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DSC STUDY OF THE KINETICS OF THE THERMAL DEHYDRATION OF $BaCl_2 \cdot 2H_2O$ AND $BaCl_2 \cdot H_2O$

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The kinetics of the thermal dehydration of various kinds of $BaCl_2 \cdot 2H_2O$ and of $BaCl_2 \cdot H_2O$ are investigated using a differential scanning calorimeter. The loss of H_2O proceeds in two steps:

$$BaCl_2 \cdot 2H_2O \rightarrow BaCl_2 \cdot H_2O \rightarrow BaCl_2$$

and is therefore revealed by two endothermic peaks.

In the experiments at varying temperature both steps follow a contracting-circle law, after an initial acceleratory stage according to a ($n = 2$) power law.

In the experiments at constant temperature, after an initial acceleratory stage according to a ($n = 2$) power law, both steps (except $BaCl_2 \cdot 2H_2O$ single-crystals which follow a contracting-circle law) follow an Avrami-Erofeev law (with $n = 2$) in the form used by Galwey and Jacobs. The activation energies for the various steps are compared and the different kinetic behaviour is discussed.

Barium chloride dihydrate has long been known [1] to lose its water under heat treatment in two steps, according to the equations:

$$BaCl_2 \cdot 2H_2O = BaCl_2 \cdot H_2O + H_2O \quad (1)$$

$$BaCl_2 \cdot H_2O = BaCl_2 + H_2O \quad (2)$$

The kinetics of the dehydration of $BaCl_2 \cdot 2H_2O$ have previously been studied by Ingraham and Rigaud [2] by means of gaseous thermal conductivity measurements using highly compressed pellets of cylindrical shape. As it is known that the different "history" of the sample very often leads to different results, the aim of this work is to study the kinetics of dehydration of crystalline powders and single-crystals of $BaCl_2 \cdot 2H_2O$, and of powders of $BaCl_2 \cdot H_2O$ obtained either by decomposition of the dihydrate or by crystallizing an alcoholic solution of the dihydrate.

Experimental

a) *Materials.* A standard batch of barium chloride dihydrate was prepared by twice crystallizing a commercial product (Erba R. P.) from a solution in conductivity water. Samples from the standard batch, having a grain size of about

2 μ, were used as such and dissolved in conductivity water in order to obtain single-crystals by slow evaporation.

The X-ray diffraction patterns of these materials agree with the A. S. T. M. standards.

Among the single-crystals of the dihydrate obtained, those which best fitted the description of Groth [3] were selected; these, in the form of pseudohexagonal plates, were 0.5 mm thick and 3–4 mm large.

Microscopic examination with crossed Nicols showed the existence of twinning [4] in almost every crystal; the effect of twin boundaries on nucleation and growing was not studied in detail, but a retarding action on the surface spreading of nuclei of $BaCl_2 \cdot H_2O$ on the (010) surface of $BaCl_2 \cdot 2H_2O$ single-crystals was observed.

Barium chloride monohydrate was obtained as the product of reaction 1 and by slow evaporation of a methanol solution of the standard dihydrate [1]. The X-ray diffractograms of both samples were obtained, showing that the monohydrate resulting from dihydrate decomposition did not attain a perfect crystallinity.

For both $BaCl_2 \cdot 2H_2O$ and $BaCl_2 \cdot H_2O$ the amount of water lost was found to be strictly stoichiometric.

b) *Methods*. The decomposition kinetics were investigated by means of a Perkin-Elmer, mod. DSC-1B, differential scanning calorimeter, operating with a flow of dry nitrogen of 30 ml/min, at various sensitivities and scan speeds, and at constant temperatures. The calibration of our calorimeter was made using the transitions and the melting of NH_4NO_3, and the melting of high-purity indium. An empty pan was used as reference.

As the different thermal emissivity between sample and reference caused a gradual shift of the base line, aluminium sample holder covers were used, in which nine holes of 1 mm diameter were bored in order to ensure a free escape of water vapour while lowering the difference of thermal emissivity. In some experiments the escape of water vapour was also detected by means of the thermal conductivity cell included in the calorimeter to perform the effluent gas analysis.

The decomposition of single-crystals of $BaCl_2 \cdot 2H_2O$ was also investigated, in a stream of dry nitrogen and at constant temperature, by means of the hot stage of a Panphot Leitz microscope.

Results and discussion

The characteristic two-stage curve of $BaCl_2 \cdot 2H_2O$ at varying temperature is shown in Fig. 1a. From the peak areas measured by means of a polar planimeter, ΔH values were evaluated as 12.8 ± 0.8 kcal/mole for the dihydrate–monohydrate step; and 13.2 ± 0.8 kcal/mole for the monohydrate–anhydrous step (14.7 ± 0.9 kcal/mole if the monohydrate is prepared by crystallization from alcoholic solution). These values appear to be somewhat lower than those reported by Ingraham and Rigaud but are in rather good agreement with the results of other authors quoted in the same paper.

The kinetic analysis was performed following the method suggested by Thomas and Clarke [5]. A number of equations commonly used for the kinetics of decomposition of solids [6] were taken into consideration and modified for use with the results of differential scanning calorimetry.

