CCCXC.—*The Density of Calcium Carbonate Hexahydrate.*

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In the course of experiments in dilatometers on the rate of decomposition of the unstable hexahydrate of calcium carbonate, it was observed that the increase in volume resulting from the complete decomposition of a known weight of hexahydrate did not correspond with the densities given in the literature for calcium carbonate and its hexahydrate.

The density of the calcite formed in the reaction was 2·72 (mean of nine experiments), which is also quoted as the best representative value by Mellor ("Treatise on Inorganic and Theoretical Chemistry," III, p. 835).

A review of the literature suggests that the properties of the hexahydrate may vary somewhat according to the conditions of preparation. The customary and most convenient method of preparation is by precipitation with carbon dioxide from calcium oxide in sucrose solutions at 0°. The results below were obtained with crystals prepared in this way.

The density of the hexahydrate can be calculated from the expansion, measured in a dilatometer with a calibrated capillary tube, per g. of anhydrous calcium carbonate remaining. It is known, however, that calcium carbonate hexahydrate crystals tend to contain, as inclusions, small quantities of dyes and such salts as copper sulphate if they are present in the mother-liquor during growth (Kohlschütter and Egg, *Helv. Chim. Acta*, 1925, 8, 697). It seems probable that crystals grown from 20% sucrose solutions would contain some sugar or its calcium derivative; indeed, if the very carefully washed crystals are allowed to decompose in contact with water, a residue is obtained on evaporation which chars on ignition, with a strong smell of burnt sugar, and leaves a residue of calcium carbonate. In order to allow for the effect (small in any case) produced by this included sugar or its calcium derivative upon the volume change in the dilatometer it has been assumed that the passage into solution of the included calcium derivative produces an increase in volume in the dilatometer, and that this increase can be calculated from the weight of the residue found on evaporation, on the assumption that the density of " calcium sucrate " solution is equal to that of a sucrose solution of the same concentration.

The density of the hexahydrate is then given by the expression :

$$D_{\text{Hexahydrate}} = \frac{D_{\text{Calcite}}\{208{\cdot}2 + (100{\cdot}1 \times 0{\cdot}00899)\}}{\{100{\cdot}1\,(1 - V\,.\,D_{\text{Calcite}}) + 108{\cdot}1\,D_{\text{Calcite}}\}}$$

where $D_{\text{Hexahydrate}}$ and D_{Calcite} represent the densities indicated by the suffix; V' = expansion actually observed (in c.c. per g. of calcite remaining); v = the correction already discussed; and $V = (V' - v)$.

The mean weight (five experiments) of " calcium sucrate " passing into solution per g. of calcite formed is 0·00899 g. Also, the corresponding expansion due to the different solubilities of the hydrated and the anhydrous forms would be about 0·0001 c.c. Taking this into consideration, v becomes 0·0039 c.c.

The following values for V' were obtained in nine dilatometer experiments : 0·313, 0·311, 0·323, 0·308, 0·319, 0·301, 0·310, 0·315, 0·316. For the density at 0° these figures give the respective values : 1·835, 1·832, 1·851, 1·827, 1·845, 1·816, 1·830, 1·838, 1·840. The mean of these is 1·834, and the average deviation from the mean 0·43%.

The density of the hexahydrate at 0° was determined also in the following way. A specific gravity bulb was in turn filled, at 0°, with water, with the mother-liquor of the crystals, and with the mother-liquor together with some of the crystals, and weighed in each case. The object of this procedure is to avoid any contact of the crystals with pure water before the hexahydrate is weighed. In contact with 20% sucrose solution at 0°, the hexahydrate is stable for an indefinite time, but in contact with pure water decomposition proceeds slowly, even at 0°. The crystals were washed into a tared Gooch crucible, which was kept in water in a beaker; the beaker was warmed to complete the decomposition of the hexahydrate, and the calcite well washed. The crucible and its contents were dried and weighed. The washings were added to the liquid in which the Gooch had been standing; the whole was evaporated to dryness and the residue weighed. The weight of hexahydrate crystals is represented by the weight of calcite, calculated to $CaCO_3,6H_2O$, plus the weight of the residue. By this method the following values for the density were found: 1·828, 1·803, 1·803, 1·806, 1·833, 1·831, 1·812, 1·817. The mean of these is 1·817, the average deviation from the mean being 0·60%.

We are unable to account for the discrepancy of 0·9% between the values obtained by the two methods, but it is improbable that the average deviations of 0·60% and 0·43% respectively can be attributed wholly to experimental error. Factors affecting growth, such as the rate of absorption of carbon dioxide, and the extent to which the sugar has formed condensation products under the influence of the alkali, would seem to cause some variation in the density.

The value 1·817 is considerably higher than those given by other workers:

1·783/10°.	Pelouze, *Compt. rend.*, 1865, **60**, 429.
1·752/18°.	Bütschli, *Abh. Königl. Gesell. Wiss. Göttingen. Math. Phys. Kl.*, 1908, **6**, Nr. 31.
1·777/3°.	Mackenzie, J., 1923, **123**, 2409.
1·789/15°.	Hume, J., 1925, **127**, 1036.

Mackenzie's crystals were prepared in 10% sucrose solution; we have accordingly determined the density of crystals prepared from 10%, instead of 20%, sugar solution in both the ways described above; the density determined directly, at 0°, is 1·821, and that calculated from the expansion on decomposition is 1·833. Thus it does not seem possible to refer the difference between our value and Mackenzie's to the fact that the crystals were grown in sugar solutions of different concentrations.

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