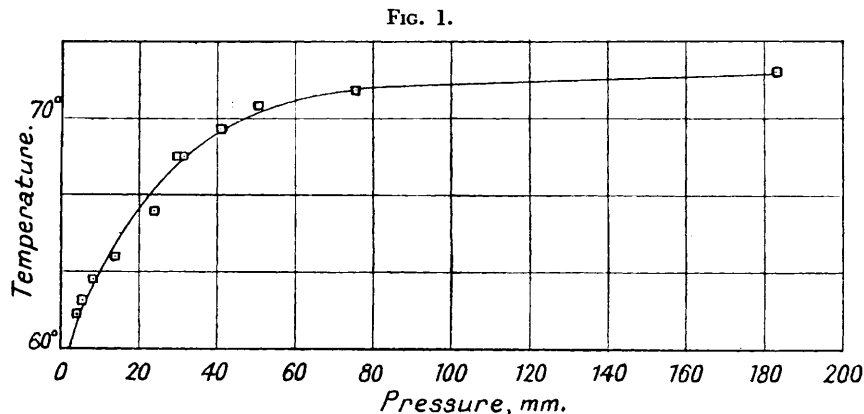


160. Hydrates of Calcium Sulphate.

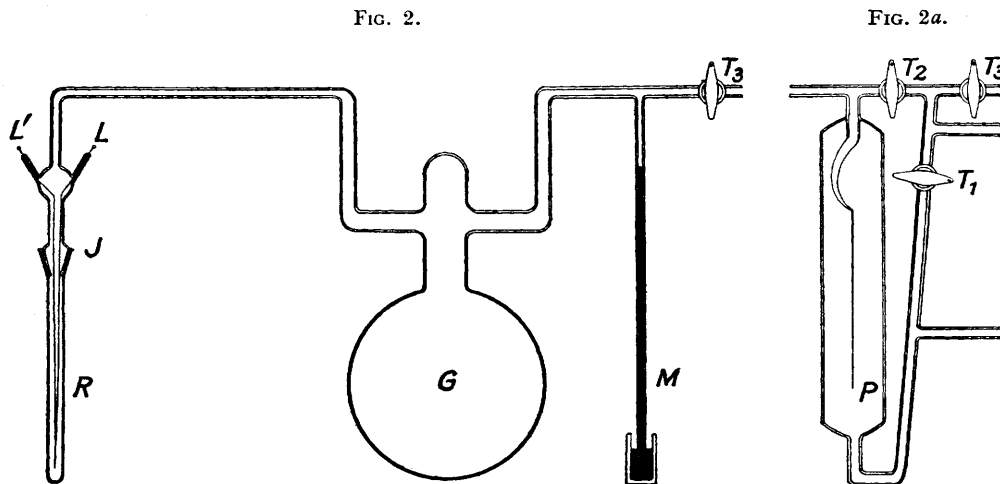
By CHARLES S. GIBSON and SIDNEY HOLT.

IN connexion with other work it has been necessary to reinvestigate the course of the dehydration of calcium sulphate dihydrate (gypsum) and to attempt to establish the conditions of existence of the hydrates with some certainty.

In the first series of expts., v. p. determinations were made, a differential tensimeter of the type described by Hartung (*Trans. Faraday Soc.*, 1920, 15, 150) being used. A satd. aq. solution



of NaCl was used as a standard, and observations of satd. v. p. in the system dihydrate-hemihydrate-water vapour were made up to 78°. The results indicated in Fig. 1 show the existence of a range of gradual change up to about 73°, in agreement with the results obtained by Shenstone and Cundall (J., 1888, 53, 544). The v. p. at 72° was 183.2 mm. and remained const. at this value for 5 days. Possibly the somewhat indecisive value for the v. p. obtained by van 't Hoff and Donnan (*Arch. Néerl.*, 1901, 6, 471) was due to the presence of $MgCl_2$ in the system.



