

5.27. When α is small, the calculation of § 5.24 applies when m is real, if we write m for iv . This leads to the values

$$\xi = \pm i \cot \frac{r\pi}{2m} \quad (r = 1, 2, 3, \dots), \quad (72)$$

corresponding to (50), and to

$$\xi^2 = \frac{1 - 4m^2}{2\alpha}, \quad \sigma^2 = \beta gkh, \quad (73)$$

corresponding to (53). The last equation gives a stable mode with the same expression for the speed, σ , as before, but (72) gives unstable modes, of which there are an infinite number for irrational m .

The Dehydration of Copper Sulphate Pentahydrate.

By JOHN HUME, B.Sc., and JAMES COLVIN, Ph.D., the University, Leeds.

(Communicated by R. Whytlaw-Gray, F.R.S.—Received March 28, 1931).

In a previous paper* were described the results of an investigation of the rate of dehydration of a hemihydrate, where the reaction presumably proceeds to completion without the occurrence of intermediate hydrates. In the course of the work it became evident that further information might be gained from the study of a dehydration reaction which could take place in several stages. For this purpose copper sulphate is eminently suitable since a penta-, a tri- and a monohydrate exist. It was hoped that by a choice of suitable conditions, the several stages of the reaction might be observed. The dehydration of copper sulphate pentahydrate has been extensively investigated, notably by Rae,† Crowther and Coutts,‡ and recently by Garner and Tanner.§

The most direct method of following the course of such a reaction is clearly the measurement of the rate of change of mass of a number of small crystals of uniform size. Then, if the reaction is assumed to occur at the interface

* Hume and Colvin, 'Proc. Roy. Soc.,' A, vol. 125, p. 635 (1929).

† 'J. Chem. Soc.,' vol. 109, p. 1229 (1916).

‡ 'Proc. Roy. Soc.,' A, vol. 106, p. 215 (1924).

§ 'J. Chem. Soc.,' p. 47 (1930).

separating the solid phases, values for the mean rate of linear propagation* can be derived. These values will have real significance only if the liberated water molecules are immediately removed from the mixture of reactant and resultant. The experiments of Rae and of Crowther and Coutts, made at atmospheric pressure are invalidated since the free diffusion of the water vapour was restricted by the air pressure. The results of Garner and Tanner obtained in high vacua will be considered in detail later.

Specimens of copper sulphate pentahydrate prepared by recrystallisation and sized by sieving, were examined under the microscope. It was considered that for simplicity the crystals might be treated as thin rectangular parallelepipeds of approximately equal length and breadth. On gently warming the crystals, it was found that nucleation proceeded rapidly over the entire surface. This suggests that the linear rate of propagation might be derived from the experimental curves by the application of a contracting rectangular parallelepiped formula (*cp.* Hume and Colvin, vol. 125 (1929), *loc. cit.*).

Let l = length (or breadth) of each crystal; θ = thickness; V = volume of each crystal = $l^2\theta$; t = time after the "arbitrary zero"; u = linear rate of propagation; α = fraction decomposed at time t ; then

$$\alpha = \frac{V - (l - 2ut)^2 (\theta - 2ut)}{V},$$

or

$$\alpha = \frac{2ut(l^2 + 2\theta l) - 4u^2t^2(2l + \theta) + 8u^3t^3}{l^2\theta}. \quad (I)$$

EXPERIMENTAL.

The experimental method was similar to that adopted for the measurement of the mass rate of decomposition of potassium hydrogen oxalate hemihydrate. In addition the balance case was in communication with an oil gauge in order that the effect of small gaseous pressures on the reaction might be determined. The loaded balance was lowered into the thermostat (maintained at $20.20 \pm 0.02^\circ \text{C.}$) and allowed to remain at atmospheric pressure for 15 minutes in order to attain the temperature of the bath. The balance case was then evacuated as rapidly as possible and readings of the extension started as soon as the buoyancy effect became negligible. Throughout the investigation crystals of the same size, and from the same preparation, were used except where otherwise stated.