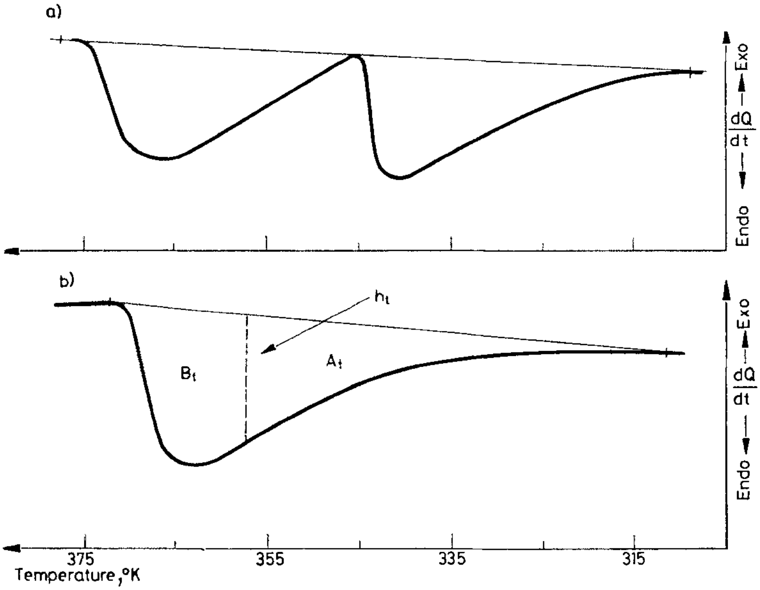

Fig. 1. a) Characteristic two-step DSC curve of the dehydration of $BaCl_2 \cdot 2H_2O$ (mg 5.15, scan speed 2°K/min, chart speed 0.0106 cm/sec, sensitivity 4 mcal/sec). b) DSC curve of the dehydration of $BaCl_2 \cdot H_2O$ crystallized from methanol, (mg 8.28, scan speed 2°K/min, chart speed 0.0106 cm/sec, sensitivity 4 mcal/sec)

The "contracting-sphere" equation:

$$1 - (1 - \alpha)^{1/3} = kt$$

was differentiated to give:

$$\frac{d\alpha}{dt} = \frac{3k(1 - \alpha)}{(1 - \alpha)^{1/3}} \tag{3}$$

The equation given by Thomas and Clarke [5] for DSC

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \cdot \frac{dH}{dt} \tag{4}$$

relates $\frac{d\alpha}{dt}$ to measured quantities. In fact ΔH is proportional to the total area A (cm^2) under the peak according to the relation:

$$\Delta H = A \cdot R/S \cdot W \tag{5}$$

where R is the sensitivity $\left(\frac{\text{millical}}{\text{sec}}\right.$ for full-scale deflection ; S is the chart speed $\left(\frac{\text{cm}}{\text{sec}}\right)$ and W is the chart width (cm) of the pen recorder. Moreover $\frac{dH}{dt}$ is proportional to the height h_t (cm) of the peak from the base-line at a certain temperature according to the relation [7]:

$$\frac{dH}{dt} = h_t \cdot R/W \tag{6}$$

Substituting (5) and (6) into (4) gives

$$\frac{d\alpha}{dt} = h_t \cdot S/A \tag{7}$$

and substituting this result into (3) one obtains

$$\frac{h_t \cdot S}{A} = \frac{3K(1-\alpha)}{(1-\alpha)^{1/3}} \tag{8}$$

Now, $\alpha = A_t/A$ and $B_t = A - A_t$ (see Fig. 1b); substituting into (8), (9) is easily deduced, relating the rate constant to directly measured quantities:

$$K = \frac{h_t S}{3B_t} \cdot \left(\frac{B_t}{A}\right)^{1/3} \tag{9}$$

By the same procedure the "contracting-circle" equation

$$1 - (1-\alpha)^{1/2} = k \cdot t$$

becomes

$$k = \frac{h_t S}{2B_t} \cdot \left(\frac{B_t}{A}\right)^{1/2}$$

and the "Avrami-Erofeev" equation in the form used by Galwey and Jacobs [8]

$$-\ln(1-\alpha) = (k \cdot t)^n$$

gives

$$k = \frac{h_t \cdot S}{n \cdot B_t} \cdot \frac{(\ln A/B_t)^{1/n}}{\ln A/B_t}$$

The above equations, together with the modified forms of the power law: $\alpha = k \cdot t^n$, the first order law: $-\ln(1-\alpha) = kt$, and the Prout-Tompkins law: $\ln \alpha/(1-\alpha) = kt + c$, were used in order to ascertain which gave the best fit to the experimental data and the best alignment of the $\ln k$ values in the Arrhenius plot.

The experiments made at varying temperature, for the first step of dehydration, show that single-crystals and crystalline powders behave in much the same way, following a contracting-circle equation, as seen in Fig. 2, where the ln k values are plotted against $1/T$ in the Arrhenius diagram. The slopes of the rectilinear portions give an activation energy of 22.6 ± 1.3 kcal/mole for powders and single-crystals.

