ments now in use, with the view of increasing the interest in the work of the committee and at the same time obtaining evidence of the directions in which reforms were most greatly needed. As the plan only received the hearty approval of one other member of the committee, it was abandoned.

The committee is now striving to bring before the council at an early date a series of recommendations which include certain definitions of fundamental standards, and the request that the U. S. Office of Standard Weights and Measures adopt regulations governing the construction, calibration, verification, etc., of chemical measuring instruments, as mentioned at the opening of this paper.

As the chairman of the committee, I take this opportunity to announce that the committee will be very glad to answer inquiries or to accept suggestions from the members of the society whenever they may find it convenient to offer them. I shall be especially pleased to see discussions of the subject of standards for volumetric apparatus or for other forms of measuring instruments, presented in this Journal. ERVIN E. EWELL.

WASHINGTON, D. C., March 7, 1899.

NEW BOOKS.

MAASSANALYTISCHE STUDIEN. Habilitationsschrift. VON Dr. JULIUS WAGNER. Leipzig: Oskar Leiner. 1898. pp. 123.

Since the adoption of the regulations of the Kaiserliche Normal-Aichungs-Commission of Berlin in June, 1893, those regulations have probably been generally accepted as representing the best results of mature thought upon questions relating to practical and desirable accuracy in the graduation and calibration of volumetric apparatus, and the precautions to be taken to ensure the preparation of trustworthy utensils. Committees appointed by three International Congresses have practically adopted the equivalent of these regulations as expressing their views, and only a few minor modifications were adopted by the Aichungs-Commission in 1897. In the little volume under consideration, Part I of which is devoted to general sources of error in volumetric analyses, Dr. Wagner has criticised certain of the conditions prescribed by the Normal-Aichungs-Commission as inadequate, and presents experimental data in support of his statements. This criticism demands some attention at this time, from its close connection with the work of the Committee on Measuring Instruments appointed by the President of the Amer-

ican Chemical Society to consider what steps should be taken, or regulations adopted, to promote uniformity of standards and practice, and greater accuracy of manufacture in connection with measuring utensils.

In the opinion of Dr. Wagner apparatus having the stamp of the Normal-Aichungs-Commission requires reexamination before it can be used in scientific investigations, because the degree of accuracy demanded is less than is attainable in the chemical processes in connection with which it is used, and also less than is practically attainable in manufacture and graduation. Dr. Wagner first refers to Classen's criticism of the regulations of the commission[1] because no account is taken of the variation in the amount of fluid which adheres to the walls of the vessels in the case of fluids of varying character. Dr. Wagner first shows that glass utensils are apparently most readily and completely cleansed by treatment with sulphuric acid and potassium bichromate, and notes the striking fact that a pipette containing a very thin layer of oil on its inner surface delivers more liquid than when thoroughly cleaned. He then studies the behavior of solutions of twentieth-normal bichromate, normal sodium carbonate, of concentrated sulphuric acid, and of several concentrated salt solutions, and determines, by weighing, the volume of the liquid adhering to the burette. His results indicate that the differences lie within the limits of error of observation, except in the case of concentrated sulphuric acid, from which it appears that the criticism of Classen is not well founded.

The first of the measuring instruments discussed is the pipette. Regarding the accuracy to be demanded in the use of pipettes, Böckmann, in his *Chemische Technische Untersuchungen, 1893*, I, 178, places the average value of the allowable error at 2/1000 for volumes from 1 to 25 cc., and 1/1000 from 50 to 2000 cc. This may be regarded as a fair statement of the requirements for technical use; yet, as is pointed out, the Aichungs-Commission's regulations allow a variation of 1/100 for a one cc. pipette; 1/200 for two cc.; 4/1000 for five cc.; 2/1000 for ten cc.; 1/1000 for twenty-five, fifty, and one hundred cc.; a lack of uniformity which may in itself become a source of error.

