

On an Accurate Method of determining the Densities of Solids.

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IN the course of some researches on the relation between the chemical constitution and the crystalline form of substances, I found it necessary to attempt an accurate determination of the densities of crystals.

Messrs. Playfair and Joule,¹ in 1843, in the course of similar researches, determined the specific gravities of numerous salts by the use of an instrument which showed the actual volume of the solid investigated. This method was found to be subject to many errors, and they abandoned it for one which is the prototype of that ordinarily used in accurate work at present. Their second method² consisted in the use of a flask, stoppered by a piece of thermometer tube, which in its turn was covered by a cap, the separate pieces being carefully ground to fit. The thermometer tube was first calibrated, and the capacity of the flask then determined by observing the rise of water in the tube for different temperatures.

After the salt had been introduced into the flask, the latter was filled to a mark while in a bath whose temperature was known, and then was put away to cool before weighing. For salts soluble in water they used turpentine, the specific gravity of which had been determined by the same method.

The only differences between this method and the latest development of it are, that carbon tetrachloride is now substituted for turpentine (except at high temperatures), and that the thermometer tube is replaced by either a perforated stopper or by one ending in a fine capillary, which capillary, while the flask is in the bath, dips under some of the liquid used for the observations.

By means of this process, Mr. Tutton³—and I take Mr. Tutton's work

¹ Playfair and Joule, "Relations between Atomic Vols. and S. G.," *Mem. Chem. Soc.*, Vol. II., 1843-45.

² Playfair and Joule, "Relations between Atomic Vols. and S. G.," *Journ. Chem. Soc.*, Vol. I., 1849.

³ A. E. Tutton, "Crystallography of the Sulphates of Potassium, Rubidium, and Calcium," *Journ. Chem. Soc.*, July, 1894.

as a type of what accurate work can do with the method—obtained the following results:—

Relative Density at 20° C.

| K_2SO_4 | Rb_2SO_4 | Cs_2SO_4 |
|-----------|------------|------------|
| 2·6659 | 3·6150 | 4·2411 |
| 2·6609 | 3·6094 | 4·2458 |
| 2·6660 | 3·6128 | 4·2438 |
| 2·6680 | 3·6132 | 4·2459 |
| 2·6622 | 3·6071 | 4·2432 |
| 2·6617 | 3·6144 | 4·2412 |
| 2·6631 | 3·6073 | |

Greatest diff. = ·0051 or ·19 %/o. ·0079 or ·21 %/o. ·0048 or ·11 %/o.

The following are the two chief causes of inaccuracy in the use of this method:—

(1.) The loss of liquid through evaporation during the time elapsing between filling in the bath and weighing.

It must be remembered that the most perfect glass-surface contact will not prevent a volatile liquid such as carbon tetrachloride from evaporating. In my own pyknometer the surfaces have been most carefully ground, and I find that 20 grams of the liquid at the ordinary temperature lose ·006 gram in half-an-hour.

(2.) The error due to the differences between the real temperature of the bath, the real temperature of the filled pyknometer, and that shown by the bath thermometer. A difference of ·05° C. makes a difference of ·0013 gram in 20 grams of carbon tetrachloride, and it must be borne in mind that the error may be either a positive or a negative one—hence in comparing any two results it may be doubled—and the results may be still further vitiated by the fact that this difference, or the error due to it, is also involved in the determination of the density of the carbon tetrachloride and in the calculation for the capacity of the flask.

However, Mr. Tutton partly overcomes this by determining the density of the carbon tetrachloride anew every time he determines that of the solid—that is, the bath heats two flasks, one containing the liquid and salt, the other the liquid only. This, on the assumption that the flasks are equally heated, leaves only the error due to the discrepancy between the true bath temperature and that shown by the bath thermometer. In the following method no error due to the evaporation of the liquid is involved, indeed this evaporation is actually an essential of the method.

I obtained a pyknometer having a thermometer stopper and a capillary

(closed by a cap) at the side—there is in principle nothing new about it, and the article in a rough form is sold by all chemical apparatus manufacturers. Having tried several pyknometers of various sizes, I found the following, which was made by Dr. Geisler of Bonn, to my instructions, to be the best:—

The thermometer stopper is graduated from 10° C. to 20° C. to $\frac{1}{10}^{\circ}$, and of such a length that the $\frac{1}{100}^{\circ}$ can be estimated, and the capacity is about 12 cc. The latter is reduced to the lowest limits compatible with accuracy, so that a smaller quantity of salt will suffice; and this is of great importance in the case of salts such as Cs_2PtCl_6 , which are difficult to obtain well crystallised in large quantities. The form is cylindrical, and is preferred to the spherical because of its relatively larger surface enabling it to take up more rapidly the temperature of the balance case.

I may here mention that I am having a conical shaped pyknometer made, from which I hope to obtain some advantages in the practical manipulation of the apparatus.