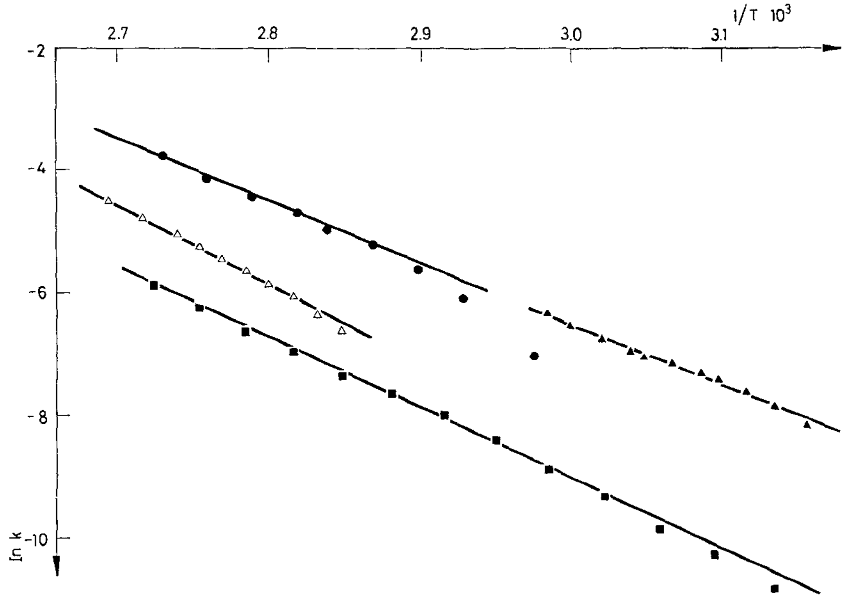

Fig. 2. Arrhenius plots for dehydrations at varying temperature: ▲ dihydrate – monohydrate (single crystals); ● dihydrate – monohydrate (powders); △ monohydrate – anhydrous (powders from preceding decomposition); ■ monohydrate – anhydrous (powders from methanol)

The same holds for the monohydrate–anhydrous reaction, and the Arrhenius plot (see Fig. 2) shows the applicability of the contracting-circle equation. An activation energy of 24.5 ± 1.5 kcal/mole is calculated from the slope for powders obtained by decomposing the dihydrate.

Contracting-envelope kinetics were also found by Ingraham and Rigaud [2] who gave for the activation energies the values of 18.0 ± 1.2 – 19.0 ± 2.2 kcal/mole and 26.6 ± 4 – 26.7 ± 3.6 kcal/mole for the dihydrate and monohydrate, respectively.

For both dehydration reactions, the contracting-circle equation was not applicable to the early stages of decomposition. This is better seen when low scan-speeds are used (0.5 – 1 °K/min), indicating that when the decomposition of solids takes place in a number of stages (e.g. according to Mampel's theory [9]), some of them may be concealed unless differential thermal methods are used with care.

For the runs at low scan-speeds, a power law with $n = 2$ was found to fit the experimental results rather well in the range $0 < \alpha < 0.10 - 0.15$, showing the existence of an acceleratory stage which, however, seems to have a similar activation energy.

In the case of the dehydration of monohydrate crystallized from methanol, it was expected that, using low scan-speeds, the acceleratory stage might be evidenced better. This was not confirmed by the experimental results; in fact in this case the contracting-circle equation fits the experimental data starting from the very beginning of the dehydration reaction: the activation energy value is 21.7 ± 1.1 kcal/mole (see Fig. 2). A lower value ($22.8 \pm 4 - 24.3 \pm 4.4$ kcal/mole) for the activation energy has also been reported by Ingraham and Rigaud for runs made using $BaCl_2 \cdot H_2O$ not obtained from the decomposition of the dihydrate.

The results obtained at varying temperature are collected in Table 1.

Table 1

Experiments at varying temperature

Reaction	Material	Kinetic law	Range of validity	E_a (Kcal/mole)
$BaCl_2 \cdot 2H_2O \rightarrow$	Single crystals	Contr. circle	$0.1 < \alpha < 1$	22.6 ± 1.3
$\rightarrow BaCl_2 \cdot H_2O$	Powders	Contr. circle	$0.1 < \alpha < 1$	22.6 ± 1.3
$BaCl_2 \cdot H_2O \rightarrow$	Powders from preced. dehydr.	Contr. circle	$0.1 < \alpha < 1$	24.5 ± 1.5
$\rightarrow BaCl_2$	Powders from methanol	Contr. circle	$0.1 < \alpha < 1$	21.7 ± 1.1

It seems that for the monohydrate–anhydrous reaction the rather rapid nucleation stage is somewhat hindered when the reactant is crystallized imperfectly; the same happens for the progress of the reaction interface towards the center of the crystal, as shown by the slightly different values found for the activation energy.

In order to gain more information, a number of experiments were performed for both decompositions, at various constant temperatures, not far above the temperatures at which the non-isothermal curves showed the first deflection from the base line.

The $T =$ const. curves were treated as previously described in order to determine α at measured t values.

α/t was then plotted against t to ascertain which law gave the best fit to the experimental points. In fact such a plot is helpful in distinguishing which of the power, the contracting-circle and the Avrami-Erofeev laws was followed.

From the $n = 2$ power law, $\alpha = kt^2$, we obtain:

$$\frac{\alpha}{t} = k \cdot t$$

so we could expect a straight line of positive slope (= k) passing through the origin (Fig. 3).

