

S 8. *The Kinetics of the Thermal Decomposition of Magnesium Hydroxide.*

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The isothermal dehydration of precipitated magnesium hydroxide and of naturally occurring brucite has been studied at various temperatures in vacuum. For precipitated hydroxide the rate of decomposition as well as the heat of activation varies for different preparations, though concordant results are obtained with the same preparation. The rate of dehydration of brucite is not greatly affected by its state of subdivision, and at a given temperature is of the same order as for the precipitated hydroxide. The results are discussed in conjunction with Mampel's theory of the decomposition of powders. The measured rate agrees reasonably with that calculated by the Polanyi-Wigner expression.

ALTHOUGH extensive work has been done in recent years on the kinetics of decomposition of solids, little attention has been paid to the thermal dehydration of the hydroxides and hydrous oxides of metals in spite of the importance of such reactions in the laboratory and in industry. Moreover, the work done has been confined for the most part to the method of thermal analysis, in which the substance is subjected to a steadily rising temperature; this procedure, although very useful for the determination of the range of temperature within which decomposition becomes appreciable, and for the detection of intermediate products of dehydration, cannot throw much light on the kinetics of the process.

The study of the kinetics is attended by various difficulties: the starting substance is frequently amorphous, or microcrystalline, or both; its properties depend in high degree on the exact details of preparation; and its chemical composition is in many cases still a matter of controversy. In the hope of minimising some, at least, of these difficulties, the substance chosen for the present work was magnesium hydroxide: it occurs in nature as brucite in a well-crystallised form, sometimes very pure; it crystallises in the hexagonal *C6* system forming lamellæ which can be readily cleaved so that fragments can be easily cut to shape; and it has been proved by *X*-ray measurements that in the system $\text{MgO-H}_2\text{O}$ there exist only two solid phases, *viz.*, brucite and magnesium oxide, and no others (Fricke and co-workers, *Z. anorg. Chem.*, 1927, **166**, 244; Hüttig and Frankenstein, *ibid.*, 1929, **185**, 403; Büssel and Köberich, *Z. physikal. Chem.*, 1932, *B*, **17**, 310).

The method of thermal analysis has already been applied to the study of the decomposition of magnesium hydroxide by van Bemmelen (*J. pr. Chem.*, 1882, **26**, 227; *Z. anorg. Chem.*, 1898, **18**, 98), Johnston (*Z. physikal. Chem.*, 1908, **62**, 330), Hüttig and Frankenstein (*loc. cit.*), Hackspill and Kieffer (*Ann. Chim.*, 1930, **14**, 227), Büssel and Köberich (*loc. cit.*), Lashchenko and Kompanskii (*J. Appl. Chem. Russia*, 1935, **8**, 628), Nutting (U.S. Geol. Survey, Professional Papers No. 197E, 1943, p. 197), and Jolisbois and Bergès (*Compt. rend.*, 1947, **224**, 78). From this work it is seen that a suitable temperature range for the measurement of the rate of decomposition of magnesium hydroxide is 300–400°.

In the following experiments the isothermal dehydration of precipitated magnesium hydroxide and of brucite of various states of subdivision has been studied between 300° and 370° in a vacuum, the method of continuous weighing being used.

EXPERIMENTAL.

For the determination of the weight of the sample as a function of time, the automatically recording electrical sorption balance of Gregg and Wintle (*J. Sci. Instr.*, 1946, **23**, 259) was employed, and is illustrated in Fig. 1. In order to eliminate losses due to spurting, the sample was contained in a small bucket of Pyrex glass, which was fitted with a lid made from a sintered-glass filter-stick and ground so as to fit the bucket accurately. Experiments with lumps and flakes of brucite, where spurting was unlikely, showed that the lid had no measurable effect on the rate of decomposition.

