A Helium Densitometer for Use with Powdered Materials

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An apparatus employing air as the pycnometer fluid instead of a liquid in the determination of the density of solids was described as early as 1797.[2] The method involves measuring the change in pressure required to increase or decrease a given volume of gas by a known amount and repeating the measurement when a portion of the gas volume is occupied by a known weight of the powdered solid. Numerous modifications of the apparatus with varying degrees of refinement have since appeared.[3,4,5]

However, the adsorption of air by many finely divided solids imposes a serious limitation upon the usefulness of this method. To remove this limitation, the use of helium as the pycnometer fluid has been proposed[4] and since then a number of instruments employing helium have been described.[6,7,8,9]

The simpler forms of densitometers[6,8] measure directly the volume of the pycnometer minus the sample volume by allowing helium at constant temperature and pressure to expand into the evacuated pycnometer. The more complicated ones[7,9] were originally intended for studies on adsorption of gases and require the measurement of pressure, volume and temperature both before and after the admission of helium to the pycnometer. All of the instruments, as described in the literature, employ pycnometers of large volume and have provisions for thermostating part or all of the apparatus. (We see no objection in the apparatus of Howard and Hulett,[6] however, to the employment of a much smaller pycnometer volume than the 40-ml. bulb employed by the authors.)

We have modified the apparatus of Karns[5] in several important respects, in order to permit the use of helium as the pycnometer fluid and to increase the accuracy of measurement over that claimed by him. The advantages that measurements can be conducted on small samples and that elaborate thermostatic baths are not essential have been retained.

A diagram of the apparatus is shown in Fig. 1. The sample is placed in the small, one-ml.,[10] flask-like container, of which an enlarged view is also given in the figure. The neck of this container is ground for about one cm. of its length to fit the inner part of a slightly tapering ground glass joint, fashioned from one-mm. capillary tubing. The manometer is also constructed of one-mm. capillary tubing, matched for size and uniformity of bore, and of 7-mm. o. d. tubing, the volume between marks M and N being made approximately equal to the volume of the sample container. The glassware to the right of C and also stopcocks A and B provide for the careful evacuation of the powder and introduction of helium prior to performing the compression.[11] Helium gas, obtained from a tank and purified by slow passage through activated charcoal cooled to the temperature of liquid air, is stored in the large bulb at a pressure somewhat above atmospheric. All stopcocks subject to internal pressures greater than one atm., particularly A and C, are provided with brass clamps not shown in the main diagram. Pressure is applied to the enclosed system by means of the levelling bulb and mercury reservoirs J and K. The raising of the levelling bulb is accomplished by the cord which passes over the pulley and is wound on the small reel, rotation of which is closely controlled by the large gear-and-ratchet device. Pressures are read by means of the maple meter stick, two meters in length, engine-divided in mm.

Theory and Method of Calculation.—The equations for calculating the unknown volume of the powdered sample can be simply derived using Boyle's law.

(1) A. D. Little Post-Doctorate Fellow in Chemistry, Massachusetts Institute of Technology, 1941–1942.

(2) Say, *Ann. chim.*, 1, 23 (1797).

(3) Regnault, *Ann. chim.*, 3, 14, 207 (1845); Rüdorff, *Ber.*, 12, 249 (1879); Teleney and McKeehan, *Phys. Rev.*, 30, 189 (1910); Oberbeck, *Wied. Annalen*, 67, 209 (1899); Carman, *Phys. Rev.*, 26, 396 (1908); Zehnder, *Ann. Physik*, 10, 40 (1903); 15, 328 (1904); Surdo, *Science Abstracts*, A10, 2 (1907).

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

(5) Karns, THIS JOURNAL, 48, 1176 (1926).

(6) Howard and Hulett, *J. Phys. Chem.*, 28, 1082 (1924).

(7) Davidson, *J. Textile Inst.*, 18, T175 (1927).

(8) Stamm, *J. Phys. Chem.*, 33, 398 (1929).

(9) Smith and Howard, *Ind. Eng. Chem.*, 34, 43 (1942).

(10) This volume could be reduced to permit working with much smaller amounts of sample, but the accuracy obtainable would probably be somewhat impaired as a result.

(11) All of the stopcocks shown in the figure are not absolutely necessary; F and H could be eliminated, if desired.

