REVIEWS.

KOLLOIDCHEMIE UND PHOTOGRAPHIE. By Dr. LÜPPO-CRAMER. Second edition, completely revised. Pp. 112. (Dresden and Leipzig: Th. Steinkopff. 1921.) Price 7s. 10d. net.

The successful practice of photography and, more especially, the manufacture of photosensitive materials are typical of those practical arts which call for an intimate acquaintance with the properties of matter in the colloidal condition, but appreciation of the importance to photography of recent scientific investigations in colloid chemistry was by no means common when the first edition of this book appeared in 1908. Dr. Lüppo-Cramer deserves congratulation on having been one of the earliest photographic investigators to appreciate the advantages of that close affiliation of photochemistry with colloid chemistry which is proving so fruitful. It is still unfortunately true that comparatively few photographic chemists in this country have much more than a hazy notion of the lines along which progress in the latter branch of physical chemistry is being made, whereas in Germany such knowledge would appear to be more widespread, if one may judge from the fact that the author gives this as the reason for omitting from the new edition the introductory chapters dealing with the elementary principles of colloid chemistry.

The remainder of the original book has also been drastically altered; many of the interesting examples culled from photographic practice find no mention in this edition, and practically all the new matter is provided from the author's own observations. As an elementary guide to the bearings of colloid chemistry on photography the book has suffered by these changes.

The pioneer studies of Carey Lea on the photohalides and colloidal silver are given the prominence which they merit, but few other English-speaking workers are mentioned. Lüppo-Cramer's experimental work is almost entirely qualitative in character and he persistently ignores the accurate quantitative work and the broader outlook of English and American investigators. For instance, in view of the fact that the minimum amount of light, as measured by the product of intensity and time, which will produce a latent photographic image is found to be inadequate to provide the energy required, on thermochemical grounds, to separate one atom of silver from one atom of bromine per exposed silver bromide particle, few British or American photochemists will agree with Lüppo-Cramer that:—"So soon as one acknowledges that . . . chemical development is a sufficient proof of the existence of nuclei, all efforts to explain the primary action of light on silver bromide otherwise than as a splitting off of bromine and a silver-nucleus formation become, to say the least, unnecessary" (p. 52); nor does it trouble him that, if the supply of energy in such minimal exposures is already inadequate to the task, it is no use ascribing to the colloidal silver, which is assumed to be present in the "ripened" grains of a high-speed emulsion, the function of a catalyst promoting the decomposition (p. 53), since "catalysis" cannot supply energy lacking in the stimulus.

Dr. Lüppo-Cramer is well known as a tireless experimenter, with a large fund of information concerning photographic phenomena, many of which he was the first to place on record. His contributions to the literature of the subject are so numerous and valuable and are scattered through so many journals that the thanks of all photographic chemists are due to him for providing this epitome of his views and results with full references to the original papers. It would, therefore, be ungenerous

to criticise too severely his explanations of the phenomena he describes, especially as, in many cases, it is difficult to suggest any reasonable alternative at present. Suffice it to say that his hypotheses are usually so simple and definite in character that they almost always lead to further progress by stimulating both himself and others to test them experimentally.

To those engaged in photographic research, the book will supply much food for thought and abundant data for further investigations of an extremely interesting character.

F. F. RENWICK.

THE ELECTRONIC CONCEPTION OF VALENCE AND THE CONSTITUTION OF BENZENE. By H. S. FRY. *Monographs on Inorganic and Physical Chemistry*, edited by A. FINDLAY. Pp. 300. (London: Longmans, Green and Co. 1921.) Price 16s. net.

THE knowledge respecting the constitution of the atom which has been obtained during the present century has made it possible to gain some insight into the nature of chemical combination, and the view that two types of chemical union exist, (1) the ionising valency, dependent upon electron transference, and (2) the non-ionising valency, dependent upon electron-sharing between the two combining atoms, is probably now widely accepted. In this book, however, chemical combination is regarded as being dependent upon electron transference only, although in the substances chiefly considered the chemical combination is exclusively of the non-ionising type. This presents a great initial difficulty to the acceptance of the author's views. In the chlorine molecule, for example, the two atoms are assumed to be respectively positively and negatively charged, and this is represented by the "electronic formula," $\text{Cl}^+ \text{Cl}^-$. Experimental support for this is seen in the production of hydrochloric acid and hypochlorous acid in the hydrolysis of chlorine, and all chlorine, which, as in the chloramines, gives hypochlorous acid on hydrolysis, is regarded as positive chlorine.

The greater part of the book is devoted to the electronic formula for benzene. It is assumed that the six outwardly directed valencies alternate in electric character, so that three alternate hydrogen atoms are positive hydrogen and the other three negative hydrogen. The application of this formula to the substitution phenomena is first considered. If substitutes which give an ortho-para-orientation are regarded as negative and those which give a meta-orientation as positive, a simple explanation is provided of many of the observed facts, for most of the radicals, such as the nitro-group, which can be introduced directly into the benzene molecule, are, on this hypothesis, positive. "When substituents are of the same sign or polarity they will occupy positions which are meta to each other; if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other."