To indicate the degree of accuracy which might properly be

[1] Mohr's Titrirmethode, 7th Edition, p. 55.

demanded for research work, Dr. Wagner examined fourteen pipettes, varying from 100 cc. to 10 cc. capacity, and finds that the contents of a pipette may be determined to 2/10000 of its value for pipettes larger than ten cc., and probably to 4/10000 for ten cc. and five cc. pipettes, and that the error arising from the use of a pipette need not exceed these amounts. These quantities are much less than the limits set by the Aichungs-Commission, and a regraduation of instruments tested by this commission is therefore essential for work of high accuracy.

Regarding the method of emptying a pipette, whether by allowing the liquid to run freely, and, at the expiration of a definite time, touching the tube against the side of the vessel, or by gently blowing out the last drop, the data obtained by Wagner are not conclusive, as no advantage is evident on the side of either method. The differences are within the errors of observation. Convenience seems to favor the removal of the liquid by blowing.

But the question may properly arise, whether it is practicable to graduate burettes with an exactness corresponding to that which has just been stated to be attainable in measuring their contents. This, it is stated, may be done, if the restrictions as to the internal diameter of the tubes are suitably made. The Aichungs-Commission demands, in general, that the internal diameter of the tubes shall not be less than five-tenths mm. nor more than six mm. but without further specifications. The position of the mark cannot be accurately fixed within five-tenths mm. while a greater variation is not infrequent, and pipettes are found on the market with tubes so large as to make this uncertainty in marking a source of considerable error. On the other hand, a diameter of five-tenths mm. is so small as to make the use of a pipette annoyingly tedious. A table is given showing the allowable internal diameter in order that the error in marking may not cause an error in volume exceeding 3/10000, the adoption of which would add to the concreteness of the Aichungs-Commission's regulations. In the opinion of Dr. Wagner, the requirements of the Commission that at the orifice the walls of a pipette shall be drawn out as thin as is practicable tends to produce a capillary opening, which is undesirable; this fact leads him to favor blowing out the last drops of liquid as a method of emptying the pipettes now on the market.

Dr. Wagner notes great inequality in practice as regards the time of drainage. He recommends that pipettes should be so constructed with respect to the size of the orifice, that the time of outflow shall be sufficiently long to avoid any after-drainage, rather than to empty the pipette rapidly and to wait for a definite interval. He makes certain statements as to the time necessary to accomplish this.

A similar irregularity in allowable error to that noted in the requirements regarding pipettes is found with respect to measuring flasks, and it is pointed out that, for a variation of one mm. in the position of the mark, the maximum diameter allowable in 500 cc. and 50 cc. flasks as stated by the Commission should be reduced from twenty and ten mm. to fourteen and eight mm. respectively, in order to conform to the allowable variation in cubic centimeters, as stated in the very same regulations of the Commission. Measuring flasks may apparently be read with an accuracy about five times as great as that demanded by the Commission's regulations, with respect to graduation. The author believes that the manufacturers would welcome more explicit statements regarding the allowable variations in the diameter of the necks of the flasks.

Following a discussion of the limit of error in burette readings, the author points out inconsistencies similar to those already noted in the limit of accuracy demanded for burettes by the Aichungs-Commission's regulations, and points out that by suitably limiting the diameter of the burette, uniform accuracy is attainable. Burettes containing fifty cc. should have a diameter of ten to eleven mm., those of thirty cc. eight to ten mm., ten cc. graduated pipettes, five to seven mm. Assuming a necessary minimum error of one-tenth mm. in reading the position of the meniscus, the percentage error is always less than 1/1000, if the above dimensions are adhered to.

The original statement in the Commission's regulations regarding the allowable error in the small divisions of a burette seems to have been unsatisfactory, and was revised in 1897 but in such a way that, according to Dr. Wagner, it is satisfactory with respect to accuracy, but almost impossible to execute, and he recommends that, instead of striving to attain unreasonable exactness, each burette be accompanied by a table of corrections

(a request made by the Verein Deutscher Chemiker, but set aside by the Commission without assigned reason), or that the results of the calibration be written upon the burette itself.

