

P. 1884. The table headings at the top should read "Aluminum" at the left and "Tin (white)" at the right; a horizontal line should appear above the headings "Tin (gray)" and "Iodine."

P. 1885. The table heading at the top should read "Potassium chloride" on the right; a horizontal line should appear above the heading "Silver chloride."

P. 1886. The table headings at the top should read "Mercurous chloride" on the left and "Tin tetrachloride" on the right; a horizontal line should appear above the headings "Lead chloride" and "Formic acid (cont.)."

The System, $\text{Fe}_2\text{O}_3\text{—SO}_3\text{—H}_2\text{O}$, by E. Posnjak and H. E. Merwin.

Make the following changes if not so printed.

P. 1977. Line 18, "See Table III" should be "See Table IV." In Table III, "Expt." should be "No.;" and < should be \angle .

P. 1979. Line 24, III should be IV. Line 27, the last (110) and (120) should be (1 $\bar{1}$ 0) and (1 $\bar{2}$ 0).

P. 1981. Line 2, after "but" insert "on"; line 6 from bottom, 4 should be 3.

P. 1982. Line 3, omit second c; lines 3 to 7, insert, in first wide space, > ; line 7, the second (110) should be (1 $\bar{1}$ 0); line 9, III should be IV.

P. 1983. Last line, 50 should be 51.

A Study of the Velocity of Hydrolysis of Ethyl Acetate, by Herbert S. Harned and Robert Pfanstiel.

P. 2201. For $\frac{T'_0 - T}{T_E} = x$, read $\frac{T'_0 - T}{T_E} A = x$.

A New Method for the Introduction of an Ethyl Group. The Reaction Between Organo-magnesium Halides and Diethyl Sulfate, by Henry Gilman and Rachel E. Hoyle.

P. 2625. The yield in the reaction between benzyl magnesium chloride and diethyl sulfate is 65% and not quantitative.

NEW BOOKS

The Chemistry of the Non-Benzenoid Hydrocarbons and their Simple Derivatives.

By BENJAMIN T. BROOKS, Ph.D. The Chemical Catalog Company, Inc., 1 Madison Avenue, New York, U. S. A., 1922. 612 pp. 16 × 23.5 cm. Price \$7.00.

As stated by the author in the preface "the beautiful, interesting and often facile chemistry of the benzene hydrocarbons has somewhat overshadowed the chemistry of the aliphatic open-chain and cyclic non-benzenoid hydrocarbons." In this volume we have an adequate and a very readable survey of the paraffin and cyclic (other than the aromatic) hydrocarbons. No attempt to attain completeness has been made but abundant references to the literature are found throughout the book. The author sees great opportunities for research on the theoretical side of petroleum, rubber, turpentine and essential oils. Methods of refining petroleum, for instance, are still wasteful since they are based necessarily on empirical knowledge.

Titles of the first 6 chapters are: I. The Paraffins; II. Chemical Properties of the Saturated Hydrocarbons; III. The Paraffin Hydrocarbons; IV. The Ethylene Bond; V. The Acyclic Unsaturated Hydrocarbons; VI. Polymerization of Hydrocarbons. The great importance of the ethylene bond is emphasized in a chapter of considerable length. The theories

of Baeyer, Lewis and Langmuir are considered; its chemical properties; modification of the latter by substituents; addition reactions; action of sulfuric acid; auto-oxidation; vulcanization of rubber; ozonides, etc. Polymerization has assumed a new interest owing to the conversion of isoprene into a rubber-like substance, but, there seems to be no bright outlook for the commercial synthesis of rubber.

Chapters VII-XIV deal with the cyclic hydrocarbons, the first two treating of cyclopropane, -butane, -pentane and -hexane. This section is very interesting and important, for it presents a summary of work done mostly since 1900. The work of Wallach, Sabatier, Markownikow, Kishner, Perkin, Willstaetter, Kohler and others is well reviewed. Attention is called to the fact that von Baeyer's view of cyclohexane and its derivatives as "hydro-aromatic" compounds "served a useful purpose in connection with the constitution of benzene" but the term should be abandoned, for the chemical behavior of cyclohexane and its simple derivatives is "almost identical" with that of *n*-hexane. I see no good reason why the author writes "*n*.butane" and "2,4-dimethylhexane" when the established usage is *n*-butane and 2,4-dimethylhexane. Throughout the book a period is used for the dash and also for a comma.

The next 4 chapters treat of the "terpenes," the chapter headings being; IX. Paramenthane Series; X. Ortho- and Meta-menthane Series; XI. Bicyclic and Tricyclic Hydrocarbons; XII. Pinenes and Fenchenes; XIII. Camphene, Bornylene and Camphor. References include the year 1921. Chapter XIV takes up cycloheptane, higher homologs and lubricating oils. The next chapter, on Rearrangements, describes two sorts, those in which the ring suffers the loss of carbon and those in which there is a gain of carbon. Chapter XVI gives a general survey of physical properties, closing with a section on colloids, greases, jellies, emulsions and the use of fuller's earth in bringing about a fractional separation of hydrocarbons. The final chapter treats of physiological and related properties.