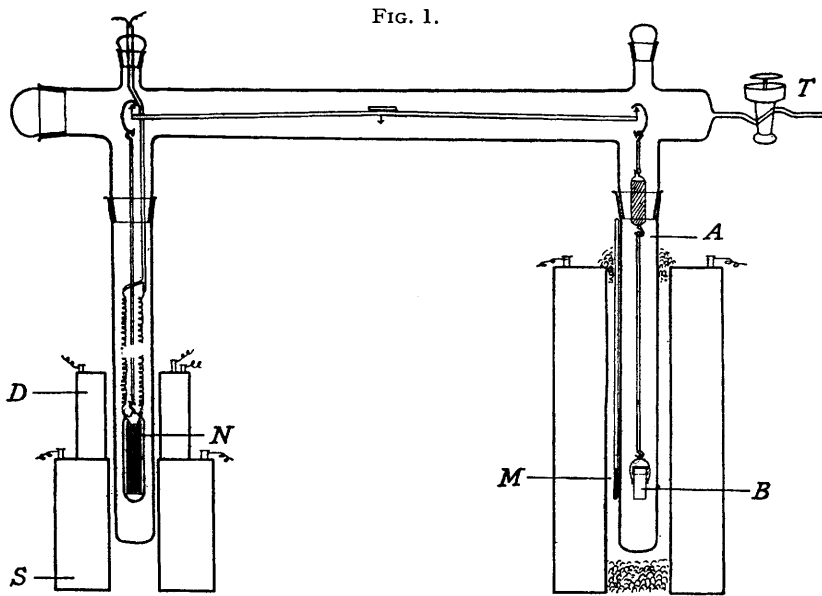


FIG. 1.
The balance: A, detachable limb; B, bucket; M, thermometer; N, inner solenoid; S, outer solenoid; D, damping coil; T, tap.

In carrying out an experiment, the bucket *B* with its sample was hung on to the hook of the balance, the limb *A* put into position, and the balance case evacuated through the tap *T* by means of a mercury condensation pump backed by a Speedivac pump. The furnace, previously heated to the temperature of the experiment, was then raised into position, whereupon the decomposition at once commenced. The temperature was recorded by the thermometer *M* placed in contact with the limb *A* at the level of the bucket. During an experiment the temperature was kept constant to $\pm 1^\circ$; but owing to the inevitable time lag in heating the sample, its temperature in the first few minutes is uncertain and the results of that period are accordingly liable to some error.

The curve obtained on the recording drum of the instrument is in the form of small steps (Gregg and Wintle, *loc. cit.*) and the apparatus registers the mass of the sample to within 0.5 mg. at intervals of approximately 2 mg., so that in effect 50–80 experimental points are obtained in each curve. The decomposition graphs given below have been obtained by joining the corners of these steps.

Precipitated Magnesium Hydroxide.—Batches II, III, IV, VIII, X, and XII were prepared by running slowly 500 c.c. of *n*-potassium hydroxide into 500 c.c. of *n*-magnesium chloride (both prepared with carbon dioxide-free distilled water) at the boiling point and with continuous stirring. The mixture was kept at the boiling point for some time, the precipitate was then allowed to settle, repeatedly washed by decantation, filtered off, and washed again on the filter until free from chloride ion. This usually required 8 hours at least. The precipitate was dried at 110° for several hours. Details are as follows:

Batch.	Time of precipitation (mins.)	Time of boiling after precipitation (mins.)	Time of drying (hrs.)	Loss of weight on ignition, %.
II	30	5	15	30.8
III, IV, XII	45	30	20	30.9
VIII	10	—	30	30.9
X	40	30	3	30.9

Batch XIV was as Batch II, but sodium hydroxide was used in place of potassium hydroxide.

Batch V was precipitated in the cold and dried at 20° over phosphoric oxide for 3 weeks.

Batch VI was another part of the precipitate of Batch V, but was boiled with water for 12 hours and dried at 110° for 3 hours.

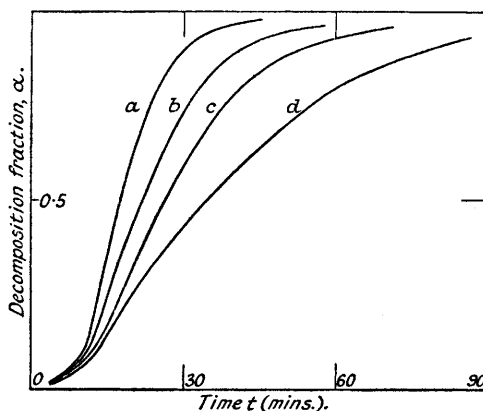
Batch XVII was as Batch III, but prepared from sodium hydroxide and magnesium sulphate heptahydrate.

Brucite C and O were kindly supplied by the Geology Department of Cairo University, and Basic Dolomite Inc., Cleveland, Ohio, respectively. The two samples were very pure and the loss in weight on ignition was 30.9% (calc.: 30.88%).

