

# DENSITY DETERMINATIONS: ACCURACY AND APPLICATION TO SPHALERITE STOICHIOMETRY<sup>1</sup>

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## ABSTRACT

A hydrostatic method of determining density has been developed which attains a precision of 0.06 percent and an accuracy of about 0.1 percent (within 2 standard deviations) for 90 to 120-mg samples having a density of 4.0 g cm<sup>-3</sup>. This method uses a Cahn RG electrobalance and practical-grade hexachloro-1, 3-butadiene ( $\rho = 1.67076$  g cm<sup>-3</sup> at 25°C).

Sulfides frequently exhibit variations in stoichiometry that may be quantitatively examined by precise density determinations. Application of density determinations to a study of the stoichiometry in synthetic, polycrystalline, iron-bearing sphalerites, shows that, if Fe<sup>3+</sup> occurs in interstitial sites, as has been suggested, then it must represent less than 1 percent of the amount of Fe present.

## INTRODUCTION

An accurate density determination of a crystalline solid, when compared to its theoretical density, can be used to assess the degree of stoichiometry of the solid. The density,  $\rho$ , in g cm<sup>-3</sup> is calculated from the well-known formula:

$$\rho = \frac{1.66042 \times Z \times \text{Formula Weight}}{\text{Volume in } \text{\AA}^3},$$

where 1.66042 is derived from Avogadro's Number ( $6.02257 \times 10^{23}$  (g mol)<sup>-1</sup>, according to the 45th Edition of the Handbook of Chemistry and Physics), and  $Z$  is the number of formula weights per unit cell.

The methods and problems of density determinations are well outlined by Muller (1967) and by Richards and Berger (1962); Smakula and Sils (1955) present an excellent report of what is involved when extreme accuracy is required.

The procedure described here was developed with the objective of devising a suitable hydrostatic method for the measurement of the density of polycrystalline and friable samples of about 100 mg weight, frequently obtained in the pyrosynthesis of sulfides—a method that would give a fairly high degree of accuracy, but not require an extremely complicated procedure. The method has been applied specifically to the density determination of synthetic, iron-bearing sphalerites.

## MATERIALS

The literature on density determinations does not report the use of a suitable hydrophobic heavy liquid. The popular use of carbon tetra-

<sup>1</sup> Sulfide research contribution no. 11, Mineral Sciences Division.

chloride should not be continued, since, in addition to its toxicity, this liquid suffers from photochemical reactions. Many of the other well-known heavy liquids, such as bromobenzene, methyl iodide, bromoform and methylene iodide, have one or more drawbacks such as extreme toxicity, low purity, high surface tension and instability. The liquid selected, hexachloro-1, 3-butadiene, has a density similar to that of carbon tetrachloride but also has other desirable features, including low surface tension, high stability, relative nontoxicity, and low vapor pressure at room temperature. It is also insoluble in water but soluble in many organic solvents. Hooker Chemical Co. of Niagara Falls, N. Y., one of the manufacturers of this liquid, gives the following data for their practical grade, 98 percent minimum purity material:

Boiling range:	210–220°C
Refractive index, $n_{20/D}$ :	$1.552 \pm 0.001$
Flash point:	None
S.G. $\left\{ \begin{array}{c} 15.5^\circ\text{C} \\ \hline 15.5^\circ\text{C} \end{array} \right\}$ :	$1.675 \pm 0.025$
Density correction factor (35° to 100°C) per °C:	$0.00149 \text{ g cm}^{-3}$
Vapor pressure at 40°C:	1.5 mm Hg
Surface tension at 25°C:	$34.7 \text{ dyne cm}^{-1}$

Silicon was used to derive the density of the liquid. The silicon was cut from a large single crystal of electronic-grade material having a resistivity<sup>1</sup> of about  $1\frac{1}{2}$  ohm cm., which indicates a maximum impurity level of about six parts in  $10^8$ .

The iron-bearing sphalerites were synthesized from high-purity elements by a method reported elsewhere (Keys, *et al.*, 1968). They were homogeneous, polycrystalline lumps (3 to 10 per sample), weighing a total of 90–120 mg per sample. Compositions were determined by electron-probe microanalysis.

