

2. From the measurements of cells of Type I, the activity coefficients of potassium, sodium and lithium sulfates have been calculated. These results have been considered from the point of view of the Debye and Hückel theory, as well as the results of Randall and Cushman on pure sulfuric acid.

3. From measurements of cells of Type II, the activity coefficients of sulfuric acid in potassium, sodium and lithium sulfate solutions have been calculated.

4. From measurements of cells of Type III, the activity coefficients of potassium and sodium hydroxides in their corresponding sulfate solutions have been calculated.

5. The activity coefficients of sulfuric acid in the uni-bivalent sulfate solutions and of the hydroxides in the corresponding sulfate solutions have been calculated by approximation equations, similar to those resulting from the theory of Debye and Hückel.

6. The ion activity-coefficient of water in the salt solutions has been computed from the results of these three cells. This quantity was found to be greater in potassium than in sodium sulfate solution at a given concentration, a fact in agreement with the behavior of potassium and sodium chloride solutions.

7. From these results, it appears that the square root of the ionic concentration product of water, $\sqrt{c_{\text{H}^+}c_{\text{OH}^-}}$, is rapidly increased by the first addition of the sulfates, and that sodium sulfate causes a somewhat greater increase in this quantity than potassium sulfate. In the sodium sulfate solutions, $\sqrt{c_{\text{H}^+}c_{\text{OH}^-}}$ reaches a maximum at 1.5 *M* and then decreases somewhat with increasing salt concentration.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A MODIFIED TYPE OF GAS VOLUME-METER FOR THE DETERMINATION OF THE DENSITIES OF SOLIDS

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RECEIVED DECEMBER 29, 1925

PUBLISHED MAY 5, 1926

Determination of the densities of solids by a method of gas displacement serves to eliminate the error due to exclusion of liquid from porous material and also avoids contamination of the sample. Density determinations have been made by computing the volume from the weight of air displaced by the sample.¹ As early as 1879 instruments were described by means of which the volumes of solids were determined by measuring the volume change with changing pressure of the residual air in a chamber in which the solid was confined.² Highly refined instruments of this type have been

¹ Baxter and Hilton, *THIS JOURNAL*, **45**, 700 (1923).

² Rüdorff, *Ber.*, **12**, 249 (1879).

described by Zender³ and by Washburn and Bunting.⁴ These writers have also developed completely the theory of instruments operating on this principle. The instrument described here is a simple modification of the above type which can be operated with an accuracy of 0.5% on metallic powders and organic solids using samples of from 0.1 to 0.5 g.

The arrangement of the instrument is illustrated in Fig. 1. The essential parts of the instrument are the two vessels, X (which extends from the graduation mark M_2 to the stopcock S_1) and Y, which is that portion which lies between the graduation marks M_1 and M_2 . C_1 is a 2mm. capillary tube 170 cm. in length and C_2 is an 8mm. tube of similar length. R is a mercury reservoir holding about 25 cc. S_2 is a 3-way stopcock by means of which mercury may be admitted from R and C_2 to C_1 and Y, or may be withdrawn from C_1 and Y through T. S_1 is a stopcock of 5mm. bore and B is a thin glass bottle of convenient size to pass through S_1 .

Making the Determination

To make the determination the weighed bottle B is placed in the instrument as in the illustration and with S_1 open, mercury is admitted until the level reaches M_1 . S_1 is then closed and mercury is admitted until the level reaches M_2 . The difference in levels is then read on C_1 . The pressure is released by drawing off the mercury and B is removed from X by means of a small wire hook. The sample is then placed in B and weighed, B is again placed in the instrument and the adjustment of the mercury levels is made as before. The readings are now reduced to a standard reading by a simple multiplication, R (corrected) = R (observed) $\times P$ (reference)/ P (barometer). P (reference) is the barometric reading at the time when the observations were made for the construction of the graph. The volume of the bottle and of the bottle and contents are then read directly from a graph which has previously been constructed and from the data so secured the density of the weighed sample may be determined.

Calibration of the Instrument

The calibration of the instrument consists in determining the volumes of X and Y. This may be calculated from three observations: (1) P_1 , the pressure required to bring the level of the mercury from M_1 to M_2

³ Zender, *Ann. Physik*, 10, 40 (1903); 15, 328 (1924).

⁴ Washburn and Bunting, *J. Am. Ceramic Soc.*, 5, 112, 527 (1922).

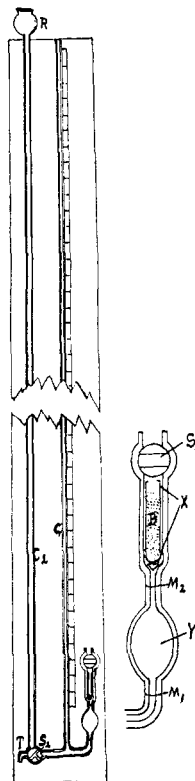


Fig. 1.—A modified type of gas volume-meter for the determination of the density of solids.

when X is empty; (2) P_2 , the pressure required when X contains bottle B of unknown volume; (3) P_3 , the pressure required when X contains bottle B and a known volume of mercury V_1 .

Let T = the volume of $X + Y - B$; R = the volume of $X - B$; P_r = the barometric pressure at the time of the observations. We may now form three equations.

$$P_r (T - V_1) = (P_r + P_3) (R - V_1) \quad (1)$$

$$P_r T = (P_r + P_2) R \quad (2)$$

$$P_r (T + B) = (P_r + P_1) (R + B) \quad (3)$$

Solve for B , R and T from which X and Y may be computed. The graph may now be constructed on which the volume of an object is plotted against the pressure required to bring the mercury level from M_1 to M_2 when the object is placed in X. The curve takes the form of the equation, $P = [P_r(X + Y) - P_r V] / (X - V)$, where V is the volume of the sample that is placed in X.

In the instrument in which the following determinations were made, $X = 0.9570$ cc. and $Y = 1.2509$ cc. A sample having a volume of 0.1 cc. gave a difference of mercury level of about 150 mm. The readings could be reproduced to 0.3 mm. without difficulty.

TABLE I
DETERMINATIONS ON MERCURY

Wt., g.	Diff. in level	Vol., cc.	Density	Error
1.6918	199.6	0.1427	13.56	+0.22%
2.4995	269.2	.1613	13.49	- .30%

The ratio between the significant reading and the volume of the sample is governed by the ratio of the volumes of X and Y. If Y is large when compared with X the difference in level will be correspondingly large. The significant reading will also increase as the residual air space in X is cut down, that is, as the bottle and sample are made to fill X as completely as possible.

This type of instrument cannot be used for substances which will adsorb air under the conditions of the experiment. The vapor pressure of the substance under investigation may also introduce an error. This will amount to less than 0.1 mm. in mercury level at 30° for substances boiling above 250°.

Summary

A modified gas volume-meter is described by means of which the density of powders and crystals may be determined with an accuracy of 99.5% using samples less than 0.2 cc. in volume.

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