Let V_1 = volume included between marks M and N,
$\quad V_2$ = volume included between mark N, stopcock C, and the sample container,
$\quad V_3$ = volume of the sample,
$\quad P_1$ = initial pressure in system (atmospheric pressure),
$\quad P_2$ = final pressure in V_2 when compression is carried out with V_2 empty,
$\quad P_3$ = final pressure in V_2 when compression is carried out with the sample in V_2
$\quad H_2$ = height of mercury corresponding to pressure P_2 (i. e., $H_2 = P_2 - P_1$),
$\quad H_3$ = height of mercury corresponding to pressure P_3 (i. e., $H_3 = P_3 - P_1$)

Then, applying Boyle's law

$$\frac{P_1}{P_2} = \frac{V_2}{V_1 + V_2} \tag{1}$$

and

$$\frac{P_1}{P_3} = \frac{V_2 - V_3}{V_1 + V_2 - V_3} \tag{2}$$

Solving these equations simultaneously, eliminating V_1

$$V_3 = V_2 \left(\frac{(P_3 - P_1) - (P_2 - P_1)}{(P_3 - P_1)} \right) \tag{3}$$

or

$$V_3 = V_2 \left(\frac{H_3 - H_2}{H_3} \right) \tag{4}$$

V_2 is a constant of the apparatus which can be determined by measuring H_3 and H_2 when a sample of known volume is employed. A weighed quantity of mercury at a known temperature constitutes a suitable calibration standard. H_2 need be accurately determined but once. If equation (1) is solved for $P_2 - P_1$, it is found that

$$P_2 - P_1 = H_2 = \frac{(V_1)}{(V_2)} P_1 = \text{(constant)} \, P_1 \tag{5}$$

Hence if the barometer is read when H_2 is determined and when all subsequent determinations of H_3 are made, the value of H_2 corresponding to any value of P_1 readily can be calculated. In an actual density determination, therefore, all that need be measured are H_3 and the weight of the sample.

To calculate the density of the sample the barometric pressure and H readings are corrected to $0°$.[12]

Letting P_A = barometric pressure when H_3 was obtained and P_B = barometric pressure when H_2 was obtained, H_2 can be corrected to the value it would be at P_A by use of equation (5) in the form

$$H_2 \, (\text{at } P_A) = \frac{[H_2 \, (\text{at } P_B)][P_A]}{[P_B]} \tag{6}$$

Then V_3 can be calculated from equation (4), and

(12) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926, Vol. I, p. 68.

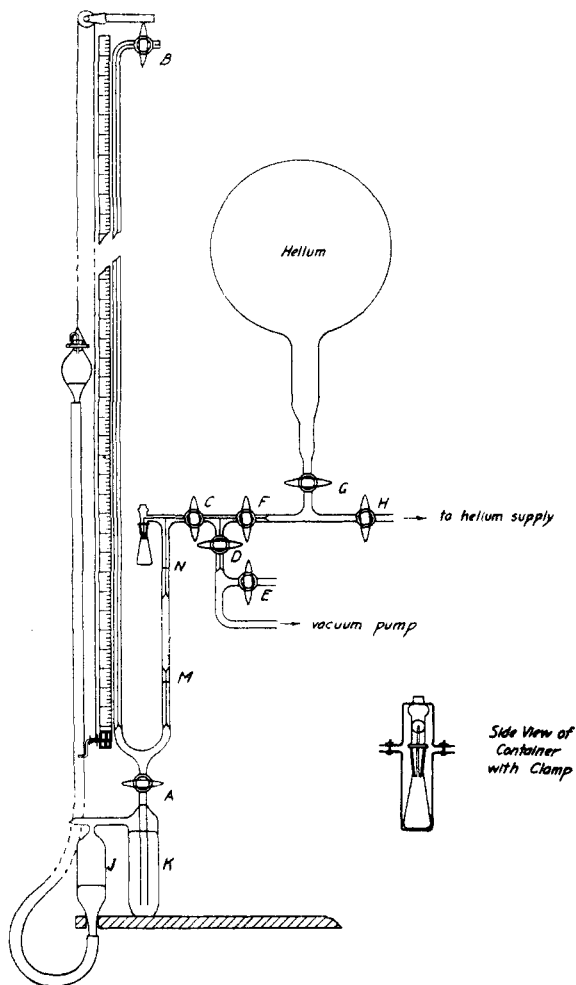finally the density is obtained as the quotient of the known weight of sample and V_3.