* Hume and Colvin, 'Phil. Mag.', vol. 8, p. 589 (1929).

RESULTS.

I.—*Experiments in vacuo over Phosphorus Pentoxide.*

In these experiments the balance case contained a mass of phosphorus pentoxide to absorb the water liberated during the reaction. The evacuation was as complete as possible using a Hyvac pump in conjunction with a single stage mercury diffusion pump.

Fig. 1 shows the type of curve obtained. Complete decomposition corre-

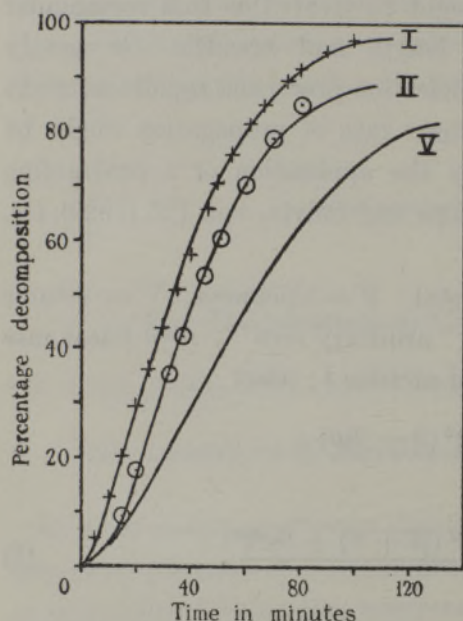


FIG. 1.

sponds to the complete conversion of the pentahydrate to monohydrate. It is to be noted that there is no evidence for the existence of more than one stage in the dehydration process. Furthermore, the general shape of the curve, having a very short induction period confirms the expectation that the rate of nucleation is very high. In consequence of this great rate of nucleation the crystals are rapidly enveloped in monohydrate, so that the effects of infection by contact are nullified. That is to say, even a single crystal can be regarded as typical of all the others in the decomposing mass. The close similarity in the form of the curves indicates the degree of reproducibility,

which is better shown by the calculation of the linear rate of propagation.

Derivation of the Linear Rate of Propagation.—In equation (I), the quantity θ is obtained by the direct measurement of the thickness of a large number of crystals whose lengths (a) and breadths (b) were also obtained. The quantity l was derived from the equation

$$l = \sqrt{(ab)}.$$

Incidentally for the size and shape of crystal used, a and b are approximately equal. Substituting the experimental values ($l = 0.136$ mm., $\theta = 0.060$ mm.) equation (I) becomes

$$\alpha = \frac{0.06932ut - 1.3248u^2t^2 + 8u^3t^3}{0.001103}. \quad (\text{II})$$

From this, by substituting arbitrary values for (ut) a curve can be obtained. From the experimental curve values for the percentage decomposition (100α) at any time t' from the start of the experiment can be read off and hence values of (ut) from equation (II). The magnitude t is the time measured from an arbitrary zero which would be required for crystals to attain the observed degree of decomposition if they had been completely nucleated at the arbitrary zero. In general t will be smaller than t' . To obtain values of u , the linear rate, from (ut) , the discrepancy between t and t' must be determined. On the basis of previous experience, assuming that u is a constant,

$$(ut)/t' - \Delta t = u \text{ (constant).}$$

Clearly, if these views are correct, the product (ut) should be a linear function of t' , the time from the start of the experiment. The intercept of the line (ut) , t' on the time axis gives the magnitude of the correction Δt . The results of the calculation for the runs (fig. 1, curves I and II) are shown in Table I.

Table I.