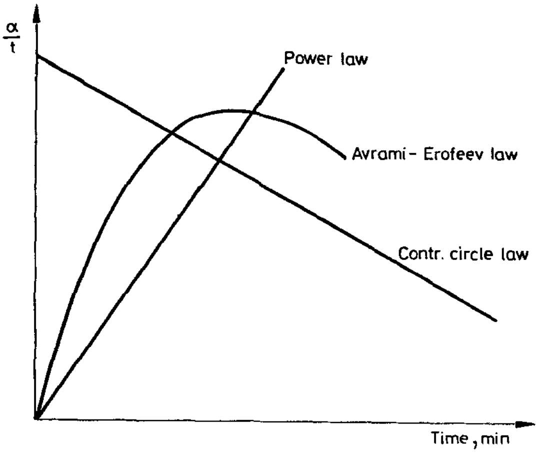

Fig 3 Theoretical $\frac{\alpha}{t}$ vs. t curves

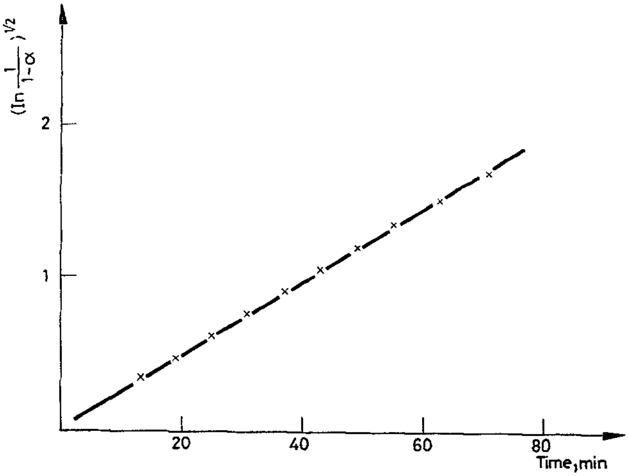

Fig. 4. Plot of $\left(\ln \frac{1}{1-\alpha}\right)^{1/2}$ vs. t for an experience at constant temperature

From the $n = 2$ Avrami-Erofeev law $-\ln(1-\alpha) = (kt)^2$, we obtain

$$\alpha = 1 - \left(1 - k^2t^2 + \frac{k^4t^4}{2}\right) = k^2t^2 - \frac{k^4t^4}{2}$$

$$\frac{\alpha}{t} = k^2t - \frac{k^4t^3}{2}$$

(assuming kt small) and a maximum is expected (Fig. 3).

From the contracting circle equation $1 - (1-\alpha)^{1/2} = kt$, we have

$$1 - \alpha = (1 - kt)^2$$

$$\alpha = 2kt - k^2t^2$$

$$\frac{\alpha}{t} = 2k - k^2t$$

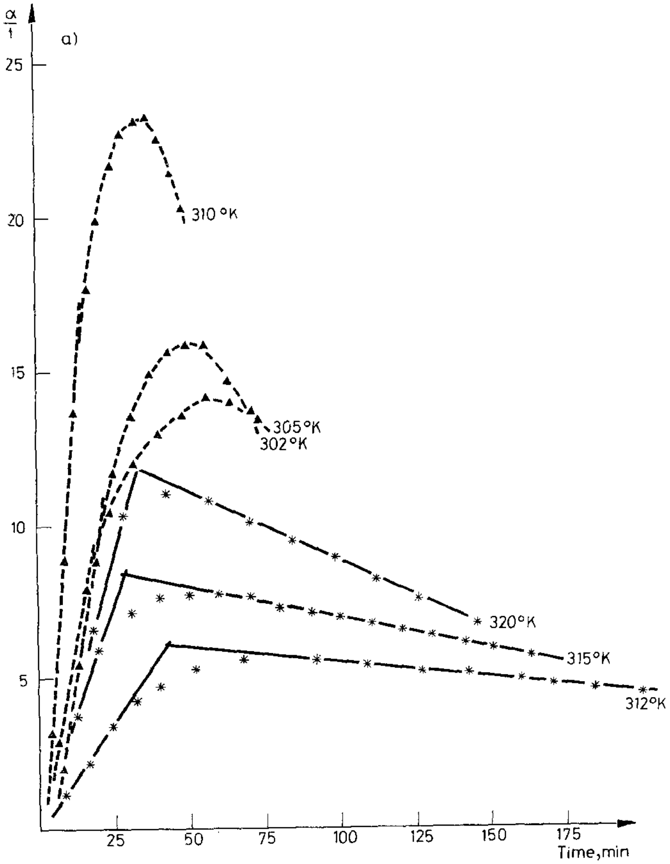

Fig. 5a. $\frac{\alpha}{t}$ vs. t plots for experiences at constant temperature. ✱ dihydrate–monohydrate (single crystals); ▲ dihydrate–monohydrate (powders).

so we could expect a straight line of negative slope, which crosses the ordinate axis in the point $2k$ (Fig. 3).

In the case of the validity of the Avrami-Erofeev law, the value for the rate constant was obtained by plotting $\left(\ln \frac{1}{1-\alpha}\right)^{1/2}$ vs. t. A straight line results which passes through the origin and has a positive slope ($=k$) (see Fig. 4).

It is noteworthy that, at constant temperature, after the initial power law period, a better fit to the experimental results is found using an ($n = 2$) Avrami-Erofeev equation rather than the expected contracting-circle one, whose applicability seems to be limited only to the dehydration of $BaCl_2 \cdot 2H_2O$ single-crystals.