Fig. 1.

Experimental Procedure

The pycnometer is filled as completely as possible with a weighed quantity of sample, the inner end of the ground joint lightly greased along the upper portion of the ground surface, and the pycnometer clamped on. With the level of mercury from reservoir K just above A (A and B closed) the sample and manometer are evacuated (at an initially slow rate by proper manipulation of C, D, and F) by means of a mechanical oil pump and then helium is admitted into the manometer from the reservoir. B is then slowly opened and the mercury level raised to mark M, the slight excess pressure being relieved by means of C, D, and E. With C closed, the mercury level is raised to N and the height of mercury in the long arm is read on the meter stick. This height minus the height

TABLE 1

DENSITIES OF POWDERED SUBSTANCES[a]

Substance	Density[b] measured, g./cc.	Temp., °C.	Precision of measurement, %	Density from literature[13] (sp. gr. 20°/4° except where noted)		Difference between measured and literature values, %	Notes
CaCO₃ (calcite)	2.713	29.5	0.1	2.711	25.2°/4°	+0.07	Total of 4 detns. on 2 samples of Iceland spar —primary standard
AgNO₃	4.347	27.5	.1	4.352	19°/4°	— .12	C. P. sample
KCl	1.984	28.5	.1	1.988		— .20	C. P. sample
Hg₂Cl₂	7.134	29.95	.15	7.150		— .22	C. P. sample[c]
KHC₈H₄O₄	1.634	27.5	.1	1.636		— .12	Primary standard
As₂O₃ (monoclinic)	4.152	27.5	.2	4.15		.1	C. P. As₂O₃ recrystallized and converted
ZnO (hexagonal)	5.590	27.3	1.0	5.606		— .29	C. P. sample, pumped for two hours

[a] Slight differences between measured and recorded values might possibly be attributed to the different temperatures at which the densities were determined and also to errors in some of the recorded values of the same order of magnitude as the differences. [b] Results are for two determinations except where noted. [c] Particle size determination microscopically performed on sample. Largest particles were a few hundredths of a mm. in diameter; smallest visible under a magnification of 200X were about 0.001 mm. in diameter.

corresponding to N constitutes H_3. In addition the barometric pressure and the average temperature of the long mercury column are determined.

Discussion of Errors.—Errors in the measurements can arise from the following causes:

(1) variations in setting the mercury column on the marks;

(2) sticking of mercury in the capillary tubing;

(3) changes in temperature of the surroundings during a determination;

(4) changes in barometric pressure during a determination;

(5) variance in the volume of V_2 from one experiment to another

    (a) in accordance with the amount of stopcock grease employed,

    (b) resulting from assembly of the ground joint,

    (c) arising from differential expansion of the flask depending upon the pressure employed;

(6) deviation from the perfect gas law;

(7) changes in temperature of the helium owing to the heat of compression;

(8) adsorption of helium by the sample;

(9) condensation of vapor of sample.

The errors which most greatly affect the precision of measurement are (1) and (2). From four determinations of H_3 (or H_2) the average deviation from the mean has been found to be of the order of ±0.3 mm. of mercury; from two determinations, ±0.5 mm. An inaccuracy of 0.5 mm. in the value of $H_3 - H_2$ can constitute as small an error as 0.1%, when $H_3 - H_2$ is about 500 mm. Such a value of $H_3 - H_2$ is easily attainable when

(13) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926, Vol. 1, p. 100.

the ratio of bulk to true density of the powder is favorable, owing to the completeness with which the free volume of V_2 can be filled with sample. The percentage error in H_3 causes a somewhat lower percentage error in V_3, as the former is partially compensated by an error in the same sense in $H_3 - H_2$. However, a small error in H_2 can give rise to a large percentage error in $H_3 - H_2$ when the latter is small. This can be checked by calibrating the apparatus with increasing amounts of mercury. The calculated value of V_2 will vary systematically with V_3 (of mercury) if there is a small constant error in H_2.

Errors due to (3) and (4) are very infrequent as the time required to compress the gas and to read the pressure is so short. Errors resulting from (5), (6), and (7) have been found to be negligible. Errors (8) and (9) are inherent in the sample and are inappreciable for all substances that do not adsorb helium appreciably at room temperature and at pressures up to about three atmospheres, and the vapor pressures of which are less than about 0.5 mm. These conditions are met by a large majority of solid substances. Whenever there is doubt concerning the absence of helium adsorption, it is recommended that measurements be made at different pressures (by varying the sample volume).