#### METHOD OF DENSITY DETERMINATION

A Cahn RG electrobalance (max. load 1.0 g) was modified for the density determinations (see Fig. 1). When loop A is used for weighing, the balance has a rated sensitivity of  $1 \times 10^{-7}$  g and a rated precision of  $2 \times 10^{-7}$  g. The weight changes were indicated on an integrated, digital voltmeter, reading to one microgram. Both a semimicro balance (sensitivity 0.01 mg) and a torsion balance were also tried, but were found to give insufficiently good reproducibility.

A constant flow of dry air was fed through the central part of the balance and vented around the metal cap near loop A. The air was bled from a compressed air cylinder at the rate of 2.2 cu ft/hour, circulated through a 50-ft-copper pipe immersed in a water bath, and then dried before entry into the balance. When weighing in liquid, a normally closed,

<sup>1</sup> Resistivity determined by T. M. Baleshta, Mineral Sciences Division, Mines Branch.

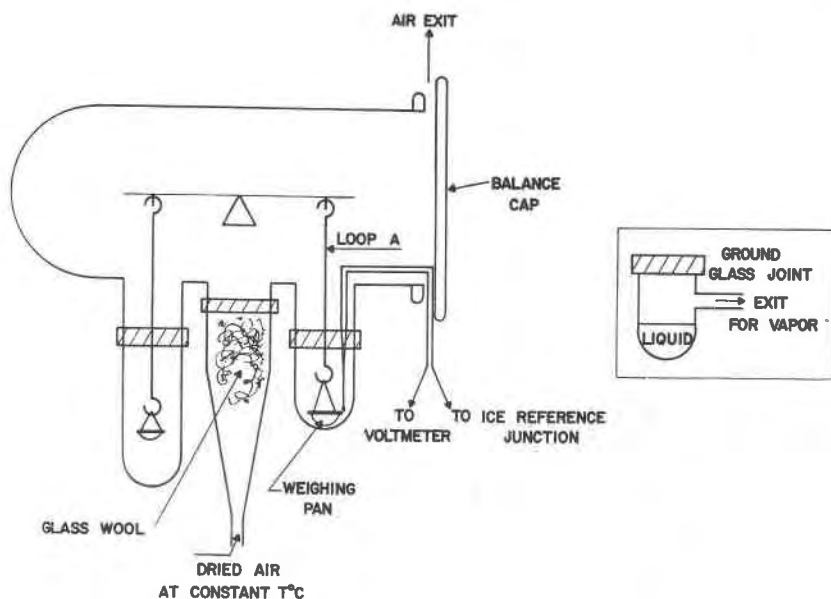


Fig. 1. Schematic representation of the experimental set-up for the Cahn electrobalance, with the weighing pan in place (see text for details).

ground-glass joint was modified by attaching an exit tube above the liquid level, so that any vapor coming off the liquid was forced out by the constant air flow (see insert, Fig. 1). The balance was calibrated five times during the course of the weighing by using 20-, 50-, and 100-mg weights (Ainsworth, Class M). A straight line was fitted to the calibration data by least squares in which the values of the weights were considered to be correct and the readings were considered to be subject to error. All samples, weights and pans, etc., when not in the balance, were kept in a desiccator containing Drierite.

A copper-constantan thermocouple was suspended in the balance so that it sensed the temperature at the level of the sample basket when immersed in liquid. This thermocouple was checked against a previously-calibrated mercury thermometer (0.1°C subdivisions and an accuracy of 0.1°C) and found to read to within 0.2°C at 22°C. The temperature in the balance never went beyond the limits of 22.5°C and 24°C, and most readings were taken around 23.3°C.

The density of the liquid was always corrected for temperature according to the relation  $0.00149 \text{ g cm}^{-3} \text{ per } ^\circ\text{C}$ . The thermal expansion of the sphalerite over the 2.5°C maximum temperature-range is insignificant for the determinations, since calculations using Skinner's (1962) values of cell edge *versus* temperature gave a change in density of only  $3 \times 10^{-6} \text{ g cm}^{-3} \text{ } ^\circ\text{C}^{-1}$  for the sample with the least iron.