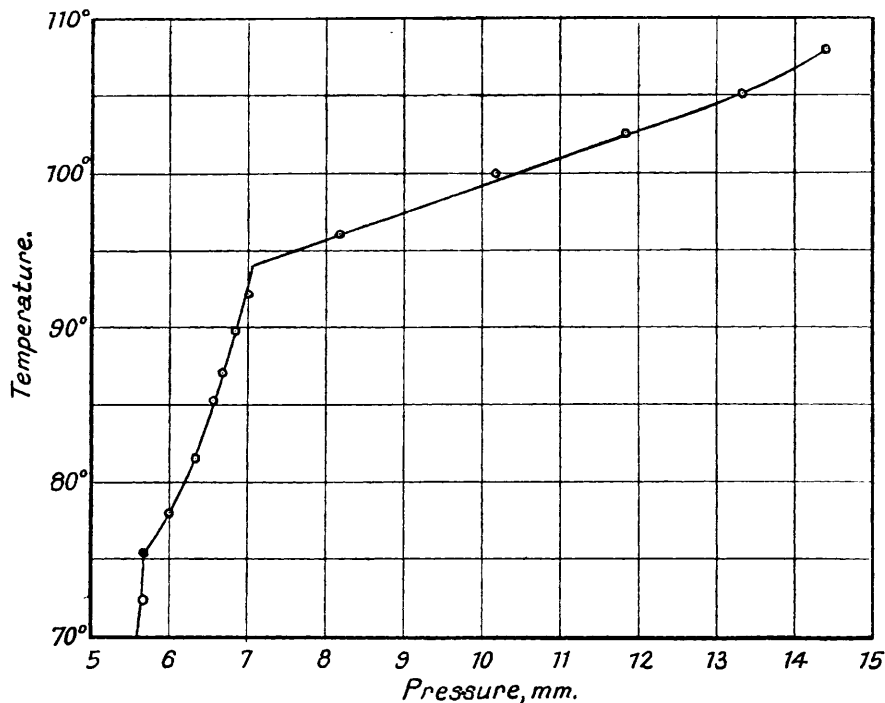
In the second series of expts., a modification of the apparatus employed by Hackspill and Kiefer (*Ann. Chim.*, 1930, 14, 227) for a study of salt hydrates was substituted for the tensimeter. This apparatus, which does not measure the satd. v. p., is illustrated in Fig. 2. It consists of a reaction tube, *R*, containing a thermocouple passing through the Pb seals, *LL'*, and provided with a ground attachment at *J*. The reaction vessel is connected with a glass globe *G*, attached

to a manometer, *M*. The vol. of the globe is an important feature and is about 7 l. The apparatus was so arranged as to allow the use of a McLeod gauge for the lower pressure measurements. *G* was enveloped in a well-lagged container in which no appreciable variation of temp. was registered during the course of an expt. The rate of heating was controlled by variation of the voltage drop across the winding of a small heater by means of a rheostat, hand control being satisfactory. Evacuation of the apparatus was done *via* the tap, *T*₃.

For all the expts. the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was prepared from pure CaCl_2 and pure H_2SO_4 ; it was obtained in cryst. form by recrystn. from pure HCl (about 5*N*), and its comp. verified by direct analysis.

A weighed amount of the dihydrate was placed in the tube, *R*, and the apparatus evacuated to less than 0.1 mm. by means of a Gaede pump. The pump was isolated from the apparatus, and the temp. in *R* raised at the rate of approx. 12° per hr. to 120°, press. and temp. being recorded at intervals of 15 min. The curves drawn from temp.-press. measurements in 12 expts. show discontinuities at $73^\circ \pm 2^\circ$ and $92^\circ \pm 2^\circ$ as seen in Fig. 3. In two cases, however,

FIG. 3.



there were indications of an additional break at 105° and 107° respectively, and a third series of expts. was carried out in order to investigate the changes above 100° in greater detail.