The above observations are confirmed by plotting (Fig. 5) the experimental data in a graph of $\frac{\alpha}{t}$ vs. t. Thus, for single-crystals, a power law (with $n = 2$) is found to be applicable in the initial part, with a corresponding activation energy

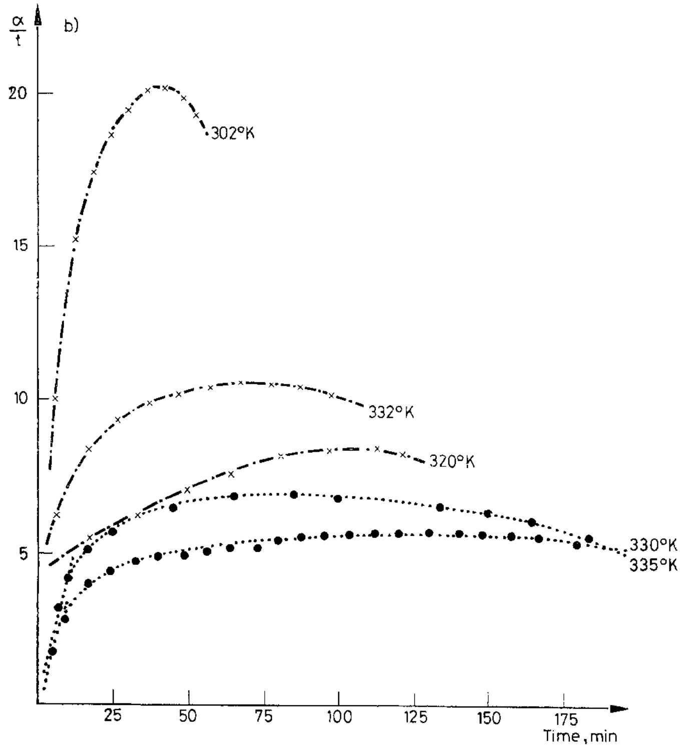

Fig. 5b. $\frac{\alpha}{t}$ vs. t plots for experiences at constant temperature: a) ● monohydrate—anhydrous (powders from preceding dehydration); × monohydrate—anhydrous (powders from methanol)

of 18 ± 4 kcal/mole; while for further decomposition a contracting-circle equation, with an activation energy of 16.5 ± 1 kcal/mole, is more suitable (Fig. 6).

For crystalline powders the dihydrate–monohydrate reaction after a power law ($n = 2$) period with an activation energy of 20.0 ± 4.5 kcal/mole, follows the Galwey and Jacobs form of the Avrami-Erofeev equation (with $n = 2$), and the $\ln k$ values, obtained by plotting $\left(\ln \frac{1}{1-\alpha}\right)^{1/2}$ vs. t, give a straight line in the Arrhenius diagram with an activation energy of 18.8 ± 1.2 kcal/mole.

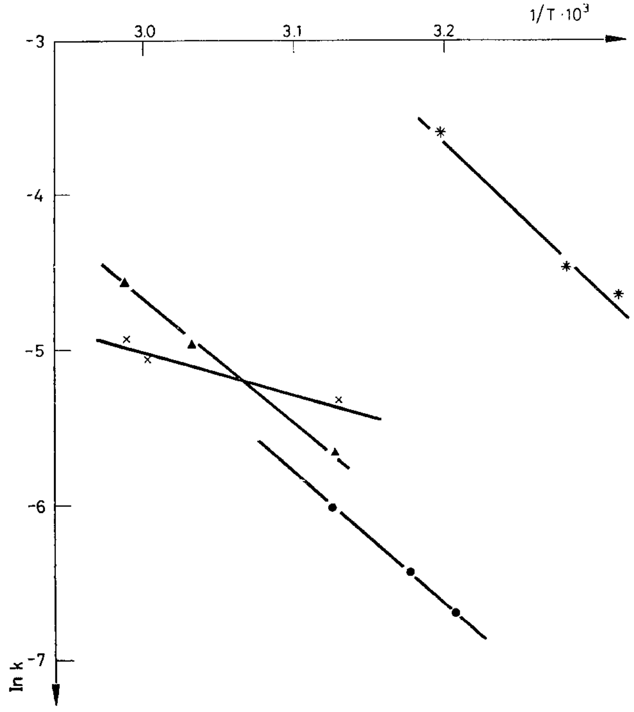

Fig. 6. Arrhenius plots for experiences at constant temperature: ✱ dihydrate—monohydrate (single crystals); ▲ dihydrate—monohydrate (powders); × monohydrate—anhydrous (powders from preceding dehydration); ● monohydrate—anhydrous (powders from methanol)

The results are collected in Table 2.

It is noteworthy that for reactions (1) and (2) the two observed stages show about the same activation energy.

For the dehydration of the monohydrate, obtained from dihydrate, the $\frac{\alpha}{t}$ vs. t plot shows some peculiarities, namely:

Table 2

Experiments at constant temperature

Reaction	Material	Kinetic law	Range of validity	E_a (kcal/mole)
$BaCl_2 \cdot 2H_2O \rightarrow$ $\rightarrow BaCl_2 \cdot H_2O$	Single-crystals	Power law ($n = 2$)	$0 < \alpha < 0.15$	18 ± 4*
		Contr. circle	$0.15 < \alpha < 1$	16.5 ± 1
	Powders	Power law ($n = 2$)	$0 < \alpha < 0.1-0.15$	20 ± 4.5*
		Avr.-Erof. ($n = 2$)	$0.15 < \alpha < 1$	18.8 ± 1.2
$BaCl_2 \cdot H_2O \rightarrow$ $\rightarrow BaCl_2$	Powders from preced. dehydr.	Avr.-Erof. ($n = 2$)	$0 < \alpha < 1$	~10
	Powders from methanol	Power law ($n = 2$)	$0 < \alpha < 0.1-0.15$	17.7 ± 5*
		Avr.-Erof. ($n = 2$)	$0.15 < \alpha < 1$	16.5 ± 1.1