The author has rendered scientific and technical men a valuable service and the book should be very extensively used.

ALVIN S. WHEELER

Colloid Chemistry of the Proteins. By Prof. WOLFGANG PAULI, Director of the Laboratory for Physico-chemical Biology, University of Vienna. Translated by P. C. L. THORNE, M.A. (Cantab.), A. I. C., Sir John Cass Technical Institute, London. Part. I. P. Blakiston's Sons and Company, 1012 Walnut Street, Philadelphia, 1922. xi + 140 pp. 27 figs. 22 × 14 cm. Price \$2.25.

Proteins and the Theory of Colloidal Behavior. By JACQUES LOEB, Member of the Rockefeller Institute for Medical Research. McGraw-Hill Book Company, Inc., 370 Seventh Ave., New York; 6 and 8 Bouverie Street, E. C. 4, London, 1922. xi + 292 pp. 80 figs. 21 × 14 cm. Price \$3.00.

In its inception the theory of electrolytic dissociation was intimately related to the behavior of the proteins. In the experiments of de Vries,

upon which so many of the early speculations of van't Hoff and of Arrhenius depended, plant cells were used as osmometers, as delicate indicators of the degree of dissociation of the electrolytes in which they were immersed. After a period of nearly 30 years, during which the theory of electrolytic dissociation has progressed and become firmly established, advances in the chemistry of certain cell constituents have made clear the nature of the delicate reactions of plant or animal cells to infinitely small changes in electrolytic dissociation. These depend upon the fact that such important cell constituents as the proteins are themselves amphoteric electrolytes and are, therefore, in direct equilibrium with the inorganic electrolytes within and without the cell.

Two recent books, the one by Wolfgang Pauli, of the University of Vienna, the other by Jacques Loeb, of the Rockefeller Institute in New York, are concerned with interpreting the behavior of proteins in terms of their dissociations as amphoteric electrolytes.¹ Both books describe researches carried on by their authors over many years. As a result of their investigations both authors are agreed that although the large molecular weights of the proteins have in the past led to the consideration of their behavior as depending largely upon surface phenomena, these must now be considered as secondary to their chemical or stoichiometrical reactions.

"If a metal or a simple compound is brought to the colloid state," writes Pauli, "the dispersed particles are always aggregates of simpler but similar smaller portions. If, on the other hand, the particles are those of a non-associated substance of high molecular weight, of the same degree of dispersity as the above, we have particles formed of a combination of several heterogeneous groups of atoms (for instance, albumin, which is formed of various amino acids). . . At first sight it appears that the second example is more complex than the case of the colloidal metal; but one must not overlook the fact that the various groups which build up the complex compound often retain their characteristic properties, and stamp the whole molecule with their physico-chemical behavior."

Loeb's investigations indicate that many of the properties, which have heretofore been ascribed to the surface phenomena resulting from the colloidal dimensions of the proteins, disappear if identical amounts of protein compounds are considered. Since proteins themselves dissociate either as acids or as bases, the extent to which they form compounds with other acids and bases is determined by the hydrogen-ion concentration, the amphoteric strength of the proteins, and their iso-electric points. "It was merely an unfortunate historical accident" writes Loeb "that the colloidal behavior of proteins was investigated before the convenient methods of measuring the hydrogen-ion concentration were developed;

¹ In any discussion of the recent advances that have been made in protein chemistry reference must be made to S. P. L. Sørensen's comprehensive "Studies on Proteins" (*Compt. rend. trav. lab. Carlsberg*, 12, 1917). In them the behavior of proteins have also been interpreted—and analyzed—in terms of their amphoteric dissociation.

otherwise, we should probably never have heard of the idea that the chemistry of colloids differs from the chemistry of crystalloids, at least as far as the proteins are concerned."

The material in Pauli's book is for the most part older and is therefore considered first. It is divided into 9 chapters of which the first 2 are concerned with demonstrating that "the colloid chemistry . . . and general physical chemistry of the proteins form an inseparable whole." "It would appear impossible to suggest a single source of the electric charge which would be applicable to all colloid systems. But in the case of the proteins, as we shall show, all experience points to the conclusion that those which behave as electrolytes owe their charge to typical ionization processes." Loeb has apparently suggested a source of charge common to proteins and to other colloids.

The third and fourth chapters of the book are concerned with the phenomenon, first described by Hardy, and extended to natural soluble proteins by Pauli, that proteins change the sign of their charge with change in the hydrogen-ion concentration. As a result, they appear to be in an iso-electric condition at a particular hydrogen-ion concentration, characteristic for each protein. Here proteins exist most nearly uncombined and, therefore, exhibit their most striking differences. Pauli has devoted a considerable portion of his book to discussing the state of proteins in their iso-electric condition, for, as he points out, "in order to understand the alterations in state of the proteins, it is of great importance to have accurate knowledge of their dissociation when in the iso-electric state."

This section of the book, despite a certain confusion in terminology, will prove invaluable to the special student. The confusion is due in part to an amplification of the theoretical treatment which the existing experimental material hardly justifies; in part, unquestionably, to the apprehension of apparent contradictions and difficulties.