The sample weight was always obtained by difference. A 250-mesh ( $\sim 60 \mu\text{m}$ ) stainless steel (18-8) wire basket was used as sample container. The basket was first weighed empty and then weighed with the sample in air. The basket-plus-sample was then immersed in a  $10 \text{ cm}^3$  beaker containing the liquid, and subjected to vacuum for 3 minutes to outgas. The wet basket-plus-sample was then transferred to another beaker, containing fresh liquid, and left to stabilize for 10 to 30 minutes.

A 130- $\mu$ m-diameter steel wire with a hook at the end substituted for the weighing pan on a loop A, and the wet basket-plus-sample was hung on the hook. The modified ground-glass joint with liquid (a constant volume of liquid was obtained by using a buret) was then very gently attached, thereby immersing the sample. After the readings in liquid had been taken, the basket was removed, the sample dumped out, and the empty basket was weighed in the liquid. The time and temperature were recorded with each weighing. After weighing the empty basket in liquid, the basket was thoroughly cleaned in acetone, and dried. The thermocouple wire was cleaned similarly, but *in situ*, and the hooked wire replaced by the weighing pan. The sample was given a more vigorous cleaning by placing it for 30 seconds in acetone, dried, and then returned to the desiccator for equilibrium with a dry-air atmosphere in readiness for subsequent density determinations. All samples were measured at least three times.

Difficulties were experienced in judging the equilibrium period for the balance when a sample or basket was added or removed. The criterion used was a return to the same, or very nearly the same, reading for the empty pan or the empty basket (usually within 5  $\mu$ g). This could not always be relied on, as there was some drift of the zero point during the course of a day, or suddenly after a steady period of 2 or 3 days. The air flow was never interrupted, and a 220-cu-ft cylinder lasted about 100 hours. In practice, weighings in air were allowed to equilibrate from 5 to 35 minutes. The ground-glass joints were handled with cotton gloves and entire on-and-off change was done as rapidly as possible—usually within 60 seconds. A different approach was used when weighing in the liquid, since convection currents in the liquid, and a damping effect, caused a slow oscillation of the hangdown wire. The first reading was taken after 5 minutes, and the next was taken when a high or low reading was reached; this procedure was repeated at least three times, so that at least two high readings and two low readings were obtained. The true value was taken as the mean between the last two readings. Generally, the difference between the high and low readings was around 10  $\mu$ g, but sometimes it was as high as 25  $\mu$ g.

#### SOURCES OF ERROR

Most of the sources of error lie with the measurements in liquid. The only error for the weighing in air would be due to the uncalibrated Class M weights used to calibrate the balance. Since the absolute error in these is less than 5  $\mu$ g each, the final error over the range 90–120 mg would be of that order.

The errors when weighing in the liquid can be due to a number of factors: differences in temperature of the liquid, thermal, mechanical and/or molecular currents in the liquid, surface tension of the solution, diffusion of vapor above the baffle, and air trapped within the sample. Many of these sources of trouble can be eliminated or reduced by using a better density cell and a thinner hangdown wire. Such a cell is now available commercially and its use has been reported (Elgert and Cammann, 1967).

Difficulty was also experienced from electrostatic effects on dry days, but this could have been eliminated by proper ground connections within the glass hangdown tubes.

## DENSITY OF SILICON STANDARD

Because the silicon standard was of high purity, its density was calculated from the best values in the literature. The cell edge used in the calculation,  $5.430736 \text{ \AA}$  at  $25^\circ\text{C}$ , is taken from Beu *et al* (1962), who had revised Bond's (1960) value obtained on a pure silicon single crystal. This cell edge, when used with Avogadro's Number (see Introduction) of  $6.02257 \times 10^{23} \text{ (g mol)}^{-1}$ , and the International Atomic Weights of 1961, gives a calculated density of  $2.32928 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ . This is not very different from the value of  $2.32902 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ , measured by Smakula and Sils (1955), who used Tilton and Taylor's (1937) revised water-density of  $d_{25} = 0.997048 \text{ g cm}^{-3}$ . Bigg (1967) suggests a better value for water density,  $d_{25} = 0.9970450 \text{ g cm}^{-3}$  by applying the relationship  $1 \text{ ml (1901)} = 1.000028 \text{ cm}^3$  to new values derived from an improved combination of the older observations. The use of Bigg's value would increase Smakula and Sils' value for silicon somewhat.