* These values are approximate because the range of validity is not sufficiently wide

i) an initial power law period is never observed and an Avrami-Erofeev equation ($n = 2$) is found to be valid for the complete range of α;

ii) the curves in the $\frac{\alpha}{t}$ vs. t diagram do not pass through the origin, but show a positive intercept on the ordinate axis;

iii) a very low activation energy (10 kcal/mole) is found. It seems reasonable to assume that the decomposition of this kind of $BaCl_2 \cdot H_2O$ begins, though slowly, earlier than shown by the curve. At constant temperature the first water molecule is lost relatively slowly and nuclei of the anhydrous form might be formed on grown nuclei of the dihydrate.

The decomposition of monohydrate from methanol justifies the above assumptions, in fact:

i) the dehydration begins at temperatures very near those observed for the starting of the dehydration of $BaCl_2 \cdot 2H_2O$ (Fig. 1b);

ii) a curve passing through the origin is found in the $\frac{\alpha}{t}$ vs. t plot and it is possible to note a small acceleratory period for $0 < \alpha < 0.1$. The residual decomposition is characterized by an activation energy of 16.5 ± 1.1 kcal/mole.

The above observations make it clear that, while the curve of the complete transformation appears to give two well-separated endothermal peaks corresponding to reactions (1) and (2) respectively, the two processes at least partially overlap. Moreover, the two dehydration steps were found to consist of two consecutive kinetic stages: a power law stage and an Avrami-Erofeev or a contracting-circle stage (the latter only for the dehydration of $BaCl_2 \cdot 2H_2O$ single-crystals). These two stages have about the same activation energy for a given kind of material.

In the case of crystalline powders of the dihydrate and of the monohydrate from methanol, a good agreement of the experimental data is obtained at various constant temperatures in the Young plot (Fig. 7); this seems to indicate that there must be only one activated process, the progress of the reactant-product interface, involved in the reaction [10].

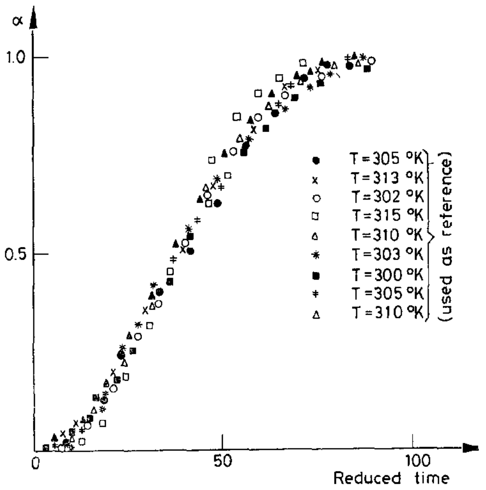

Fig. 7. Young plot, α vs. reduced time, for some experiences at constant temperature

However, this distinction between the two steps is uncertain: in fact the ($n = 2$) power law and the ($n = 2$) Galwey and Jacobs form of the Avrami-Erofeev equation are both obtained from the general Avrami equation: the first for low values of α and the second for high values of α.

Besides, the experimental results tend to indicate that at constant temperature the ingestion of nucleus-forming sites and the overlapping of growth nuclei (according to the Avrami-Erofeev equation) predominate for powders. For $BaCl_2 \cdot 2H_2O$ single-crystals, whose large, flat (010) faces allow a rapid initial ($\alpha < 0.2$) two-dimensional growth, this stage is followed by the movement of the reactant-product interface toward the inner part of the crystal. Indeed a sequence of photomicrographs (Fig. 8) of growth nuclei on the (010) face at constant temperature (312°K) shows the expected strong initial variation of average radius with time.

The different kinetic behaviour observed is thought to be due mainly to the effect of the grain size; in fact powders are in the form of very thin plate-like