Curve I, $\Delta t = 5$ minutes.				Curve II, $\Delta t = 11.5$ minutes.			
t'	100α	ut	$u \times 10^4$ in mm./min.	t'	100α	ut	$u \times 10^4$ in mm./min.
10	12.2	0.00210	4.20	20	17.9	0.00310	3.26
15	20.4	0.00370	3.70	25	24.1	0.00420	3.11
20	29.2	0.00515	3.43	30	32.2	0.00580	3.13
25	37.1	0.00670	3.35	35	40.2	0.00735	3.13
30	45.5	0.00855	3.42	40	47.2	0.00990	3.10
35	52.9	0.01030	3.43	45	54.0	0.01060	3.16
40	59.7	0.01210	3.46	50	60.7	0.01240	3.22
45	66.9	0.01415	3.45	55	66.1	0.01400	3.22
50	71.4	0.01560	3.47	60	70.8	0.01540	3.18
55	76.0	0.01710	3.42	65	74.9	0.01675	3.13
60	80.2	0.01875	3.41	75	80.8	0.01895	2.98

The constancy of the values of u , the linear rate, obtained during the run, from 25 per cent. to 75 per cent. decomposition is satisfactory. Deviations in the earlier stages are to be anticipated from the nature of the assumptions, and in the later stages owing to the extinction of small particles and the increasing effect of errors in the estimation of the interfacial area. Table II contains the values of u derived from experiments carried out under identical conditions but at widely different dates.

Table II.

Date.	u in mm./min.
December 17, 1929	0.000345
January 28, 1930	0.000348
January 29, 1930	0.000317
July 26, 1930	0.000305
January 30, 1931	0.000290

The concordance amongst the results is satisfactory.

II.—*Influence of Pressure on the Decomposition Curve.*

Before proceeding to the specific effect of water vapour on the reaction, it is necessary to evaluate the effect of small pressures of a non-reacting gas. Accordingly the previous experiments were repeated with small pressures of air, dried by phosphorus pentoxide in the balance case and gave the results contained in Table III. The experiments dated December 18, 1929 and February 3, 1930, are shown graphically in fig. 1 as curves III and IV respectively. Only the points are shown since these so nearly coincide with curves I and II.

Table III.

Date.	Pressure in mm. mercury.	u in mm./min.
	0.002	0.000321*
December 18, 1929	0.9	0.000356
December 19, 1929	1.5	0.000328
February 3, 1930	2.7	0.000314
January 30, 1930	4.3	0.000263

* Mean value from Table II.

It will be seen that with the exception of the last experiment at a pressure of 4.3 mm. the agreement between the individual values is as good as that between the various runs under the same conditions *in vacuo*. At the highest pressure used, a distinct retardation of the reaction is noticeable, probably due to interference with the diffusion of the water vapour from the vicinity of the reaction.

III.—*Influence of Water Vapour on the Decomposition Curve.*

Since it has been established by the previous experiments that the rate of decomposition is substantially constant over a range of gaseous pressures, the

effect of low pressures of water vapour can be investigated. In the first place it was hoped that the primary reaction, namely, the conversion of the pentahydrate into trihydrate might be resolved by repeating the previous experiments with the substitution of a mixture of copper sulphate trihydrate and monohydrate in place of the phosphorus pentoxide. Under these conditions no reaction was observed. Various sulphuric acid-water mixtures capable of giving lower vapour pressures were used. Fig. 1, curve V, is typical of the results obtained. It was found that in those cases where reaction took place with measurable velocity, decomposition proceeded beyond the trihydrate stage without the slightest evidence of the formation of an intermediate hydrate. Increase in the water vapour pressure retards the reaction until finally complete stoppage is caused.

It is to be remembered that the velocity of a reaction of this kind is determined by two factors, namely, the rate of nucleus formation and the rate of propagation, each of which may be susceptible to the influence of water vapour. In view of this, vapour pressures too high for nucleation may allow the reaction to proceed once the nucleation has been effected. Preliminary experiments showed this to be the case.