## DENSITY OF HEXACHLORO-1,3-BUTADIENE

The density of practical-grade hexachloro-1,3-butadiene was determined using two pieces of silicon weighing 100 mg in the same manner as described above. The density of the liquid was determined nine times, and found to be  $1.670756 \pm 0.00030 \text{ g cm}^{-3}$  (95% confidence limits) at  $25^\circ\text{C}$ . The liquid temperature for the measurements varied between  $23.05^\circ\text{C}$  and  $23.5^\circ\text{C}$  with a mean value of  $23.3^\circ\text{C}$ , and a median value of  $23.4^\circ\text{C}$ . The difference in measured density of the liquid at  $23.05^\circ\text{C}$  (the worst case) to the value at  $25^\circ\text{C}$ , obtained by applying the coefficient of expansion for silicon ( $\alpha = 4.15 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , Straumanis and Aka, 1952), was only 1 part in  $10^6 \text{ g cm}^{-3}$ , so that the effect of the coefficient of expansion of silicon could be ignored in this case.

## DENSITY OF IRON-BEARING SPHALERITES

Figure 2 shows the calculated and measured variations of density versus composition, in terms of mole percent FeS in sphalerite. The calculated curve is based on the cell volumes at the compositions, obtained from Barton and Toulmin's (1966) equation,  $a = 5.4093 + 0.0005637 \text{ (mole \% FeS)} - 0.000004107 \text{ (mole \% FeS)}^2$  and then multiplying the cell edges obtained by the factor 1.000117 in order to relate them to the silicon cell edge of Beu *et al.* (1962), which is considered to be more reliable than that used by Barton and Toulmin.<sup>1</sup> The cell edge of each

<sup>1</sup> Barton and Toulmin had actually used  $\text{CaF}_2$  as internal standard. The  $\text{CaFe}_2$  had previously been calibrated against silicon using Swanson and Fuyat's (1953) value of  $a_0 = 5.4301 \text{ \AA}$  at  $26^\circ\text{C}$ .