Experimental Results

Representative data obtained by means of the helium densitometer are given in Table I, wherein they are compared with density data taken from the literature. The data indicate that the den-

sities of finely powdered substances can be determined with an accuracy which in general agrees with the precision of measurement and is of the order of ±0.1% in cases of favorable ratios of bulk to true density (about 0.5).

The elimination of the air adsorption error by the use of helium is well illustrated by the case of zinc oxide. As is seen in the table, when compression was carried out in helium, the measured density differed from the literature value by −0.29%, but when the determination was carried out in air, the divergence was found to be +15%,

even when the sample had been first evacuated and then dry air admitted.

Summary

1. A modification of the Karns densitometer for solid materials has been described, which is applicable to fine powders which do not appreciably adsorb helium and do not possess appreciable vapor pressures at room temperature.

2. The method is accurate to ±0.1% using samples of about 0.5-cc. volume and a ratio of bulk to true density of about 0.5.

The Solubility of Potassium Iodide in Potassium Hydroxide Solutions at 20°

BY H. DARWIN KIRSCHMAN AND RICHARD POMEROY

During the course of work at this Laboratory it became desirable to determine the solubility of potassium iodide in solutions of potassium hydroxide from 0 to 14.35 N. To facilitate the use of these data, density determinations were later made at a number of concentrations.

Brönsted[1] gives the results of seven determina-

tions at concentrations of potassium hydroxide from 9.41 to 15.02 N. His results differ from ours by 10–20%. The complete absence of experimental procedures in his report makes it difficult to suggest the cause of this variation.

The results of our measurements are presented in Table I and Fig. 1.

TABLE I

Solubility Data at 20°		Density Data at 20°	
KOH[a] moles/liter	KI moles/liter	KOH[a] moles/liter	Density g./ml.
14.35	0.556	14.35	1.593
13.28	.651	13.28	1.576
12.51	.759	12.04	1.555
11.05	.981	11.11	1.539
10.53	1.107	10.01	1.529
8.814	1.541	9.010	1.524
8.161	1.733		
7.050	2.171	7.767	1.525
6.624	2.292	6.810	1.531
6.453	2.369[b]	6.524	1.533
5.853	2.634		
5.816	2.650	5.002	1.553
4.753	3.145		
4.111	3.485		
4.000	3.525	3.642	1.582
2.405	4.454	2.480	1.613
1.860	4.818		
1.358	5.132	1.386	1.653
0.783	5.539	0.1235	1.703
.000	6.089		
.000	6.109[c]	0.000	1.716[c]

[a] Including about 1% of potassium carbonate as equivalent potassium hydroxide.   [b] 0.40 N in added carbonates.   [c] From Seidell, "Solubilities of Inorganic Compounds," Third edition, Vol. I, p. 812.

(1) Brönsted, THIS JOURNAL, **42**, 1448 (1920).
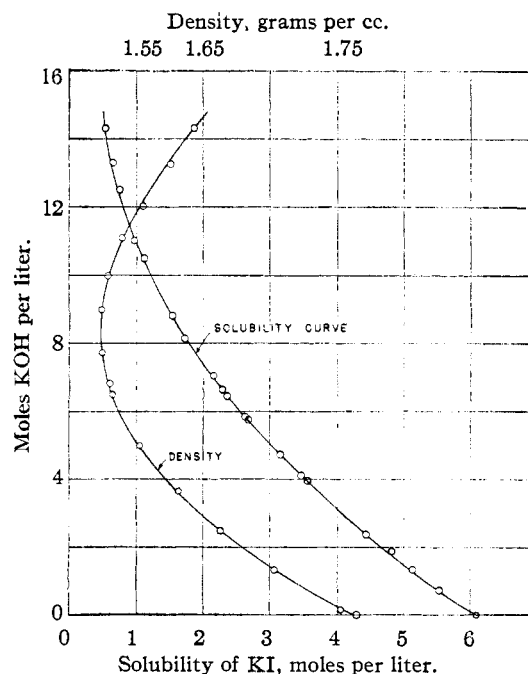
Density, grams per cc.

Fig. 1.

Experimental

In general, a saturated solution of potassium iodide in distilled water was added to a warm solu-