Results.—Precipitated magnesium hydroxide. The decomposition curves of the various preparations of magnesium hydroxide are of the usual sigmoid type, and the acceleratory region is generally limited to less than 15% of the total decomposition. Whether this region is due to the process of nucleus formation and growth, or simply to a temperature lag in the heating of the sample, cannot be decided without far more experimentation; and discussion of the results will accordingly be confined to the main period of the reaction, *i.e.*, the “decay” period, during which the rate of decomposition progressively diminishes. It should be noted that the reaction comes practically to a standstill at some 3—5% short of complete dehydration, and in order to expel the last traces of water within a reasonable time, it is necessary to raise the temperature to 500°.

In Fig. 2, a typical set of results—for 0.4 g. of Batch III decomposed at four temperatures between 305° and 350°—is plotted as the fraction decomposed $\alpha = (1 - w/w_0)$ against time t , where w_0 = initial mass of reactant, and w = mass at time t .

FIG. 2.



Dehydration curves of precipitated magnesium hydroxide.
Batch III: a, 350°; b, 335°; c, 320°; d, 305°.

Over the decay period, which corresponds to 80—90% of the complete reaction, the decomposition can be represented by the equation

$$(w/w_0)^{1/3} = -kt + a \dots \dots \dots (1)$$

which may be alternatively written as

$$1 - (1 - \alpha)^{1/3} = kt + b \dots \dots \dots (2)$$

On differentiation, (1) gives

$$-dw/dt = k_0 w^{2/3} \dots \dots \dots (3)$$

where k_0 (the velocity constant) = $3kw_0^{1/3}$; k , a , and b are constants.

Thus by plotting $(w/w_0)^{1/3}$ against t in the case of more than 40 decomposition experiments, a straight line is obtained, the slope of which gives k . Fig. 3 is typical and represents the results of Batch III, shown in Fig. 2. It must be emphasised, however, that small variations in the index n produce only very slight curvature in the plot of $(w/w_0)^n$ against t ; but when $n \geq 1/2$ or $\leq 1/6$, the line is definitely curved, and examination of the numerous results plotted with varying values of n leaves little doubt that n lies close to 0.33. The value of the index has been verified by plotting $\log_{10}[-d(w/w_0)/dt]$ against $\log_{10}(w/w_0)$ in a number of typical cases, and the curves approximate closely to straight lines having slopes which deviate by not more than ± 0.04 from 0.67, as may be judged from Fig. 4.

For a given preparation, the results were reproducible within close limits, even when some time elapsed between successive experiments, as will be seen from the values of k in Table I. This absence of ageing may well be due to the fact that all the batches were dried at 110° in an air-oven (except Batch V, which was dried at 20° over phosphoric oxide for 3 weeks).

TABLE I.

Values of k in duplicate experiments.

Batch.	Temp.	k (hour ⁻¹).		Time interval (days).	Batch.	Temp.	k (hour ⁻¹).		Time interval (days).
		Expt. I.	Expt. II.				Expt. I.	Expt. II.	
III	320°	0.76	0.78	7	VIII	365°	0.95	1.01	190
	335	1.07	1.11	68		X	365	0.78	0.83

With different preparations, on the other hand, different rates were sometimes obtained even when the conditions of preparation had been made as like as possible; whilst slight, but deliberate, variations in the details of preparation sometimes gave no difference in the velocity constants. This is made clear by reference to Table II together with the details of preparation described above.

FIG. 3.

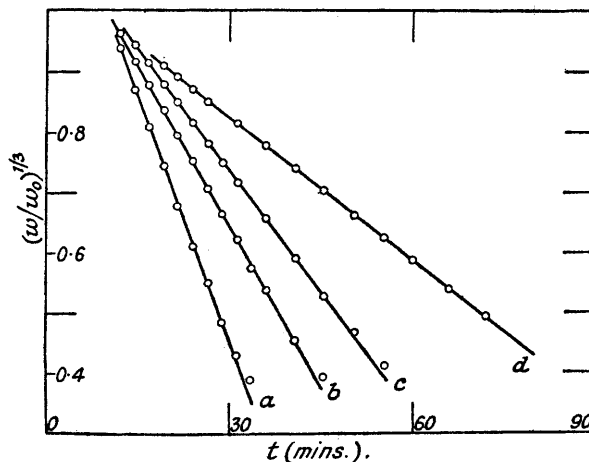
Curves of $(w/w_0)^{1/3}$ versus t for Batch III: a, 350°; b, 335°; c, 320°; d, 305°.