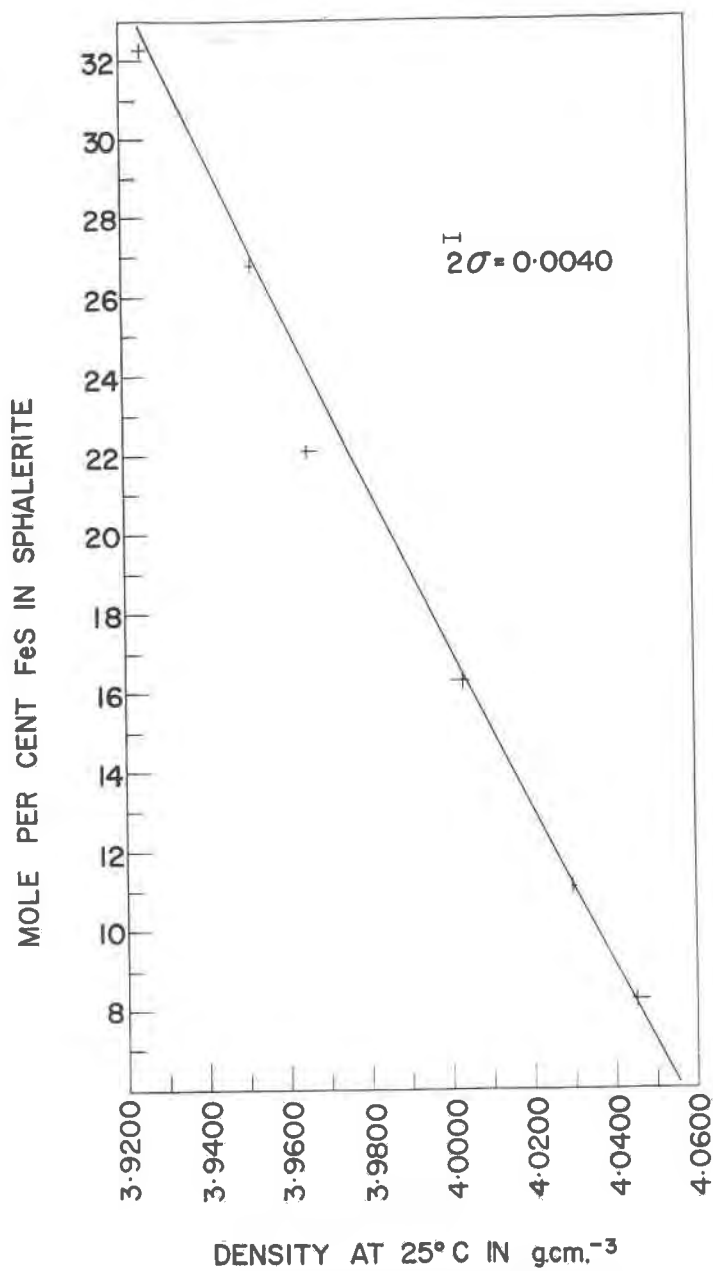


FIG. 2. Curve of density, at 25°C, versus sphalerite composition, in mole % FeS (see text for details).

sphalerite was measured and, though these values were all within 0.0067 Å of Barton and Toulmin's curve, the latter curve was used since it was obtained from a great many samples and measurements.

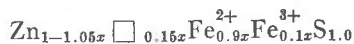
Each measured density is indicated by an abscissa bar, which shows the range of values obtained, and an ordinate bar, which represents the position of the mean. It is readily apparent that all samples except one fit the curve reasonably well. The density of the anomalous sample was determined seven times (all the others 3 times); its mean value is more than three standard deviations ( $3\sigma$ ) from the curve and so must be considered truly anomalous. This sample was treated in various ways in attempts to solve this discrepancy, but with no success. Two of the measurements were made on the sample split in two, but gave values within  $2\sigma$  of the first two. The sample was then crushed to  $-10+100$  mesh and three measurements were made on the powder which, again, were within  $2\sigma$  of the previous four measurements. If air pockets within the sample are responsible for the lower density, they must be very small and evenly distributed. It should also be reported that, prior to these measurements, all the samples had been measured many times previously (at least six) and all the handling, washing, drying etc., may have affected the surface properties of this one sample more than the others.

The anomalous sample, however, because it had been measured seven times was used to determine the precision of these density determinations. A standard deviation of  $0.0013 \text{ g cm}^{-3}$  or 0.03 percent was obtained.

The fifteen other measurements (5 samples, three times each) were examined for accuracy by assuming the theoretical curve to be correct and calculating the standard deviations for all fifteen by relating each sample to its theoretical density. A standard deviation of  $0.00196 \text{ g cm}^{-3}$  was obtained. This is equivalent to 0.048 percent at  $4.0445 \text{ g cm}^{-3}$  or 0.05 percent at  $3.9256 \text{ g cm}^{-3}$ .

#### DISCUSSION AND CONCLUSIONS

The iron-bearing sphalerites gave measured densities compatible with theoretical densities based on stoichiometry to within about 0.1 percent (2 standard deviations). If 10 percent of the Fe present occurs as interstitial  $\text{Fe}^{3+}$ , as Manning (1967) has suggested, then there should be a measurable decrease in density. The formula for such a sphalerite would then be:



where  $x$  refers to total iron, and  $\square$  represents the Zn vacancies created in