A specimen of copper sulphate pentahydrate was partially dehydrated over phosphorus pentoxide *in vacuo*. When decomposition had proceeded to 27 per cent. the phosphorus pentoxide was replaced by a sulphuric acid-water mixture, too dilute to permit nucleus formation, and the run continued. Decomposition continued extremely slowly. The decomposition curve (fig. 2, curve I) shows a point of inflection in the neighbourhood of 50 per cent., corresponding to the formation of trihydrate. At 60 per cent. decomposition

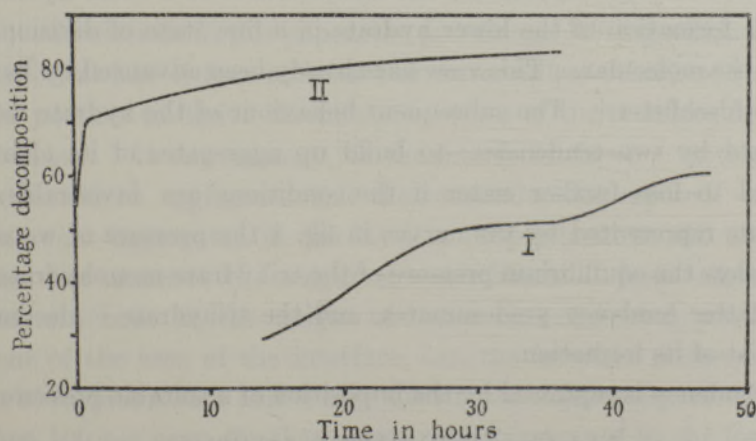
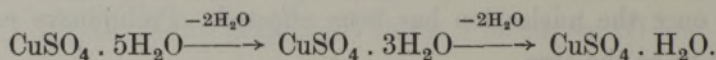


FIG. 2.

the sulphuric acid-water mixture was replaced by phosphorus pentoxide and the experiment continued *in vacuo*. During the replacement, water was absorbed from the atmosphere so that the apparent decomposition on re-evacuation was 54 per cent. Rapid decomposition to 71 per cent. was followed abruptly by very slow dehydration. Fig. 2, curve II, shows this stage of the reaction, zero time being the time of re-evacuation.

Discussion of Results.

The results obtained *in vacuo* and at low pressures of water vapour support the theory that the rate of loss of four molecules of water is controlled by the linear rate of advance of the interface between the solid phases. The existence of this interface has been observed by Garner and Tanner (*loc. cit.*) at temperatures below 56° C. The reaction at the interface requires further consideration, in that, although the curves in fig. 1 show no evidence of more than one stage in the reaction, this does not preclude the possibility that the process actually occurs in two stages, namely,



Provided that the second stage proceeds immeasurably fast compared with the first stage and that the water liberated can diffuse through and evaporate rapidly from the decomposed material then the type of curve obtained is to be anticipated. This view necessarily leads to the assumption that the effective interface is one between penta- and trihydrate, the latter having but momentary existence.

It is to be expected that in most cases, where the reactant and the resultant have different crystal structures, the dehydration of a solid hydrate would lead to the formation of the lower hydrate in a fine state of division approximating to the molecular. This view has already been advanced by Partington* and by Kohlschütter.† The subsequent behaviour of the hydrate would then be governed by two tendencies—to build up aggregates of its characteristic lattice and to lose further water if the conditions are favourable. In the experiments represented by the curves in fig. 1 the pressure of water vapour is so far below the equilibrium pressure of the trihydrate-monohydrate mixture that the latter tendency predominates, and the trihydrate is decomposed in the moment of its formation.

If this tendency is repressed by the imposition of a suitable pressure of water

* 'J. Chem. Soc.,' vol. 99, p. 466 (1911).