FIG. 4.

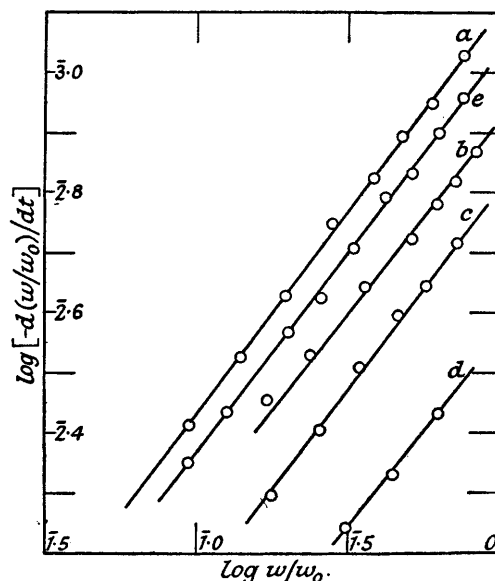
Typical curves of $\log_{10}[-d(w/w_0)/dt]$ versus $\log_{10}(w/w_0)$: Batch III: a, 350°; b, 335°; c, 320°; d, 305°; Batch II: e, 365°.

TABLE II.

Values of k for various preparations.

Batch.	k (hour ⁻¹), 335°.	k (hour ⁻¹), 365°.	Batch.	k (hour ⁻¹), 335°.	k (hour ⁻¹), 365°.
II	0.45	1.32	VIII	0.50	1.01
III	1.07	(2.27)*	X	0.50	0.78
IV	0.52	1.20	XII	0.35	0.52
V	0.48	—	XIV	—	1.03
VI	—	1.10	XVII	(0.50)†	1.43

* Extrapolated.

† Interpolated.

Erratic behaviour of this kind has frequently been reported. Thus Spencer and Topley (*J.*, 1929, 2633) found variations as great as 8-fold in the velocity of decomposition of silver carbonate, even with preparations made in as nearly as possible the same way. Also, the results of MacDonald and Hinshelwood (*J.*, 1925, 127, 2764) show about 10-fold increase in the maximum rate of decomposition

of silver oxalate when precipitated in presence of excess of sodium oxalate instead of excess of silver nitrate (see also MacDonald, *J.*, 1936, 832).

It was thought that these variations in the velocity constant might be related to changes in the internal area, and therefore in the micellar size, of the magnesium hydroxide. Accordingly, the adsorption isotherms of nitrogen at -183° were determined on several samples, having different velocity constants, by the "B.E.T." method (Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309). Typical isotherms of Type II (cf. Brunauer, Deming, Deming, and Teller, *ibid.*, 1940, **62**, 1723) were obtained and the monolayer capacity x_0 (proportional to the specific area) could consequently be derived from them by the usual "B.E.T." procedure. As will be seen from Table III, however, x_0 and k appear to be quite unrelated, so that the rate of decomposition is not determined primarily by micellar size.

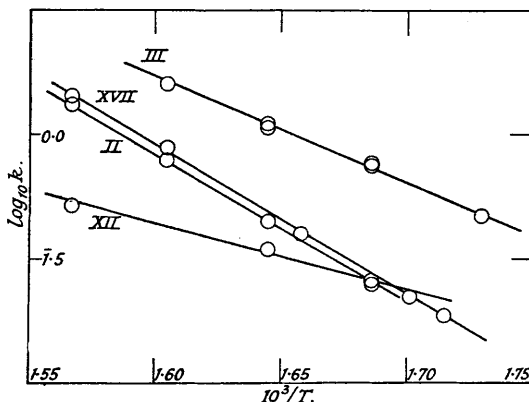
TABLE III.

Values of k and of monolayer capacity.

Batch.	k (hour $^{-1}$), 335 $^{\circ}$.	Monolayer capacity, x_0 (c.c./g.).	Batch.	k (hour $^{-1}$), 335 $^{\circ}$.	Monolayer capacity, x_0 (c.c./g.).
III	1.07	16.0	XII	0.35	16.9
VIII	0.50	16.9	Brucite O (10—20 mesh)	0.38	Unmeasurable

All the preparations had the same sieve size (80—150 mesh to the inch) and therefore the same average size of particles; but at the same time different batches showed variations up to 4-fold in the rate of sedimentation of the washed precipitate before drying. However, no correlation could be found between the rate of sedimentation and the velocity constant of decomposition.

