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VOLUMETRIC APPARATUS.[1]

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THERE have been various ideas as to what volumetric apparatus should represent, and the subject has been carefully studied in Europe for several years. Several reports have been made by German chemical societies and by committees of the international congresses of applied chemistry which have been held in Brussels and Paris during recent years. The Imperial Bureau of Weights and Measures of Germany has taken up the matter, and has minutely defined the conditions under which it works in testing apparatus submitted for that purpose. A report which I have not seen was submitted at the congress held recently in Vienna.

The various ideas as to what volumetric apparatus should represent may all be brought under the following three types: Apparatus of the first type contains the named volume at the specified temperature; of the second, contains such a volume of water at the specified temperature, that if (disregarding the container) the water were cooled down to 3.93° C., its volume would be the named volume; of the third, contains the same number of grams of pure water free from air when weighed in dry air at the specified temperature and 760 mm. pressure, as the number of cubic centimeters or grams marked upon them.

Table I shows the volume of water contained at the various specified temperatures by liter flasks of these three types, the

[1] Read at the Boston Meeting of the American Chemical Society, August, 1898.

TABLE I.

The Calculated Contents of Liter Flasks of Various Types.

In these calculations it is assumed that the density of the weights is 8.3, that the barometer stands at 760 mm., that the coefficient of cubical expansion of glass is 0.000025, and that 1000 cc. of pure water, free from air, weigh 1000 grams *in vacuo* at 3.93° C.

Type.	Specified temperatures. °C.	= °F.	Volumes contained at the specified temperatures.	Weight in air of water to fill flasks at the specified temperatures.	Volume contained at 22° C.	Weight in air of water contained at 22° C.
			Cc.	Grams.	Cc.	Grams.
I. Contain the named volume at the specified temperatures.............	3.93	39.074	1000.000	998.879	1000.452	997.197
	4.0	39.2	1000.000	998.879	1000.450	997.195
	15.0	59.0	1000.000	998.051	1000.175	996.921
	15.5	59.9	1000.000	997.978	1000.163	996.909
	15.555+	60.0	1000.000	997.967	1000.161	996.907
	16.666+	62.0	1000.000	997.790	1000.133	996.879
	17.5	63.5	1000.000	997.648	1000.113	996.858
	20.0	68.0	1000.000	997.173	1000.050	996.796
	22.0	71.6	1000.000	996.747	1000.000	996.747
II. Contain such a volume of water at the specified temperature that if the water (disregarding the container) were cooled down to 3.93° C. the volume of the water would be the named volume.	15.0	59.0	1000.872	998.921	1001.047	997.790
	15.555+	60.0	1000.958	998.923	1001.119	997.862
	22.0	71.6	1002.206	998.945	1002.206	998.945
III. Contain the same number of grams of pure water, free from air, when weighed at the specified temperature as the number of cubic centimeters or grams named upon them	3.93	39.074	1001.122	1000.000	1001.575	998.316
	4.0	39.2	1001.122	1000.000	1001.573	998.314
	15.0	59.0	1001.953	1000.000	1002.128	998.868
	15.5	59.9	1002.026	1000.000	1002.189	998.928
	15.555+	60.0	1002.037	1000.000	1002.199	998.938
	16.666+	62.0	1002.215	1000.000	1002.348	999.087
	17.5	63.5	1002.357	1000.000	1002.470	999.209
	20.0	68.0	1002.835	1000.000	1002.885	999.622
	22.0	71.6	1003.264	1000.000	1003.264	1000.000

weight of water which they would contain at the specified temperature, the volume which they would contain when at 22° C., and the weight which they would contain at 22° C. In this table appear temperatures that have never got much, if any, beyond being proposed. 3.93° C. is the temperature at which a liter of water is assumed to weigh a kilo, when weighed in a vacuum; 4° C. is the temperature commonly taken as that of the greatest density of water; 15° C. is probably the temperature most commonly used; 15.5° C. is used as an approximate equivalent of 60° F.; 15.555+° C. is the true 60° F.; 16.666+° C. equals 62° F., commonly used in England; 17.5° C. is the temperature proposed by Mohr originally; 20° C. is the temperature adopted by the Physikalish-Technische Reichsanstalt for polariscopic apparatus; and 22° C. is a temperature proposed and advocated by Oldberg before the U. S. Pharmaceutical Association but not adopted by them. Under the second type are inserted only the values for temperatures at which apparatus is actually for sale together with those for 22° C.