† 'Helv. Chim. Act.,' vol. 13, p. 978 (1930).

vapour, the aggregation takes place to form relatively massive particles of trihydrate, whose rate of dehydration will depend on the rates of nucleus formation and of linear propagation. If these rates are small compared with the corresponding rates for the reaction, pentahydrate \rightarrow trihydrate, a curve showing a break in the neighbourhood of 50 per cent. decomposition should be obtained. That these conditions can be realised experimentally is shown by fig. 2, curve I. An interesting intermediate case is afforded by curve V, fig. 1, in which the life of the finely divided trihydrate is prolonged enough to permit aggregation to some slight extent. Thus the extent of decomposition of the pentahydrate to trihydrate and of finely divided trihydrate to monohydrate, after 12 hours corresponds to 84.8 per cent. decomposition. Beyond this stage no further reaction could be detected, suggesting that the vapour pressure of water is too high to allow nucleation of the aggregated trihydrate so that its decomposition is prevented although it is in a metastable condition. Consequently copper sulphate pentahydrate dehydrated over sulphuric acid-water mixtures yields a mixture of tri- and monohydrate, whose composition is a function of the water vapour pressure imposed on the system. Since similar considerations are applicable to the dehydration of monohydrate it might be expected that with low pressures of water vapour a small amount of anhydrous copper sulphate would be formed. This is shown by the results in Table IV.

Table IV.

Percentage H_2SO_4	100	100	90	90	80	80
Percentage D = 100a	102.9	101.6	96.8	97.0	92.5	92.6

As in all the calculations in this paper, the percentage decomposition is referred to the theoretical loss of four molecules of water unless otherwise stated.

It is now possible to derive the rate of advance of the interface in presence of water vapour. At any moment, in the interfacial layer a certain amount of trihydrate will be aggregated and the remainder decomposed. Assuming that the amount aggregated in the layer is proportional to the area of the interface at that moment, the weight of water liberated from trihydrate will bear a constant ratio to the weight of water liberated from pentahydrate, independent of the area of the interface, *i.e.*, the interface advances leaving a mixture of monohydrate and evenly distributed aggregates of trihydrate. Clearly then 100 per cent. for these cases corresponds, not to the loss of four molecules of water, but to the point represented by the final composition of

the mixture. The data afforded by curve V, fig. 1, are recalculated on this basis in Table V.

Table V.

t' .	D.	t .	100 α .	ut .	u in mm./min.
mins.		mins.			
40	29.3	21.5	34.5	0.00615	0.000286
50	38.3	31.5	45.1	0.00845	0.000268
55	42.9	36.5	50.6	0.00978	0.000268
60	47.3	41.5	55.8	0.01108	0.000267
70	55.6	51.5	65.5	0.01380	0.000268
80	62.9	61.5	74.2	0.01650	0.000268
90	68.7	71.5	81.0	0.01900	0.000266
102	74.4	83.5	87.7	0.02200	0.000263
—	84.8	—	100.0	—	—

The constant value obtained for u is, as would be expected, lower than that obtained in the absence of water vapour.

Garner and Tanner have remarked on the absence of an interface in the dehydration of trihydrate produced by the decomposition of pentahydrate. On the arguments advanced above such an interface is not to be expected.

Experimental.

A series of experiments was undertaken to investigate the effect of rehydration of monohydrate. It was to be expected that an accelerated mass reaction rate would be observed for the dehydration of pentahydrate thus formed. Whilst this was realised the effects proved much more complex than had been anticipated. Four typical experiments are shown in fig. 3.

Curve I.—A specimen of copper sulphate pentahydrate was completely converted to monohydrate on the

balance *in vacuo* over phosphorus pentoxide. Rapid rehydration to pentahydrate was then effected by exposure to saturated water vapour, the

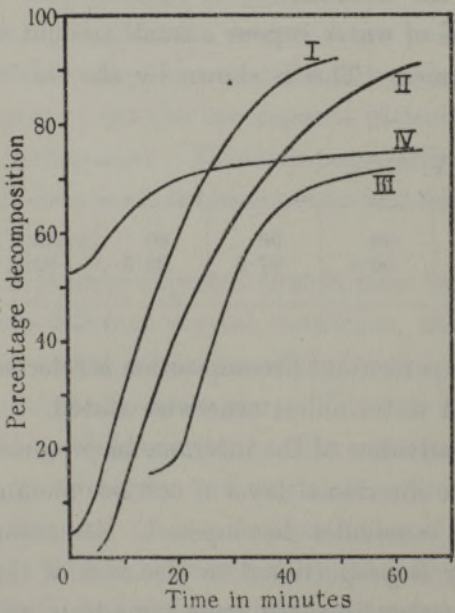


FIG. 3.—Curve II is displaced 5 minutes to right; curve III is displaced 15 minutes to right.