The Commission places the time to be allowed for a burette to drain at two minutes, but the author regards it as a more advantageous and less time-consuming practice to allow the liquid to run out at the rate of ten cc. in about ten seconds, in which case the reading may be taken at once without appreciable error.

As a result of his work Dr. Wagner makes these recommendations regarding the graduation and calibration of measuring vessels: (1) That they be divided into grades, with respect to accuracy, and that the grade to which each instrument belongs be plainly marked upon it; (2) that the highest grade for pipettes and measuring flasks include only those accurate within 5/10000 of their capacity; and (3) that, since burettes cannot be graduated with an exactness corresponding to the accuracy desired for scientific work, they should be so calibrated as to assure accuracy within one-tenth mm. at any point of measurement, and that the value of each individual cubic centimeter shall be tested.

The sources of error connected with the process of weighing are next considered and, assuming, in general, an accuracy of one part in one thousand as attainable in analysis, it appears that the reduction of weighings in air to those *in vacuo* is not requisite, since the error is less than the fraction just named. Following this discussion a warning is sounded against the acceptance of reagents of "guaranteed" purity as reliable; the methods of testing reagents are also discussed, and Krauch's "*Die Prüfung der chemischen Reagentien auf Reinheit*" is severely criticised. The closing pages of this part of the volume are devoted to a consideration of the influence of temperature-changes upon the accuracy of volumetric work. It appears that, in general, decinormal solutions may be regarded as having a coefficient of expansion equal to that of water, but solutions of greater concentration require special tables of corrections; a few values for such solutions are given in this work. The author advocates the adoption of 20° C. as a standard temperature for calibration, rather than 15° C. as named in the Aichungs-Com-

mission's regulations, considering the higher temperature to be more convenient for laboratory use.[1]

Part II of the dissertation is devoted to methods of standardization employed in iodimetry. The conclusions arrived at may be summed up as follows: (1) That the standardization of a thiosulphate solution may be made accurate to one-tenth per cent.; (2) that the best of the bichromates, iodates, and bromates found in the market are very likely to be impure; and (3) that the presence of potassium bichromate promotes the oxidation of hydriodic acid by atmospheric oxygen and by interfering with the end-point introduces a possible error when the bichromate is used for standardizing purposes.

Part III presents the results of study of the reaction between potassium permanganate and hydrochloric acid, under the influence of certain substances exerting a catalytic influence. Dr. Wagner sums up his results as follows: (1) The decomposition of permanganate in iron titrations in the presence of hydrochloric acid is the result of the intermediate formation and oxidation of a ferrohydrochloric acid; (2) other salts, such as those of chromium, cadmium, as well as gold and platinum chlorides, cause the same decomposition; (3) platinohydrochloric acid was found to be oxidized more readily than hydrochloric acid; (4) by means of cryoscopic methods the existence and gradual formation of a cadmiohydrochloric acid was indicated; (5) the presence of barium chloride with ferrous salts, causes an essential increase in the decomposition of the permanganate, amounting even to forty-five per cent.; (6) in many chemical changes secondary reactions may take place, without, however, as in the case of real catalysis, increasing the speed of the primary reaction. The secondary reactions seem then to add their effect to that of the primary reaction. Dr. Wagner proposes the term "Pseudo-Katalysen" to indicate reactions of this character.

The dissertation is marked by a somewhat aggressive spirit of criticism, but it contains much which bears evidence of careful thought and labor, and is well worth perusal.

H. P. TALBOT.

[1] The regulations of the Normal-Aichungs-Commission have also been criticised by Professor L. L. de Koninck in an article entitled "Observations relatives aux conditions du contrôle des appareils de mesure en volume par la Commission d' étallonnage normal d'Allemagne," published in the *Bull. de l' Assoc. Belge des Chemistes, Dec., 1898.*