In discussing the merits of the different types No. II may be neglected, since it is only used to a limited extent, and the principle upon which it is based holds good only for water. The real contention is between types I and III, and it will be noted at 15° C., for instance, that the errors possible are very considerable if part of the apparatus used in an analysis is of one type and part of another. Suppose, for example, a solution is made up to one liter in a flask of the first type and then 100 cc. taken for a determination in a pipette of the third type. The result will be that an error of 1/500 of the whole amount will be introduced into the result. Other instances might be mentioned but this is certainly sufficient to show the necessity for agreement as to the type to be used. It should be stated also before leaving this point, that the German Bureau of Weights and Measures only receive, for testing, apparatus graduated for 15° C. and of type I and that the published opinions of those who have made a study of the subject are almost universally in favor of the same type.

In view of the above facts, Table II, showing the results of tests actually made upon a series of flasks representing at least five and possibly six German and American makers, is of interest. In the first column the flasks are numbered for convenience in reference; in the second are shown the labels; in the third the number of the type inferred from the label; in the fourth the volume or weight actually contained, provided the inference of the type from the label is correct; in the fifth the type inferred from the actual contents found by experiment; and in the last, the volume or weight contained, provided the second inference of the type is correct, appears.

TABLE II.

TESTS OF FLASKS FROM DIFFERENT MAKERS.

No.	Label on flasks.	Type inferred from label.	Volume or weight at marked temperature if type inferred from label is correct.	Type inferred from contents.	Volume or weight at marked temperature if type inferred from contents is correct.
1	500 ccm. E+ 15° C.	I	500.002 cc.	I	500.002 cc.
2	1000 Gr. 15° C.	III	1000.453 grams	III	1000.453 g'ms
3	1000 c.c. 60° F.	I	1002.149 cc.	III	1000.112 cc.
4	1000 c.c. 60° F.	I	1002.388 cc.	III	1000.350 cc.
5	1000 ccm. 15° C.	I	1002.309 cc.	III	1000.355 cc.
6	1000 cc 60° F.	I	1001.056 cc.	II	1000.098 cc.
7	1 liter 60° F.	I	1001.120 cc.	II	1000.162 cc.
8	1000 c.c. (No. temp.)	I	998.991 cc. (at 15° C.)	Unknown	
9	1000 c.c. 60° F.	I	1002.599 cc.	III	1000.561 cc.
10	1000 cc 15° C.	I	1000.017 cc.	I	1000.017 cc.

It will be seen that the labels on flasks 1, 2, and 10 are the only ones from which the type was correctly inferred, and that flask 2 showed a variation of over ± 0.3 of a gram from the supposed contents. This limit of variation, it should be mentioned, is the one adopted for liter flasks by the German Bureau of Weights and Measures, and can be easily attained in practice. Flask 8 may be called grossly inaccurate, as it is impossible to infer from the contents what type the manufacturer had in mind. No temperature for working is given upon it. The other six flasks are all wrongly or insufficiently marked for distinguishing the type to which they belong, and 4, 5, and 9 are not within the above-mentioned limits.

Aside from the type, the most important question to be settled would seem to be the temperature at which volumetric apparatus should be standard. It is assumed for the purposes of this discussion that every one prefers ware graduated according to type I or, in other words, containing the named volume, as distinguished from the weight, at the specified temperature. We may then proceed to discuss the various figures given under this type in Table I.

