

Calibration of Volumetric Apparatus

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THIS paper describes a convenient method for calculating volumes of flasks, burets, pipets, pycnometers, etc., from the usual calibration data obtained with water as a reference standard. The method is sufficiently precise so that it can be used for calibrations of high accuracy; yet with suitable approximations it is readily adapted to all ordinary volumetric calibrations. The method has also been used with satisfactory results in presenting the theory of volumetric calibrations to students in elementary quantitative analysis. For this latter purpose it offers perhaps a somewhat more direct and logical means of making the necessary corrections and changes in units than the usual method, where calculations are based on tables in which the separate corrections and changes in units are combined, and where, therefore, the purpose and effect of each are concealed.

In the present method, the calculations are made in three steps: (1) the mass of water used in the calibration is calculated from the apparent weight by the application of a vacuum correction, (2) the volume at the temperature of filling the apparatus is calculated by multiplying the mass of the water by the absolute volume of one gram of water at this temperature, and (3) the volume of the apparatus at the desired temperature is then calculated from the volume at the temperature of filling.

For a calibration in which high accuracy is required, the mass of the water is calculated from its apparent weight by the formula:

$$M = W(1 + C) \quad (1)$$

where M and W are in grams, and C is the vacuum correction in grams per apparent gram, obtained from the following table, which was calculated with the relation

$$M = W[1 + D(V_m - V_w)]$$

rather than with the usual less precise approximation. It is assumed that the full and empty apparatus will have been weighed in air of the same density, as a matter of convenience, to simplify subsequent calculations, and that the density of the brass weights is 8.4 grams per milliliter. While this second assumption is the least precise link in the present method of calculation, it introduces an uncertainty of only about two parts per million if Class S brass weights are used. This uncertainty may, of course, be further reduced by the use of Class M weights of known volume.

VACUUM CORRECTION PER APPARENT GRAM FOR WATER

Temp., °C.	0.001220	0.001200	0.001180	0.001160	0.001140	0.001120
15	0.001077	0.001060	0.001042	0.001024	0.001007	0.000989
20	0.001078	0.001061	0.001043	0.001025	0.001008	0.000990
25	0.001080	0.001062	0.001044	0.001027	0.001009	0.000991
30	0.001081	0.001063	0.001045	0.001028	0.001010	0.000992
35	0.001083	0.001066	0.001048	0.001030	0.001012	0.000995

The temperature in the above table is that of the water during the weighing, and the air density, D , is calculated from the relation:

$$D = \frac{0.001293}{1 + 0.00367T} \cdot \frac{B - 0.00375HP}{760.0}$$

where D is given in grams per milliliter; T is the temperature of the air in the balance case, in degrees Centigrade, measured to the nearest tenth of a degree; B is the barometric pressure in millimeters of mercury, reduced to 0°C.; H is the relative humidity, determined with a good hygrometer or sling psychrometer;¹ and P is the vapor pressure of water at T° , in millimeters of mercury at 0°C., taken from the following table. Since D is a linear function of $B - 0.00375HP$ when T is constant, it is convenient to plot D against assumed values for this "corrected pressure," obtaining the parallel isotherms for 0.5° intervals; D may then be read quickly from the graph after a slide rule calculation of the corrected pressure.²

VAPOR PRESSURE OF WATER

Temp., °C.	P , Mm. Hg	Temp., °C.	P , Mm. Hg	Temp., °C.	P , Mm. Hg
15	12.8	22	19.8	29	30.0
16	13.6	23	21.1	30	31.8
17	14.5	24	22.4	31	33.7
18	15.5	25	23.8	32	35.7
19	16.5	26	25.2	33	37.7
20	17.5	27	26.7	34	39.9
21	18.7	28	28.3	35	42.2

It is evident that for all calibrations in which water is used as a reference standard at ordinary air densities the formula:

$$M = 1.00104W \quad (1a)$$

is a good approximation.

V , the volume of the apparatus in milliliters, is calculated from the mass of water by the formula:

$$V = M \cdot 1/D \quad (2)$$

where $1/D$, the reciprocal of the absolute density of water in milliliters per gram, is taken from the following table. The temperature is that of the water at the time of filling the apparatus, in degrees Centigrade.

VOLUME OF ONE GRAM OF WATER

Temp., °C.	1/D	Temp., °C.	1/D	Temp., °C.	1/D
15	1.000874	22	1.002206	29	1.004043
16	1.001031	23	1.002439	30	1.004343
17	1.001199	24	1.002682	31	1.004652
18	1.001379	25	1.002935	32	1.004970
19	1.001569	26	1.003197	33	1.005297
20	1.001771	27	1.003470	34	1.005632
21	1.001983	28	1.003752	35	1.005976

¹ MARVIN, "Psychrometric tables," Weather Bureau No. 235, 4th ed., Government Printing Office, Washington, 1915, 87 pp.

² WEATHERILL AND BRUNDAGE, "A revision of the atomic weight of silicon. The ratio $\text{SiCl}_4:\text{SiO}_2$," *J. Am. Chem. Soc.*, **54**, 3935 (Oct., 1932).

Once the volume at the temperature of calibration has been found, the volume at any desired temperature is calculated from:

$$V' = V[1 + K(T' - T)] \quad (3)$$

where V' is the volume at T' °C. and V the volume at T °C. For soda glass apparatus K has the value 0.000025; for pyrex, 0.0000096.

For most calibrations, calculations with the above

formulas and tables can be greatly simplified by mathematical approximations in which addition is substituted for multiplication. For example, the volume of a flask holding an apparent weight of 996.18 grams of water at 25°C. is: $996.18 + 1.04 + 2.94 = 1000.16$ ml. The value found by multiplication is 1000.15 ml.

Values used in making up the above tables were calculated or taken directly from data given in the International Critical Tables.