FIG. 5.



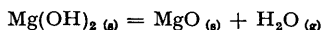
Curves of $\log_{10} k$ versus $10^3/T$ for Batches II, III, XII and XVII. Radius of circle is equivalent to 1° .

A more likely cause of the fluctuations in the velocity constant is a variation in the heat content of the hydroxide, or of the oxide, or of both. Fricke and Lücke (*Z. Elektrochem.*, 1935, **41**, 174) found a considerable difference, 2.7 kg.-cals. mol $^{-1}$, in the heat contents of two samples of magnesium oxide from the hydroxide, as measured by the difference in their heats of dissolution in acids, even though they had the same particle size as judged by X-rays. They showed that this resulted in a large difference in the dissociation pressure p_0 of the hydroxides, e.g., 1875 ~ 209 mm. of mercury at 350 $^{\circ}$. This large change in p_0 would, of course, alter the rate of dehydration at the same temperature by several-fold. The difference in heat content would be expected to depend on the history of the samples such as the adsorption of ions during precipitation which would cause lattice distortion, disorientation of the crystallites, and the like.

The variation in the heat content and therefore in p_0 explains also the experimental fact that the apparent energy of activation E varies from batch to batch. Since $k_0 = 3k\omega_0^{1/3}$, k may be substituted for k_0 in the Arrhenius equation, giving

$$d \log_e k / d(1/T) = E/R \quad \dots \quad (4)$$

Fig. 5 shows the plot of $\log_{10} k$ against the reciprocal of the absolute temperature, $1/T$, for each of preparations II, III, XII, and XVII; in each case the points fall satisfactorily on a straight line, but the slopes, and therefore the energies of activation, vary considerably. The values of E thus obtained are, in kg.-cals. mol $^{-1}$, II, 26.9; III, 19.6; XII, 12.4; XVII, 27.4. Except for Batch III they differ widely from the heat of dissociation of the reaction



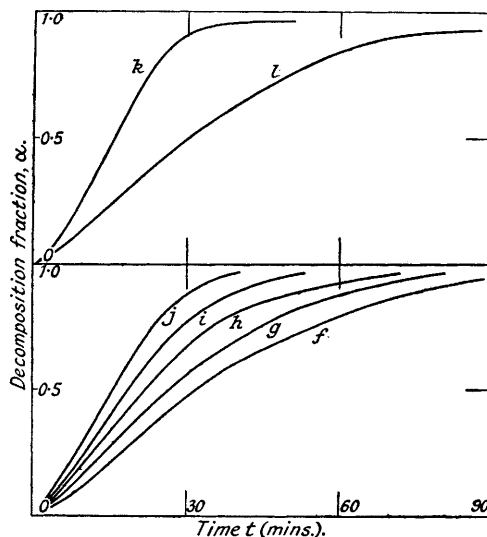
which is 20.24 kg.-cals. mol $^{-1}$ at 25 $^{\circ}$ according to Giauque and Archibald (*J. Amer. Chem. Soc.*, 1937, **59**, 561).

Brucite.—The dehydration of brucite does not give rise to a change in the external shape of the crystals, though they lose their semi-transparency and become opaque and brittle. The dehydration

curves are similar in shape to those of precipitated hydroxide, and the rate of decomposition is of the same order of magnitude. As already explained, the massive brucite can be easily cut and shaped, and accordingly a series of experiments was carried out in order to examine the effect of shape and size on the kinetics of decomposition. The brucite was first cleaved with a razor blade and the thin sheets so obtained were then cut across; this gave small pieces having measurable external surface area. Fig. 6 shows the dehydration curves of 0.5-g. samples of brucite comprising 1, 3, 7, 22, and 100 pieces respectively. Over the decay period (except near the end) the curves are represented by an equation similar in form to (1) but the index now varies quite definitely from case to case between the limits $1/2$ and $1/3$.

