a unit, and is called casein. At any rate the term *casein*, strictly speaking, designates a product isolated from milk rather than a biochemical substance occurring in milk. The product is clearly a mixture, but it is not yet possible to say whether some of its ingredients should be regarded as foreign substances or degradation products contaminating a pure casein, whether it is one chemical substance in various stages of polymerization or aggregation, whether it is a mixture of three or four chemical individuals that will ultimately be identified and named, or whether it is a mixture of a still more complicated nature.

There are several methods of isolating casein not only from cow's