The method of procedure is as follows:—

After the thermometer has been compared with a standard, the pyknometer is weighed against another one as closely similar as possible, which is used as a counterpoise throughout the observations. This is necessary for two reasons. First, to insure that the error in weight due to the deposition of moisture on the glass is negligible; secondly, to do away with the correction for the air displaced by the glass of the pyknometer. The capacity of the pyknometer at different temperatures is then determined by weighing it when filled to the mark with pure water (freed from air and CO_2), and noting the temperature of the water at the instant of weighing. As the evaporation of the water is not rapid enough to cause its level to coincide with the mark within a reasonable time, it was found necessary for this purpose to fall back upon the contraction and expansion of the liquid; and to obviate any error due to the "lag" of the thermometer, two series of weighings at different temperatures were obtained—one when the pyknometer had been filled above the mark with water slightly warmer than the balance case, and the other with it filled below the mark with water colder than the case. In the first series the weighings and temperatures were taken when the contracting water brought the level and mark into coincidence; and in the second, when the expanding water did the same. Then by rejecting all observations in which the contraction or expansion was rapid, *i.e.* all observations in which less than half-an-hour had elapsed between placing in the balance case and weighing, and by taking the means of the weighings obtained

from contracting and expanding water at about the same temperatures, it was hoped the error for "lag" could be neglected.

The results obtained are:—

12·2880 grams at 12°·03 C.
 12·2861 „ „ 13°·03.
 12·2821 „ „ 16° 05.

These, when corrected for the density of water at the respective temperatures, give the capacity of the pyknometer at those temperatures:—

12·2933 cc. at 12°·03.
 12·2935 „ „ 13°·03.
 12·2942 „ „ 16° 05.

From which the expansion of the pyknometer for intermediate temperatures can be found. Having obtained these constants, the relative density of the CCl_4 used is determined by filling the pyknometer above the mark, and waiting until the CCl_4 *evaporates* down to the mark, and then weighing and observing the temperature at the same time.

The following numbers were obtained for the weight of 12·2940 cc. of the carbon tetrachloride used:—

| | |
|----------------------------|----------------------------|
| 19·8048 grams at 11°·17 C. | 19·7350 grams at 14°·07 C. |
| 19·7956 „ 11°·59 „ | 19·7339 „ 14°·11 „ |
| 19·7744 „ 12°·32 „ | 19·7201 „ 14°·70 „ |
| 19·7713 „ 12°·84 „ | 19·7169 „ 14°·84 „ |
| 19·7666 „ 12°·78 „ | 19·6898 „ 15°·64 „ |
| 19·7548 „ 13°·21 „ | 19·6610 „ 17°·33 „ |
| 19·7459 „ 13°·62 „ | 19·6430 „ 18°·18 „ |
| 19·7408 „ 13°·84 „ | ... |

and from these a curve was drawn by the use of which the weight at intermediate temperatures could be estimated.

The density of the salt is determined in a similar manner. A known weight of the powdered crystals is placed in the pyknometer, and just covered by CCl_4 , and the whole put under the receiver of an air pump, which is exhausted until no more bubbles of air come from the salt. The pyknometer is then filled above the mark with CCl_4 and weighed as before.

The following results were obtained:—

| K_2PtCl_6 | Cs_2PtCl_6 | Rb—alum. |
|---------------------------|----------------------------|---------------------|
| 3·4711 at 14°·13 C. | 4·1930 at 13°·92 C. | 1·8853 at 13°·91 C. |
| 3·4695 „ 15°·08 „ | 4·1926 „ 13°·79 „ | 1·8852 „ 14°·16 „ |
| 3·4698 „ 14°·43 „ | 4·1940 „ 13°·56 „ | 1·8849 „ 14°·17 „ |
| ... | ... | 1·8858 „ 13°·61 „ |
| Greatest diff. 0·0016 | 0·0014 | 0·0009 |
| Percentage diff. 0·041 % | 0·033 % | 0·047 % |

All observations are corrected for air displaced by the liquid and the weights. Also all observations in which the level of the liquid passed the mark before half-an-hour had elapsed between placing on the balance and weighing were rejected, and so were those in which the temperature of the liquid and that of the balance case differed by more than $\frac{1}{5}^{\circ}$ C.

To avoid any error due to the film of air which adheres to the inside of the glass vessel, the pycnometer was, after careful washing with water, always rinsed out three times with pure alcohol and dried.

Each separate density given above was made on a different crop of crystals; and hence the probability is that the slight disagreements in the results obtained are not due so much to the method employed, but to different states of hydration of the salt or to slight differences in the amount of residual air adhering to the powder, or perhaps to real differences in the density of the different crops of the same crystals. Therefore the method may be considered to give the density of any given sample to an accuracy of $\frac{1}{2000}$.

May I perhaps point out to mineralogists the importance of accurate density measurements? Although minerals are, as a rule, impure, yet if several accurate determinations of the densities of different specimens of the same mineral have been obtained, and if the chemical composition of the specimens are known, then it is quite possible to calculate the density of the pure substance, and the knowledge of this constant is of the utmost importance for any theoretical dealing with crystals, the more so in that the majority of minerals cannot be produced artificially.