From Fig. 6 it is seen that the rate of decomposition increases somewhat as the particle size diminishes, but much less than proportionately to the total external area of the sample—a state of affairs similar to that noted in a variety of other decompositions by Hinshelwood and Bowen (*Proc. Roy. Soc.*, 1921, *A*, 99, 203), Farmer (*J.*, 1922, 121, 174), Garner and Gomm (*J.*, 1931, 2123), Garner and Hailes (*Proc. Roy. Soc.*, 1933, *A*, 139, 576), and others.

FIG. 6.



Dehydration curves of Brucite C in various states of subdivision at 365°: f, 1 piece; g, 3 pieces; h, 7 pieces; i, 22 pieces; j, 100 pieces; k, 40—80 mesh; l, 100—200 mesh.

In the present case, however, a correlation has been found between the average rate over a representative range of dehydration (20—40%) and the total area of the edges of the pieces perpendicular to the place of cleavage. [Owing to the variation of the index n of equation (1), comparison of absolute rates rather than of values of k is to be preferred.] This is seen by reference to Table IV. The results with one and with 100 pieces are particularly striking in this connection: the total external area is increased about 12-fold, but the rate has increased by some 2-fold only, as has the area of the edges. Data for powdered brucite C and O are added for comparison.

TABLE IV.

Effect of particle size on the rate of dehydration of brucite.

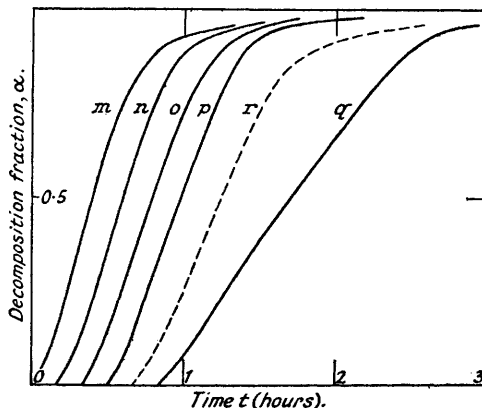
Series A: Brucite C, 365°	Area of planes of cleavage, cm. ²	Area of edges, cm. ²	$\Delta(w/w_0)/\Delta t$ (20—40% decomp.), hour ⁻¹ .
1 piece	1.74	1.04	1.12
3 pieces	3.12	1.16	1.30
3 "	3.12	1.17	1.30
7 "	4.60	1.47	1.52
22 "	15.6	1.42	1.80
100 "	30.0	2.15	2.02
40—80 mesh powder	—	—	2.26
100—200 "	—	—	1.34

Series B: Brucite O, 355°	$\Delta(w/w_0)/\Delta t$ (20—40% decomp.), hour ⁻¹ .
10—20 mesh flakes (ca. 550 pieces)	1.51
20—30 "	1.37
30—40 "	1.27
40—80 mesh powder	1.15
100—200 "	0.62

However, this increase of the rate with decreasing particle size does not continue indefinitely. Indeed, after passing through a maximum, the rate of dehydration falls considerably as the brucite is finely powdered. This is shown in Table IV and in Fig. 6a, which represents the dehydration curves of 0.5-g. samples of Brucite C of sieve size 40—80 mesh and 100—200 mesh at the same temperature, 365°.

That this fall in the rate is not fortuitous is confirmed by results with samples of 0.5 g. of Brucite O of varying particle size, obtained by crushing the brucite and sieving the product; the curves for mesh sizes 10—20, 20—30, 30—40, 40—80, and 100—200 are shown in Fig. 7 (the zero of time is displaced in order to prevent the overlapping of the curves). Equation (1) is again valid over the decay period except for the 100—200 mesh powder where the fit is not very good. The constant k in the first four cases varies between 0.81 and 0.74 hour⁻¹, and the average rate of dehydration for 20—40% decomposition between 1.51 and 1.15 hour⁻¹ (Table IV). It therefore seems clear that the rate of dehydration of brucite increases with decrease of particle size up to a maximum and then falls again with small particles.*

FIG. 7.



Dehydration curves of Brucite O at 355° (zero of time is displaced to prevent overlapping): m, 10—20 mesh; n, 20—30; o, 30—40; p, 40—80; q, 100—200; r, 10—20 mesh powder covered with 100—200 mesh Pyrex glass.