process occupying approximately 30 minutes. Care was taken to prevent the absorption of excess of water. The rate of dehydration was measured over phosphorus pentoxide in the usual way.

Curve II.—Similar procedure was followed in this case, except that the rehydration was effected more slowly and required 90 minutes for completion. Experiments allowing as long as 90 hours gave substantially the same results.

Curve III.—In this case incomplete rehydration over sulphuric acid for 270 minutes resulted in the formation of a mixture of penta- and trihydrate which was then dehydrated as before.

Curve IV.—Very rapid partial rehydration was followed immediately by dehydration as before.

Discussion.

In general complete rehydration of the finely divided monohydrate must produce pentahydrate in a state of division much finer than that of the original crystals. The actual size will depend on the extent to which aggregation in the hydrated mass is possible, so that the time occupied by the rehydration process will be a factor of importance. Comparison of curves I and II shows that aggregation can proceed in the absence of water for more than 30 minutes, but its effect becomes inappreciable after 90 minutes.

In curve III, the effects of aggregation of the trihydrate are again apparent. The steep portion of the curve corresponds to the decomposition of pentahydrate and the finely divided trihydrate resulting therefrom, but the trihydrate aggregates decompose at a slower rate. Curve IV is a somewhat similar case where rehydration was carried out approximately to the trihydrate stage. Apparently some pentahydrate was produced, so that a core of monohydrate must have remained. The presence of this small amount of pentahydrate accounts for the initial rapid rate, the subsequent slow rate representing the normal slow decomposition of the aggregated trihydrate. In this experiment although the rehydration was as rapid as possible, aggregation to a considerable extent must have occurred. Curve II of fig. 2 is to be explained in a similar way.

Discussion of Results of Garner and Tanner.

The results of Garner and Tanner, published during the course of this investigation, afford a considerable amount of data which may be used to test the conclusions reached in the preceding sections. In their experiments the rate of dehydration of single large crystals of copper sulphate pentahydrate was measured in high vacua over a range of temperatures.

Although the shape of the crystals is not detailed, measurements of the mass, thickness and superficial area of each crystal are given. Making the assumption that the crystals are rectangular parallelepipeds of equal length and breadth, values for the length can be calculated from the mass and thickness which yield a superficial area in reasonable agreement with that observed. Values for the linear rate can then be derived from equation (I). Details of two experiments (I and II) are given in Tables VI and VII.

Table VI.

Temperature 36.5°C. ; weight 0.339 gm. ; area 2.4 cm.^2 ; $\Delta t = -0.75\text{ hour}$; thickness $= 0.205\text{ cm.}$; length $= 0.855\text{ cm.}$

t' in hours.	100 a .	ut .	u in cm./hr.
2	18.5	0.0135	0.00509
4	33.3	0.0254	0.00535
6	46.4	0.0365	0.00541
8	57.8	0.0477	0.00545
10	68.2	0.0588	0.00547
12	76.9	0.0690	0.00541
13	80.6	0.0737	0.00536

Table VII.

Temperature 36.5°C. ; weight 0.216 gm. ; area 1.96 cm.^2 ; $\Delta t = -1.0\text{ hour}$; thickness $= 0.144\text{ cm.}$; length $= 0.814\text{ cm.}$

t' in hours.	100 a .	ut .	u in cm./hr.
2	26.8	0.0150	0.00500
4	47.7	0.0285	0.00570
6	64.6	0.0406	0.00580
8	78.8	0.0520	0.00578
9	84.3	0.0567	0.00567

The agreement of the values of u , the linear rate is striking in view of the difference of the dimensions of the crystals.