However, exceptions to this rule at once suggest themselves, especially in the case of the halogen derivatives; the dichlorobenzene, for example, formed by direct substitution should, on this theory, be the meta-compound. These difficulties are met by the hypothesis of "electronic tautomerism." Chlorobenzene is regarded as containing positive chlorine. This is shown by the electronic equation for its formation,

and is confirmed by its molecular volume, for the conclusion is drawn from the molecular volumes of

the chlorobenzenes that the atomic volume of positive chlorine is about 2.6 units greater than that of negative chlorine. But to explain the formation of para-derivatives on further substitution the chlorine in chlorobenzene must be negative. Hence the electronic tautomerism

is assumed, and it is supposed that of the two "electromers" that containing negative chlorine alone undergoes further substitution. The hypothesis of electronic tautomerism evidently gives great elasticity to the theory; at the same time, it largely deprives it of any power of prediction, and such a facile reversal of electric charge many chemists will find difficult to accept.

The theory appears to require a more sharply marked division into two classes of the members of a given series of compounds than in fact exists. In the chloro-compounds, for example, the chlorine in some is regarded as positive, in others as negative, but in view of the marked polarity of chlorine the difference in behaviour of the two types should surely be very great. Professor Fry gives as the chief distinction that negative chlorine in the benzene nucleus can be removed by hydrolytic reactions, whilst positive chlorine resists removal. Actually, however, instead of this difference being sharply marked, almost every gradation in readiness of hydrolysis is shown by the halogen derivatives of benzene, from the great resistance of the positively substituted chlorobenzenes on the one hand to the high reactivity of compounds like picryl chloride on the other.

The difference of chemical character associated with alternate positions in the ring in substitution-derivatives of benzene where the substituent shows strong polarity (as in the nitro-derivatives of benzene or in pyridine), in which the author finds important confirmation of his theory, has long been recognised. But it is surely more in accordance with the facts to look upon this alternating character as brought about by the introduction of the substituent rather than pre-existent in benzene itself.

Although all the views advocated in this work may not carry conviction, it contains much that is very suggestive; the arguments are developed with ingenuity, and organic chemists will find that the book is one that can be read with considerable interest.

W. H. MILLS.

A DICTIONARY OF CHEMICAL SOLUBILITIES—INORGANIC. By A. M. COMEY and D. A. HAHN. Second edition, enlarged and revised. Pp. xviii+1141. (New York: The Macmillan Co. 1921.) Price 72s.

"Comey" is more than a mere dictionary of solubilities; owing to the complete character of the work and the very large number of original papers that have been consulted, of which the source is generally fully indicated, it has become a reference work in inorganic chemistry almost rivalling "Beilstein" and Richter's "Lexicon" in the organic division. It is indeed difficult to over-estimate the debt that chemists are under to the compilers of such records, or to picture the enormous labour entailed in overhauling the huge volume of past and current scientific literature to make the presentation inclusive.

In the preparation of the second edition Dr. Comey has had the assistance of Dr. Dorothy Hahn, the latter being mainly responsible for extracting the material available since the appearance of the first edition in 1895 down to the end of 1915, whilst

Dr. Comey has edited the enlarged volume. Dr. Seidell's "Dictionary of Inorganic and Organic Solubilities," which has appeared meantime, covers a smaller field in inorganic chemistry than Comey's, dealing with the more important compounds only, with less detail and more restricted references. Whilst therefore the former is useful and sufficient for many practical purposes, it does not compete with the latter for research workers.

There is little to criticise in the arrangement. Many chemists would doubtless wish that the authors had broken with the tradition of the older dictionaries in respect to the haloid salts. The convenience of having all the cyanides, carbonates, sulphates, and other oxygen-containing salts, grouped together would be equally felt in the case of the chlorides, etc. The inclusion of a book-marker with direction notes and a list of contractions would, as in the case of Watt's work, save much reference to the explanatory preface. Nomenclature has been satisfactorily handled—indeed, some chemical dealers might with advantage revise their labels with the help of a copy. Many pages in the book draw attention to the need for further work. For example, aluminium in its behaviour towards nitric acid is described by different observers as, (1) not attacked even when concentrated and boiling, (2) slowly soluble in 27 per cent. acid, (3) easily soluble *in vacuo*, (4) not attacked by dilute or concentrated at ordinary temperatures, (5) very easily soluble, (6) slowly soluble.

But few blemishes have been noted. Menschutkin's table of the solubility of aluminium bromide in organic solvents is useless in the form given, and is better exhibited in Seidell. Voerman's table for potassium permanganate should have an explanatory note. Decimal points have here and there gone wrong, the solubility of calomel being given as 21 mg. per litre, instead of 2.1. In cases where salts undergo hydrolysis, with some separation of basic salt, the facts might well have been recorded.

A useful synchronistic table of scientific journals is included as an appendix.

W. C. REYNOLDS.

DIE PHYSIKALISCHE CHEMIE IN DER INNEREN MEDIZIN. By H. SCHADE. Pp. vii.+569. (Dresden and Leipzig: Th. Steinkopff. 1921.) Price 21s. net.

This volume is perhaps of only indirect interest to most readers of the Journal, but it is noteworthy as evidence of the remarkable extent to which the data and concepts of physical chemistry are being applied in medical science. The three sections of physical chemistry which are set out as of special value in the rational study of physiological and pathological phenomena are those dealing with (a) the properties of solutions, (b) colloids, (c) the course of chemical change from the standpoint of velocity and catalysis.

The main portion of the volume is occupied with a discussion, on this physico-chemical basis, of such matters as inflammation, infection, diseases of the heart, lungs, nerves, and digestive organs. The author, who has himself made a number of contributions to this development of clinical medicine, maintains very strongly that all processes in the living cell, both in health and in disease, are based on conditions and changes which are essentially physico-chemical in character. The abundant evidence brought forward in support of this contention is very striking.

A valuable part of the volume is a description of those physico-chemical practical methods which are applicable more especially for biochemical and medical purposes.

JAMES C. PHILLIP.