In this series the apparatus was modified by substitution of a smaller globe (of about 2 l. capacity) for *G*, and replacement of the manometer, *M*, by a glass-spring manometer, shown in Fig. 2*a*. Approx. equal pressure on each side of the manometer diaphragm during exhaustion was attained by adjustment of taps *T*₁ and *T*₂. Movement of the pointer, *P*, was measured by means of a travelling microscope. The conditions and rate of heating were as in the former series. Although the two breaks in the curves below 100° were again realised, it was adequately confirmed in 8 expts. that there is no discontinuity in the dehydration of dihydrate above $92^\circ \pm 2^\circ$, the course of which is shown in the typical curve, Fig. 3, which summarises the results of the second and third series of expts. It must be concluded that the exceptions noted above were due to exptl. deficiencies in the particular runs.

Hackspill and Kiefer (*loc. cit.*) showed that discontinuities in these curves represented the transition of hydrates, and, knowing the volume of the apparatus and the weight of dihydrate taken, it was possible to calculate approximately the composition of the solid

in the reaction vessel. The first discontinuity is the end of a period of gradual change with rise of temperature and probably indicates a change of phase—such as a polymorphic change in the dihydrate—which, however, has not been a subject of the present investigation. The material in the reaction vessel at $92^{\circ} \pm 2^{\circ}$ has approximately the composition of the hemihydrate. Between $73^{\circ} \pm 2^{\circ}$ and $92^{\circ} \pm 2^{\circ}$ the dihydrate is dehydrated to hemihydrate. Since there is no discontinuity in the pressure-temperature curve above $92^{\circ} \pm 2^{\circ}$, *i.e.*, when hemihydrate is being converted into anhydrous salt, this is evidence that the hemihydrate is not a hydrate of calcium sulphate in the ordinary sense. These results indicate that the water in the hemihydrate is zeolitically held and is not true water of crystallisation. This view of the nature of the hemihydrate has also been expressed by Linck and Jung (*Z. anorg. Chem.*, 1924, **137**, 413) and by Krausz and Jörns (*Tomind.-Ztg.*, 1930, **54**, 1467). In this connexion it is significant that the molecular volumes of hemihydrate and its dehydration product, calculated from the values of the densities determined by Linck and Jung (*loc. cit.*), are the same. On the other hand, no evidence of the new kind of dehydration referred to by Balarew (*Kolloid. Z.*, 1929, **48**, 63) as “zeolitic-hydratic dehydration” has been found. No period of gradual change has been observed in the dehydration of hemihydrate, which has been shown by several investigators to take place readily at low pressures. The two discontinuities in the pressure-temperature curve indicate that the dehydration of the dihydrate proceeds *via* the hemihydrate, and the question of the metastability of the hemihydrate raised by van 't Hoff and his co-workers (“Ozeanische Saltzablagerung,” Leipzig, 1912) to explain the anomaly of the transition temperatures in the two systems, dihydrate-soluble anhydrite-water (89°) and dihydrate-hemihydrate-water (107°), does not arise. It is suggested that the temperature, 89° , quoted for the first system is, in fact, that of the system dihydrate-hemihydrate-water.

In the present work we have not been concerned with the question of the existence of different forms of the hydrates or anhydrous forms of calcium sulphate (*cf.* Balarew, *loc. cit.*, and Jung, *Z. anorg. Chem.*, 1925, **142**, 73; see also Grengg, *Z. anorg. Chem.*, 1914, **90**, 327).

The conclusions from our experiments are : (1) Calcium sulphate dihydrate has a period of gradual change up to $73^{\circ} \pm 2^{\circ}$. (2) The dihydrate is dehydrated to hemihydrate between $73^{\circ} \pm 2^{\circ}$ and $92^{\circ} \pm 2^{\circ}$. (3) The water in the hemihydrate is conveniently described as “zeolitic.” (4) Dehydration of dihydrate proceeds *via* the hemihydrate to anhydrite.

This work has been carried out under the auspices of the Dental Investigation Committee of the Department of Scientific and Industrial Research, the funds being provided by the Dental Board of Great Britain and Ireland. The authors are also particularly indebted to Dr. J. J. Fox for his help and interest in the work.

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[Received, April 19th, 1933.]