The volumes and weights at 22° C. given in the sixth and seventh columns of this table, are supposed to be the volumes and weights contained at the most commonly occurring temperature of the average laboratory. This temperature was selected for two reasons: First, Kilgore, by "a long series of experiments," found that the average temperature of his laboratory during the working day was 21.8° C.; and secondly, it is approximately the temperature which has been found most comfortable for people not doing manual labor and located in rooms having artificial ventilation.

From the volumes given in the sixth column it will be seen that the errors incident to using apparatus, standard at the temperatures given, when it is at the ordinary temperature of a room, may amount to from 0.45 cc. per liter with that standard at 3.93° C., to nothing with that standard at 22° C., and furthermore that the error in the case of apparatus standard at 15° C., would amount to nearly two-tenths cc. per liter. It may be claimed that it is perfectly possible to use flasks at 15° C. and that in other apparatus, since it is commonly used for volumes below 100 cc., the error would not be appreciable. This view might perhaps be accepted if the temperature never went above 22° C., but many of us, particularly in commercial laboratories, have been obliged to use burettes and pipettes at temperatures as high as 30° C., with the result that this error becomes appreciable, while if the apparatus were standard at 22° C., the error in using it at 29° C. would be the same that now obtains in using apparatus standard at 15° C. when at 22° C.

Considering the different temperatures individually, it is found that 3.93° C. is the temperature at which the brass gallons furnished the different states by the U. S. Government are standard, but that neither this temperature nor 4° C. is in general use. The temperatures 15.5° C. and 60° F. are gradually going out of use in this country. 62° F. is a temperature which has little or no foothold outside of England and certainly would be useless as a standard temperature in this country. 17.5° C., the temperature originally proposed by Mohr, appears to be gaining some favor in this country for a general temperature, although apparatus standard at that is not regularly on the market as far as the writer knows. 20° C. does not appear to be used except for polariscopic apparatus. 22° C. would seem to be the most natural temperature for use in this country if it were not for the confusion which would arise from other standards being used in other countries. But this confusion already exists and can hardly become worse by an attempt to crystallize chemical usage in this country at the most convenient temperature. It would seem that if confusion in regard to this point were such an obvious disadvantage, that a practical uniformity of usage would have already resulted by general consent. Looking at the question from a national rather than an international point of view, it is difficult to see the advantage of using any temperature below the average or the most common one of our laboratories; and surely there can be no reason, from this point of view, for discarding 15° for 17.5°, or any other temperature below 20° C. Any line of reasoning which led to the adoption of 15° C., or any other temperature above that of the greatest density of water, would seem to be still more favorable to 22° or a similar temperature.

In the writer's opinion, the most commonly occurring temperature represented by even centigrade degrees, rather than the average temperature of the laboratory, ought to be considered the best temperature for general use.

In order to secure uniformity and accuracy in using volumetric apparatus, there are three minor points which must certainly be taken into account. These are, the method of reading the meniscus, the rapidity with which delivery takes place in a burette or pipette, and the time allowed for draining in using apparatus graduated to deliver rather than to contain.

There seems to be a practical agreement in reading the extreme bottom of the meniscus, but in the times of delivery and of draining, anything but uniformity prevails. The German Bureau of Weights and Measures have a standard practice in regard to all three of these points, an account of which they have published, together with other regulations in regard to graduated ware tested by them. A translation by Mr. E. E. Ewell, of this article, is to be found in an appendix to the "Proceedings of the Fourteenth Annual Convention of the Association of Official Agricultural Chemists." The original reference is *Zeitschrift für angewandte Chemie*, 1893, pp. 557–559.

For the sake of showing the probable errors in checking graduated glassware, Table III, giving the results of ten determinations of the contents of the same liter flask, together with the probable error in any one observation, and the probable error in the mean, is introduced.

TABLE III.

DUPLICATE TESTS OF FLASK NO. 3.