Table VIII contains the values of u derived in this way from the data of Garner and Tanner.

Table VIII.

Experiment number.	Temperature, ° C.	u in cm./hr.
VIII	20·5	0·00188
VII	21·5	0·0018
VI	26·5	0·0029
III	36·5	0·0055
II	36·5	0·0057
I	36·5	0·0054
IV	35·1	0·0048
X	46·0	0·0078
IX	46·25	0·0087

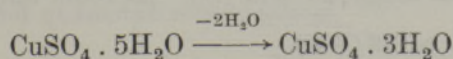
The numbers in the first column refer to the number of the experiment in the original paper. On plotting $\log u$ against $1/T$ a line results, giving an energy of activation of 11,400 calories, which will be a minimum value because of the effect of self-cooling. Extrapolating this line to 20° C. gives the value $u = 0·000305$ mm. per minute in numerical agreement with the mean value given in Table I, namely, 0·000321 mm. per minute. This agreement might be fictitious unless it is established that different specimens of copper sulphate pentahydrate give the same linear rate. To test this a number of preparations of pentahydrate were examined. Reasonably constant values for the linear rate were obtained, justifying the comparison of our value with that of Garner and Tanner. We wish to acknowledge our indebtedness to Mr. M. M. Krupeney for carrying out these latter experiments.

It is hoped to make the quantitative investigation of the influence of water vapour on the linear rate the subject of a further communication. In conclusion we wish to thank the Government Grants Committee of the Royal Society for a grant to one of us (J. H.) which defrayed part of the costs of this investigation, and to Professor R. Whytlaw-Gray, F.R.S., for his continued interest in this work.

Summary.

Measurements have been made *in vacuo* of the rate of dehydration of copper sulphate pentahydrate at 20° C., using uniform particles of known size.

The results have been analysed by a method which enables the linear rate of propagation of the reaction



through the pentahydrate lattice to be determined.

A brief investigation of the effects of increasing the air and water vapour pressure was attempted.

Evidence has been obtained that a solid hydrate on decomposition gives rise to a layer of material of almost molecular size. This will possess two tendencies, namely, to aggregate and to decompose. Whether one or the other will predominate depends on the surrounding conditions.

Aggregation and slow nucleation account for the persistence in mixtures of hydrates of a hydrate which is metastable under the vapour tension conditions of the environment.

On the Change of Resistance of Nickel in a Magnetic Field.

By H. H. POTTER, Ph.D., Lecturer in Physics, University of Bristol.

(Communicated by A. P. Chattock, F.R.S.—Received March 30, 1931.)

In a recent paper Gerlach and Schneiderhan* have described a series of experiments on the resistance of nickel considered both as a function of the temperature and as a function of an external field applied parallel to the wire.

In the absence of an external field the change of resistance with temperature can be considered as made up of two terms, the first being due to the result of the ordinary temperature coefficient of resistance, and the second (ΔR) being proportional to the energy of spontaneous magnetisation.† According to the Weiss theory this energy of spontaneous magnetisation is equal to $-\frac{1}{2}n\sigma^2$, where n is the constant of the intramolecular field and σ the volume intensity of magnetisation. Plotting ΔR against T , and σ^2 against T , Gerlach and Schneiderhan obtained curves which were coincident over the whole range from room temperature to the Curie point. The agreement is extraordinarily close and leaves no doubt as to the intimate connection between ΔR and σ^2 .

In addition to this change of resistance with temperature, Gerlach and Schneiderhan examined the change of resistance at constant temperature in an external longitudinal magnetic field (H). At room temperature an increase

* 'Ann. Physik,' vol. 5, p. 772 (1930).

† The energy of magnetisation is not magnetic in origin, but according to Heisenberg it is due to the exchange of electrons controlled by the alignment of spins.