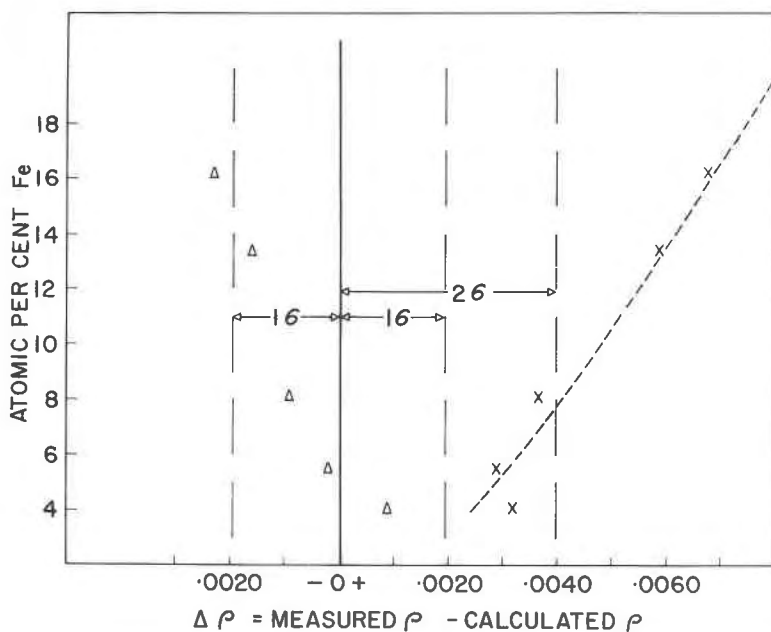


FIG. 3. Diagram showing departure from stoichiometry in  $\text{g cm}^{-3}$  between measured iron-bearing sphalerites, theoretically stoichiometric sphalerite, and those of theoretical sphalerites in which 2 percent of the Fe is  $\text{Fe}^{3+}$  (see text for details).

order to maintain a charge balance. Using the above formula on the most Fe-rich sample, the calculated density comes to  $3.8837 \text{ g cm}^{-3}$ . This is far lower than the measured value for that sample of  $3.9255 \text{ g cm}^{-3}$ .

Calculations were made for 5 samples assuming 2 percent of the Fe present was  $\text{Fe}^{3+}$ . The formula in this case is:



The calculated density for the same sample on this basis would now be  $3.9188 \text{ g cm}^{-3}$ , still significantly below ( $3.4\sigma$ ) the measured value. Figure 3 shows the differences ( $\Delta\rho$ ) between the measured densities and those of theoretical stoichiometric iron-bearing sphalerite (triangles), and those of a theoretical sphalerite in which 2 percent of the iron is  $\text{Fe}^{3+}$  (crosses). One standard deviation is shown as  $1\sigma$ ; two, as  $2\sigma$ . As indicated by the departure of the crosses from the vertical line representing  $\Delta\rho=0$ , the measured densities are substantially greater than the calculated ones for 2 percent interstitial iron (more than two standard deviations for sphalerite containing in excess of 8 atomic % Fe). Yet, calculations based on a stoichiometric model (triangles) indicate a trend toward  $-\Delta\rho$  ( $\rho_{\text{calc}} > \rho$



meas) with increasing iron content. At present it is not certain whether this trend is significant, since only one point has a  $-\Delta\rho$  greater than one standard deviation, but if it is significant, then the possibility of a very small amount of interstitial iron in high-iron sphalerites is indicated.

Considering the accuracy of the density measurements, and assuming the validity of the "vacancy formula" given above, it appears that, if  $\text{Fe}^{3+}$  occurs interstitially in sphalerite, it must be in quantities below 1 percent of the amount of iron present.

Attempts to determine if this limit also applies to buffered- and more-iron-rich sphalerites synthesized at lower sulphur fugacity, and for a natural sample containing 15 weight percent Fe, were not as conclusive since the errors involved in analysis are greater than the accuracy of the density measurements. It is hoped to resolve this at a later date by more accurate analysis.

In conclusion, it is evident that density measurements can be made with a reasonable degree of precision and accuracy on synthetic sphalerites using practical-grade hexachloro-1, 3-butadiene. It is advocated that this liquid be used more commonly when determining densities by the hydrostatic method not only because it is very suitable, but also because a greater demand would then be created for the pure liquid, thereby probably reducing its cost. At present the pure liquid, in contrast to the practical grade material used in this study, can only be obtained by special order, and is thus quite expensive.

#### ACKNOWLEDGMENTS

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Drs. E. H. Nickel and E. J. Gabe served as valuable sounding boards.

#### Addendum:

After this paper had been submitted for publication, a paper appeared by Aitcin, Garnier, and Carles-Giebergues, (1968). This paper describes a hydrostatic method for determining the density of 5- to 10-g powdered samples using a semimicro balance and attaining a high degree of precision. The samples used in that paper were 50 to 100 times heavier than in the present study.

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