Experiment No.	Contents in cubic centimeters at the specified temperature.
2	1002.108
8	1002.110
4	1002.118
9	1002.129
5	1002.133
7	1002.163
10	1002.164
3	1002.174
6	1002.183
1	1002.206

Probable error of any one observation ±0.0228.
Mean 1002.149
Probable error of Mean ±0.0072.

The method used in these determinations, as well as in those of Table II, was to weigh the flask, fill it with boiled distilled water, and allow it to remain near the balance-case until the temperatures of the air and water were within 1° C. of each other. Then water was removed until the proper reading was obtained and the flask introduced into the balance and weighed by the method of Gauss. On removing the flask from the balance-case, the reading was checked to show that no appreciable expansion of the water had taken place, and the temperature of the water noted. The dry and wet bulb thermometers, the barometer and its thermometer, were also read. From the data thus obtained the values given in Tables II and III were calculated.

The most important source of error in this work was found to be in taking the temperature of the water, for a variation of 0.1° C. made a difference in the final contents of the flask of approximately 0.02 cc. The thermometer used in the work was thoroughly tested and found to be correct within 0.1° C.

The variations in the buoyant effect of the air, due to variations in the barometer, were also taken into account, but it required a variation of fifteen mm. in the corrected reading to produce the same effect upon the weight of a liter of water that was produced by 0.1° in temperature. The barometer readings were not corrected for variation of the latitude from 45°, which, as the latitude was approximately 40°, would have introduced a correction of —0.35 for 760 mm.; or for elevation above the sea-level, which as it was only about twenty-five meters, would have introduced a correction of —0.004 mm. Corrections for tension of aqueous vapor and temperature were, however, introduced, the values given in "Smithsonian Meteorological Tables" for 1896 being used.

The coefficient of cubical expansion of glass was assumed to be 0.000025. The very improbable error of two in the second significant figure of this number, would amount to only 0.014 of a gram in the final weight of a liter of water under average conditions.

The density of the weights was assumed to be eight and three-tenths, and it was found that an error here of one-tenth would result in an error of approximately 0.0017 of a gram in the final weight of the water.

The buoyant effect of the air upon the weight of the flask was assumed to be a constant.

The table giving the density of water at various temperatures was furnished by the Office of Standard Weights and Measures, at Washington, and is the one used by them. The values are those determined by M. P. Chappuis and published by the International Bureau of Weights and Measures in "Proces-Verbaux des Seances" for 1892. The table giving the weight of a liter of air at various temperatures, was furnished by the same office. It was computed by Dr. O. J. Broch, from Regnault's observations, and published in Vol. I of "Travaux et Memoires du Bureau International des Poids et Mesures." It was found that by using different data for the densities of water and the weight of a liter of air or by using some of the published tables for obtaining the weight of a volume of water at different temperatures, an error of two-tenths of a gram might be introduced into the calculated weight of a liter.

The weights used had been compared with a standard set, originally tested and furnished with a table of corrections by the U. S. Office of Standard Weights and Measures, so that all weights were in terms of the International kilogram.

The balance was made especially for this kind of work, with large bows and pans. A variation of one division in the rest-point corresponded to six milligrams with a load of 1200 grams in each pan.

It remains for us to consider how the individual members of this society may advance the cause of uniformity in volumetric apparatus. There are two parties to be kept in mind, who look at this matter from entirely different points of view; namely, the manufacturer and the consumer. The manufacturer can be influenced only by the demands of his customers. If any considerable number of them ask for one thing, although he may decline the first few orders, the constant dropping will finally wear away the stone, and the article asked for will be added to his regular stock list.

Therefore, it must remain for us as individual customers, after committees, etc., have furnished the necessary information, to produce uniformity in the graduation and use of volumetric apparatus by instituting an overwhelming demand for the proper kind.

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THE ALKALINE REACTION OF SOME NATURAL SILICATES.[1]

BY F. W. CLARKE.

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THAT pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers brothers published a series of observations upon this subject,[2] and showed that some species of minerals would

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[2] *Am. J. Sci.* (2). 5, 401.