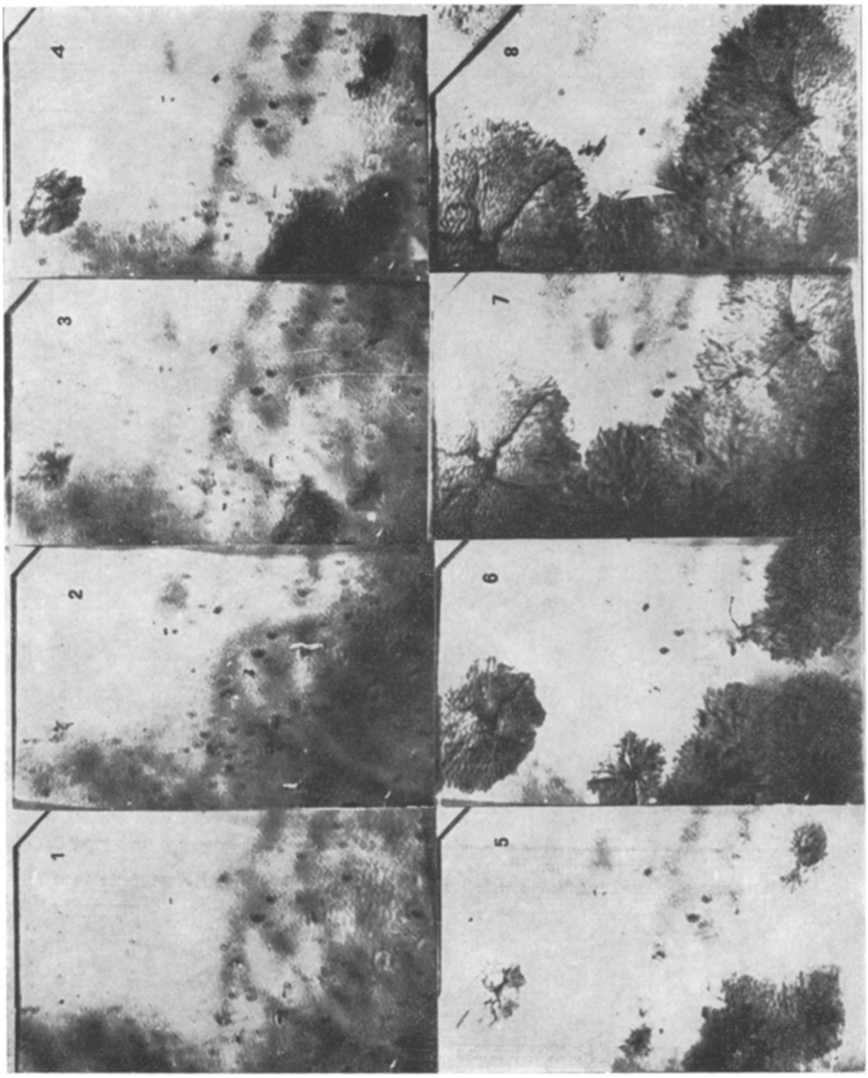

Fig. 8. Sequence of photomicrographs showing the advancement of the reaction on the (010) surface: 1) after 8′27″, 2) 24′, 3) 31′13″, 4) 34′45″, 5) 36′25″, 6) 40′55″, 7) 48′50″, 8) 51′25″

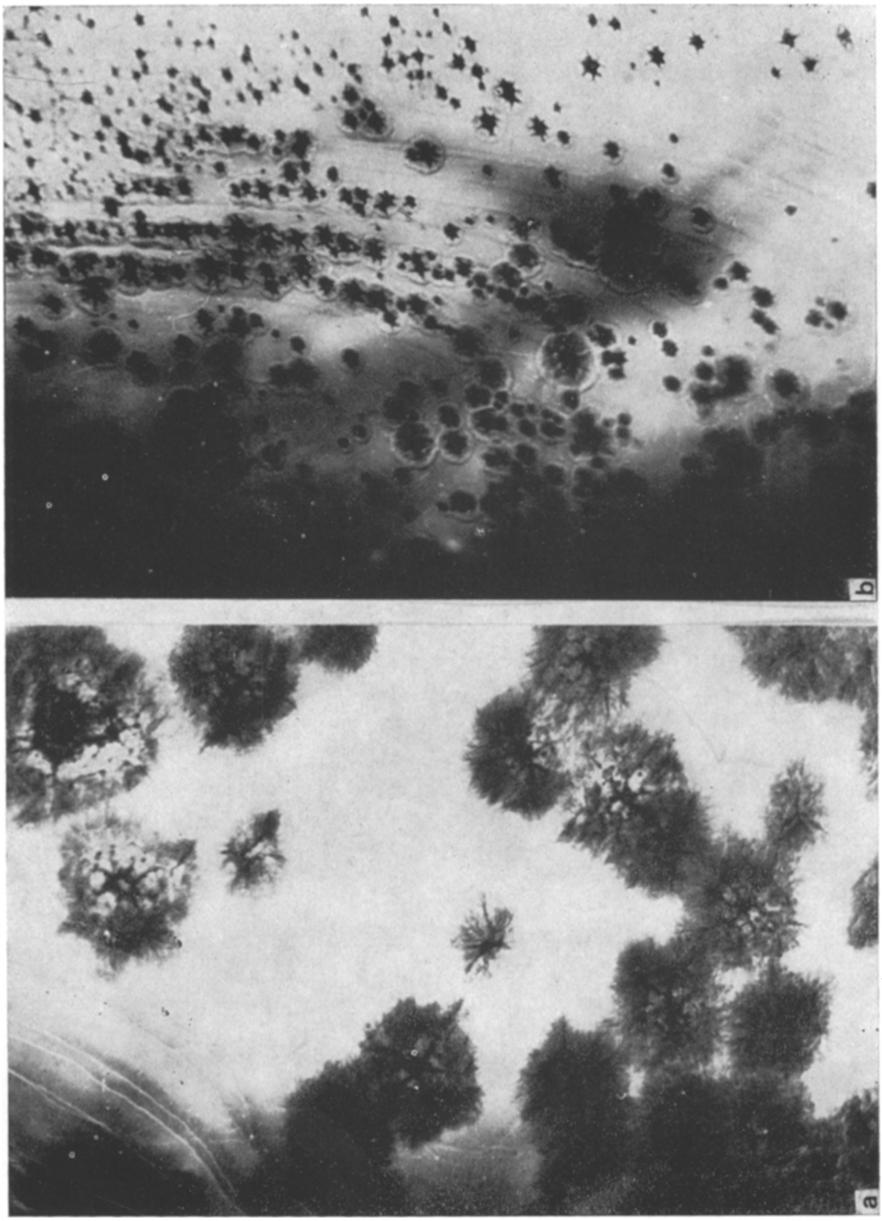

Fig. 9. Photomicrographs obtained at varying and at constant temperatures

crystals and the inward motion of the reactant-product interface is almost nonexistent, as the decomposition is practically complete when the nuclei have spread over the whole surface.