The final chapters of the book are concerned with the properties of the compounds that proteins form with acids and bases, and of the effects upon them of neutral salts. The theory of the behavior of protein compounds that has hitherto been most acceptable was due to Pauli, and is admirably presented. This theory has been called the hydration theory. It rests upon the assumption, originally made for inorganic ions by Kohlrausch, that the mobility of ions depends on the degree to which they are hydrated. Since the salt of a weak acid and a strong base, or of a strong base and a weak acid, is nearly completely dissociated, such compounds as the sodium salt of a protein, or its hydrochloride, should be more dissociated than iso-electric protein. According to Pauli, the observed greater swelling and viscosity of protein compounds are manifestations of greater hydration due to increased ionization. Further, the decrease in swelling and viscosity that appear when a very large excess of acid or

base is added to protein, or if a neutral salt is added, is to be ascribed to depression of the dissociation, and therefore decreased hydration.

Although their observations often supplement one another, Loeb has apparently demonstrated that a few of the phenomena with which Pauli is concerned are apparent rather than real, and has offered a new hypothesis to explain others.

In the first half of his book, Loeb has presented a great number of experiments to show that the proteins combine with acids and bases in stoichiometrical proportions, and that the properties of protein solutions depend upon this combination. The array is imposing, the experiments often ingenious, and the results more than adequate to demonstrate the essentially chemical nature of the reactions involved. Loeb has followed the progressive combination of proteins with acids and bases by the hydrogen electrode and the chlorine electrode, by volumetric analyses for silver ion and for bromide ion, by the retention of acid dyes on one side of the iso-electric point and of basic dyes on the other. He has defined the relation between the formation of protein compounds and changes in their osmotic pressure, in their swelling, viscosity, and in their conductivity. Many would have accepted the essentially chemical nature of the reactions with less evidence; few will remain to doubt it.

Whereas Pauli also contends that the physical properties of proteins depend upon their dissociation as amphoteric electrolytes, he has interpreted certain of his measurements to mean that the salts of the same protein with different acids or bases dissociate differently. Loeb believes no such thing, and this is the first major disparity in their views. Loeb has apparently been able to show that no appreciable difference exists—except that due to valency—between the dissociation of equal amounts of the compounds of a protein with different acids, or bases. His experiments show no substantial difference between the osmotic pressure of gelatin chloride and acetate, at the same hydrogen-ion concentration, nor their swelling nor their viscosity. The bivalent gelatin sulfate, however, is only approximately half as swollen and half as viscous. The phenomena investigated were many, and their presentation is lucid and forceful.

The second great difference between Loeb and Pauli is in the theoretical interpretation of these phenomena. Pauli, as we have seen, has attempted to explain differences in protein behavior by differences in hydration. Loeb has built his explanation of protein behavior on an entirely different property of these substances. His theory, which occupies the second half of the book, is general and is presumably applicable to other colloids besides the proteins. According to it:

“Colloidal behavior is due to the fact that protein ions cannot diffuse through many membranes which are permeable to the majority of crystalloidal ions or that protein ions form solid gels in which cohesive forces prevent their diffusion, while such gels are permeable to crystalloidal ions. The theory of the equilibrium conditions

resulting from this difference in the diffusibility of the two opposite ions of an electrolyte was developed by Donnan. These equilibrium conditions give rise to forces, such as P. D., osmotic pressure, etc., which are the only cause of colloidal behavior."

The implications of the Donnan equilibrium for the behavior of proteins have been the subject of a detailed investigation, theoretical and experimental. A measure was sought of the extent to which the equilibria between proteins, acids, bases, and inorganic salts with a common ion were due to the enormously slower mobility of the protein ion. Membrane potentials were electrometrically measured and the mechanism by which they were set up investigated by simultaneous use of the hydrogen and chloride electrodes. In many respects these experiments, and those in the succeeding chapter on osmotic pressure, are the most important in the book since they furnish the most rigorously quantitative proof of the hypothesis. The distribution of ions across a membrane surrounding a protein solution was used in one case to calculate the potential difference, in the other the osmotic pressure of the solution, on the assumption that the equilibria involved followed the mathematical law of Donnan, and the results show good agreement between the calculations and the observations.

The remainder of the book is devoted to a most suggestive consideration of the behavior of proteins from the point of view of the Donnan equilibrium; swelling is discussed, as are viscosity and the stability of protein solutions, and one closes the book impressed with the fertility of the conception, and also with the wealth of the writer's experience.

Perhaps one should end, as Loeb unquestionably did, with the historical introduction to the book. In it the development of ideas regarding colloidal behavior that have followed one another with such bewildering rapidity since Graham's pioneer work in 1861, is brought by the author to a perspective in which the "colloidal state" must go the way of "colloidal substances," and "colloidal behavior" be explained "by two laws of classical chemistry"... "the stoichiometrical law and Donnan's theory of membrane equilibria." Certainly the forces defined by these two laws are of the order of magnitude the phenomena demand. Whether they alone will suffice to explain completely the behavior of the proteins must await further experimentation.

EDWIN J. COHN