The effect of temperature on the rate of dehydration has been investigated for various particle sizes. The plots of $\log_{10} k$ against $1/T$ for samples of sieve size 10—20, 20—30, and 40—80 fall very nearly on straight lines yielding almost the same values of E , viz., 27.6 kg.-cals. mol.⁻¹. The results for the 100—200 mesh sample, when similarly plotted, give $E = 21$ kg.-cals. mol.⁻¹; although this value is of diminished accuracy owing to the divergence from equation (1), just noted, there is little doubt that the difference between it and the value for the coarser samples is in excess of experimental error.

DISCUSSION.

It is generally accepted that in the decomposition of solids, the reaction is initiated at certain centres, or nuclei, formed usually on the external surfaces of the solid and in some cases also on the surfaces of cracks and lattice imperfections. The reaction then spreads from these nuclei both along the surface and into the interior of the solid; for, according to Langmuir (*J. Amer. Chem. Soc.*, 1916, **38**, 2263), the reaction can proceed only at the interface between the reactant and its decomposition product, unless these form solid solutions. Various theories have been put forward to account for the kinetics of such reactions, and agreement between theory and experiment is very satisfactory in many cases. These theories (cf. Topley and Hume, *Proc. Roy. Soc.*, 1928, *A*, **120**, 211; Hume and Colvin, *Phil. Mag.*, 1929, **8**, 589; *Proc. Roy. Soc.*, 1929, *A*, **125**, 635; 1931, *A*, **132**, 548; Spencer and Topley, *J.*, 1929, 2633; Bradley, Colvin, and Hume, *Proc. Roy. Soc.*, 1932, *A*, **137**, 531; Garner and co-workers, *J.*, 1930, 47; 1931, 2123; 1933, 1393; *Proc. Roy. Soc.*, 1933, *A*, **139**, 576; *Science Progress*, 1938, **33**, 209; MacDonald, *J.*, 1936, 839; Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488; 1946, **42**, 468; Mampel, *Z. physikal. Chem.*, 1940, *A*, **187**, 43, 235; Erofejev, *Compt. rend. Acad. Sci. U.R.S.S.*, 1946, **52**, 511) differ somewhat in their postulates as to the laws of the formation and of the growth of nuclei.

* A similar effect has been found in these laboratories in the thermal decomposition of limestone and of calcite (unpublished work).

Perhaps the most comprehensive mathematical treatment of the decomposition of solids in the form of powder is that of Mampel (*loc. cit.*), who based it on two experimental generalisations found by earlier investigators, *viz.*, that the rate of formation of nuclei follows a unimolecular law, and that the interface which is the seat of the reaction, advances at a constant linear velocity v .

Considering the powder as composed of a large number of isotropic spheres of uniform radius r , Mampel derived a general expression for the decomposition fraction, based on probability considerations, and taking into account the *possibility of the overlapping* of the zones of decomposition spreading out from neighbouring nuclei. This expression reduces to simpler equations for three special cases: (1) The early period of the reaction covering the induction period for which the fraction decomposed (α) is approximately proportional to the fourth power of the time t , *i.e.*, $\alpha \propto t^4$; (2) the intermediate period, for which the equation

$$(v/r)t' = 1 - (1 - \alpha)^{1/3} \quad \dots \quad (5)$$

is a close approximation (cf. Topley and Hume; Spencer and Topley; *loc. cit.*); (3) the final period in which the decomposition tends towards the unimolecular law

$$\ln(1 - \alpha) = -k_1 t' + \text{const.}$$

In the last two cases $t' = (t - t_0)$, where t is the measured time and t_0 is evaluated from the experimental data.

Mampel showed that the limits of these three periods are determined by the ratio of r/v , so that for powders of relatively large radius most of the decomposition is confined to the region (1), whilst for very fine powder, practically the whole decomposition follows the unimolecular law of period (3); and for intermediate particles the decomposition is represented reasonably well by either of these expressions. The reason is that with large particles, the surface of each sphere becomes completely covered with zones of spreading nuclei long before the decomposition has proceeded to an appreciable depth, and henceforth the reaction interface moves as a contracting membrane approximating to a spherical shell; but with small particles, the rate-determining factor is the rate of nucleus formation and a particle is wholly consumed by the reaction which has spread from a single nucleus, before any other nuclei are formed at its surface.

The results of the present work are in general agreement with Mampel's theory. Thus the decomposition of precipitated magnesium hydroxide and of powdered brucite follow equation (5) over the decay period except near the end when the rate becomes much less than calculated. Indeed, the curve of decomposition approaches the line of complete dehydration asymptotically, instead of intersecting it at a finite angle and therefore at a finite time, as required by equations (1) and (5).