Different answers are given by non-isothermal runs as compared to the isothermal ones. Two effects could explain the observed inconsistencies:

a) at varying temperature the calorimeter response is an average over the different processes which take place during the decomposition of a solid; this is to be expected as, even at constant temperature, the successive stages of decomposition of a solid overlap and the overlapping is thought to extend when the decomposition is performed by increasing the temperature;

b) there is a real change in the mechanism of the decomposition; this is what seems probable to happen, as shown in Fig. 9, in which two photomicrographs obtained at varying and at constant temperature are compared. At varying temperature a great number of nuclei are found; possibly, the nucleation process is enhanced with increasing temperature. All these nuclei appear to have only a limited spreading over the surface while they seem to grow inward. As a result overall contracting-kinetics are expected, leaving a number of unchanged crystallites of the reactant which should successively decompose according to a first-order decay law. Indeed, in some instances a first-order law was observed in the final parts ($\alpha > 0.8$) of the decomposition at varying temperature both for single-crystals and powders.

Possibly both effects superimpose to an extent which is uncertain.

Ingraham and Rigaud explain the difference in activation energies deduced from isothermal and non-isothermal runs as an effect of the distance between the reaction front and the product recrystallization front. Our results, in contrast, seem to indicate that the difference in activation energies is due to a different mechanism of advance of the reacting interface.

The fact that different results are obtained in runs at varying temperature and at constant temperature underline once more the care to be taken in order to obtain meaningful kinetic parameters by means of differential thermal methods, at least when decomposition of solids, where several processes take place successively, are concerned.

Further studies are necessary to ascertain whether the anomalies observed may be overcome by means of appropriate experimentation.

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RÉSUMÉ — On a étudié la cinétique de la déshydratation thermique de différentes variétés de $BaCl_2 \cdot 2H_2O$ et $BaCl_2 \cdot H_2O$ par analyse enthalpique différentielle. Le départ de l'eau s'effectue en deux étapes:

$$BaCl_2 \cdot 2H_2O \rightarrow BaCl_2 \cdot H_2O \rightarrow BaCl_2$$

caractérisées par deux pics endothermiques. Pour les expériences à température variable les deux étapes suivent une loi avec contraction circulaire, après une phase initiale d'accélération suivant une loi en puissance 2 ($n = 2$). Pour les expériences à température constante, après une phase initiale suivant une loi en puissance 2 ($n = 2$), les deux étapes (y excludant les monocristaux de $BaCl_2 \cdot 2H_2O$) suivent la loi d'Avrami-Erofeev (avec $n = 2$) sous la forme utilisée par Galwey et Jacobs. On compare les énergies d'activation des différentes phases et l'on discute les différences du comportement cinétique.

ZUSAMMENFASSUNG — Die Kinetik des Dehydrationsvorgangs von $BaCl_2 \cdot 2H_2O$ und $BaCl_2 \cdot H_2O$ wurde durch die DSC-Methode untersucht. Der Wasserverlust verläuft in zwei Stufen

$$BaCl_2 \cdot 2H_2O \rightarrow BaCl_2 \cdot H_2O \rightarrow BaCl_2$$

und besitzt deshalb zwei Endotherme. Die Versuche bei unkonstanten Temperaturen folgte der kontraktiven Kreisregel mit einer anfänglichen beschleunigten Periode nach der Potenzregel $n = 2$. Die Versuche bei konstanter Temperatur zeigten nach einer anfangs beschleunigten Etappe nach der Potenzregel $n = 2$, daß beide Stufen (abgesehen von $BaCl_2 \cdot 2H_2O$ Einkristallen) dem Avrami-Erofeev Gesetz (mit $n = 2$) in der von Galwey und Jacobs benützten Form folgen. Die Aktivierungsenergien der verschiedenen Stufen wurden ermittelt und das verschiedene kinetische Verhalten besprochen.

Резюме — Исследована кинетика термической дегидратации таких соединений как $BaCl_2 \cdot 2H_2O$ и $BaCl_2 \cdot H_2O$ с помощью дифференциального сканнирующего калориметра. Потеря воды (H_2O) происходит в две ступени

$$BaCl_2 \cdot 2H_2O \rightarrow BaCl_2 \cdot H_2O \rightarrow BaCl_2$$

и поэтому обнаруживаются два эндотермических пика.

В экспериментах, проведенных при различной температуре, обе ступени подчиняются правилу стягивающихся кругов, после быстрого начального периода процесс описывается правилом (Н = 2) степени.

В экспериментах, проведенных при постоянной температуре, после быстрого начального периода обе ступени (исключая монокристал $BaCl_2 \cdot 2H_2O$) подчиняются правилу Аврами-Ерофеева (Н = 2) в преобразованном виде Гелве и Джекобса.

Сравниваются величины энергии активации, полученные для различных ступеней, и обсуждается различный кинетический характер процесса.