Another feature of particular interest in Mampel's work is his prediction that, as the particles of a powder decrease in size, the rate of reaction must increase to a maximum for a certain particle size and thereafter diminish. The results of experiments on brucite in various states of sub-division are in accord with this prediction, as is evident from Table IV.

At the same time it must be pointed out that there is an alternative explanation of this behaviour. The fact that the rate of reaction changes but slightly with large changes in particle size may denote that the nuclei can develop, not only on the external surface of brucite fragments, but also on the surface of smaller units (crystallites?) the total area of which would be scarcely affected by sub-division. And, in fact, microscopic examination of partly decomposed fragments reveals the presence of fairly numerous decomposition zones distributed at random in the interior of the sample. Ultimately, however, as the particle size increases, a point must be reached when the rate of escape of water molecules from the zones of decomposition begins to have an effect on the overall rate of the reaction; and as the easiest path of such escape would be the cleavage cracks, one would expect a rough proportionality between the measured rate and the total external area of the edges of the fragments composing the sample. It will be recalled that such a relationship was indeed found for unpowdered Brucite C (Table IV, Series A). On the other hand, when the particle size is sufficiently diminished, a bulk diffusion effect is to be expected: the water will be impeded not so much in its passage to the exterior of the particle, but rather in its passage through the powder as a whole. Some experiments were in fact done in which 0.5 g. of 10–20 mesh Brucite O was covered with a layer of 100–200 mesh powdered Pyrex glass weighing 0.5 g., and the rate of dehydration slowed down to a figure intermediate between that of the 10–20 mesh and that of the 100–200 mesh brucite (Fig. 7, broken line). If a bulk diffusion effect is present it would—because of its low temperature coefficient—diminish

the measured energy of activation; and such a diminution was indeed found with the 100—200 mesh powder as compared with the coarser samples, as already noted.

The two effects—that of Mampel and that due to diffusion—have quite different causes and could both operate at the same time. Without further experimentation, it is not possible at present to say whether one or both are present, and if the latter, what are the relative extents of the two.

Finally, it is of interest to compare the experimental rate of decomposition of brucite with that calculated by the Polanyi-Wigner expression (*Z. physikal. Chem.*, 1928, *A*, **139**, 439; cf. Topley and Hume, *loc. cit.*; Spencer and Topley, *loc. cit.*; Garner, *Science Progress*, *loc. cit.*), viz.,

$$- dx/dt = \nu N e^{-E/RT} \dots \dots \dots (6)$$

where $- dx/dt$ is the number of molecules decomposing per sec. per cm.^2 of interface; N , the number of "molecules" of reactant per cm.^2 ; ν the frequency of vibration of the lattice. N may be estimated roughly by taking the average distance of separation of the ions as 3.9 \AA . (the mean of the a and the c lattice parameter); whence $N = 1/(3.9 \times 10^{-8})^2$. Putting $\nu = 10^{13} \text{ sec.}^{-1}$ and $E = 27.6 \text{ kg.-cals. mol.}^{-1}$, we have $- dx/dt = 1.9 \times 10^{18} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$ at 355° .

Comparison of equations (2) and (5) shows that $h = \nu/r$. At 355° the experimental value of h is $0.74\text{--}0.81 \text{ hour}^{-1}$ for 10—80 mesh powder brucite. According to the arguments already adduced, $2r$ is most probably smaller than the aperture of an 80-mesh sieve, so that $r < 8 \times 10^{-3} \text{ cm}$. Provisionally accepting this figure, we have $\nu = 1.8 \times 10^{-6} \text{ cm. sec.}^{-1}$, whence the experimental rate of decomposition is $1.8 \times 10^{-6} \times 6.02 \times 10^{23} \times (2.43/58)$, i.e., $4.5 \times 10^{16} \text{ molecules cm.}^{-2} \text{ sec.}^{-1}$ (density of brucite = 2.43 , molecular weight = 58). This is some 40 times less than the calculated rate: but in view of the unavoidably approximate nature of this type of calculation (and the tacit assumption that brucite is isotropic), an agreement within two powers of ten is regarded as satisfactory (cf. Garner, *loc. cit.*, p. 220).

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