Kinetics of $BaBr_2 \cdot 2\,H_2O$ Dehydration: Comparison between Isothermal and Non-isothermal Methods

Giorgio Flor, Amedeo Marini, and Vittorio Berbenni

Centro di Studio per la Termodinamica ed Elettrochimica dei Sistemi salini fusi e solidi del CNR. Istituto di Chimica Fisica e di Elettrochimica, Università di Pavia (Italy)

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For the dehydration processes

$$BaBr_2 \cdot 2\,H_2O \rightarrow BaBr_2 \cdot H_2O + H_2O \qquad \text{(I)}$$

$$BaBr_2 \cdot H_2O \rightarrow BaBr_2 + H_2O \qquad \text{(II)}$$

a comparison was made between the experimental non-isothermal α vs. t curves and those calculated on the basis of a previous isothermal study.

It was observed that for low heating rates, when the "thermal lag" is negligible, the dynamic measurements are in good agreement with the isothermal ones.

Furthermore, for process (I), two mathematical methods proposed for the interpretation of the non-isothermal TG curves were applied and the kinetic parameters so obtained were discussed.

In the last years several dynamic methods, based on TG, DTA, DSC measurements [1], have been proposed for the study of thermal decomposition reactions.

Generally these methods do not allow the determination of the topochemical reaction mechanism and therefore they cannot replace the classical isothermal methods; they present, however, some advantages in the evaluation of kinetic parameters.

In fact they don't require preliminary tests in order to individuate the proper temperature range for the kinetic study, and furthermore it is often possible to obtain the activation energy, E, from a single curve.

However the applicability of the dynamic methods to the study of solid state reactions is still under discussion [2].

For some thermal decompositions Johnson and Gallagher [3], by comparing the kinetic parameters obtained by isothermal and dynamic measurements, found remarkable discrepancies and, as concerns the dynamic method, obtained different values of the parameters depending on the mathematical treatment used. Other authors [4], on the contrary, obtained a satisfactory agreement.

In this work the validity of the dynamic methods is discussed, for two thermal decompositions, by a direct comparison between the non-isothermal α (fraction of the initial compound reacted) vs. t (time) curves experimentally obtained and those calculated on the basis of the mechanism and kinetic parameters deduced from isothermal measurements.

To this purpose the processes

$$BaBr_2 \cdot 2\,H_2O \rightarrow BaBr_2 \cdot H_2O + H_2O \qquad \text{(I)}$$

and

$$BaBr_2 \cdot H_2O \rightarrow BaBr_2 + H_2O\,, \qquad \text{(II)}$$

already studied isothermally by one of us [5] in the temperature ranges 60—67 °C and 107—126 °C, respectively, have been investigated.

Experimental

a) $BaBr_2 \cdot 2\,H_2O$ was prepared by slow evaporation, at room temperature, from a $BaBr_2$ aqueous solution (Alfa 99.9%).

The crystals so obtained were classified by sieving and the fraction 230—170 mesh utilized. These crystals were prismatic in shape and averaged $120 \cdot 70 \cdot 70$ µm. Crystals identically obtained and selected had been used for the isothermal measurements [5].

b) The TG curves were recorded with a "950 Thermogravimetric Analyzer" joined with a "900 Differential Thermal Analyzer", both DuPont. The samples were carried out under the same experimental conditions as in the isothermal study, i.e. the same amount of reactant (35 mg) was uniformly distributed in a flat holder (Pt), so that the reactant layer thickness was less than 0.5 mm [6].

The TG curves for both reactions were recorded at five different heating rates: $q = 1.2$, 3, 6, 8, and 11 K min^{-1}.

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Results and Discussion

a) Experimental α vs. t curves. Figures 1 and 2 show the experimental α vs. t values for the reactions (I) and (II), respectively. In Fig. 1 the data for $q = 1.2$ are not presented because at this heating rate process (I) begins ($T_0 = 326$ K) and partly proceeds at temperatures lower than those ($T > 333$ K) recognized, in the isothermal study, to satisfy the kinetic equation proposed.

b) Calculated α vs. t curves. According to the literature [1], the reaction rate of a thermal decomposition can be written as

$$d\alpha/dt = k(T)\, f(\alpha)\,, \tag{1}$$

where $k(T) = Z \exp(-E/RT)$ is the rate constant.

Since $T = T_0 + qt$ (where T_0 is the temperature of the onset of the decomposition) and hence $dT = q\,dt$, by integration of Eq. (1) we have:

$$\int_0^\alpha \frac{d\alpha'}{f(\alpha')} = g(\alpha) = \frac{Z}{q} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT' \,. \tag{2}$$

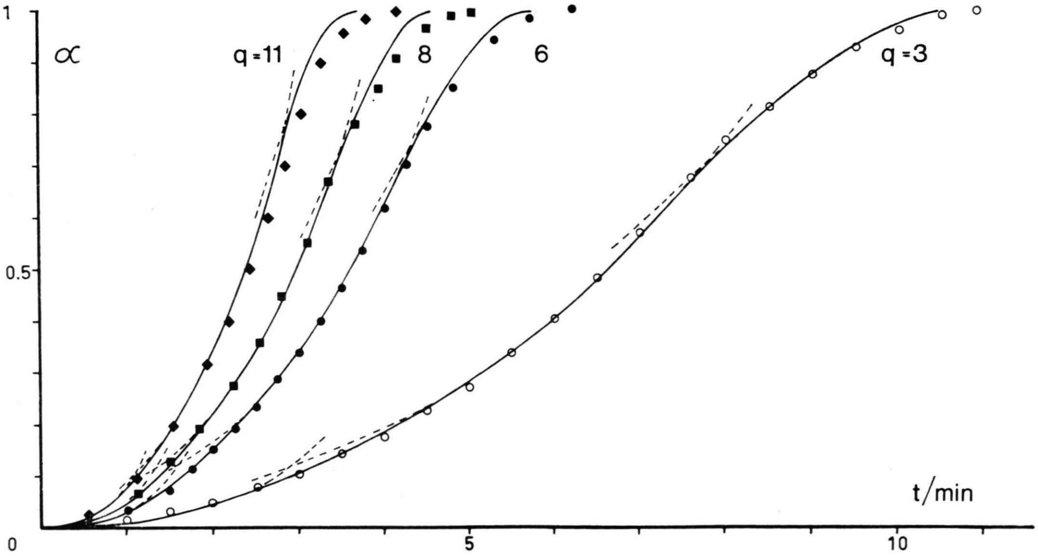

Fig. 1. Reaction (I): comparison between experimental and calculated (full lines) α vs. t curves.

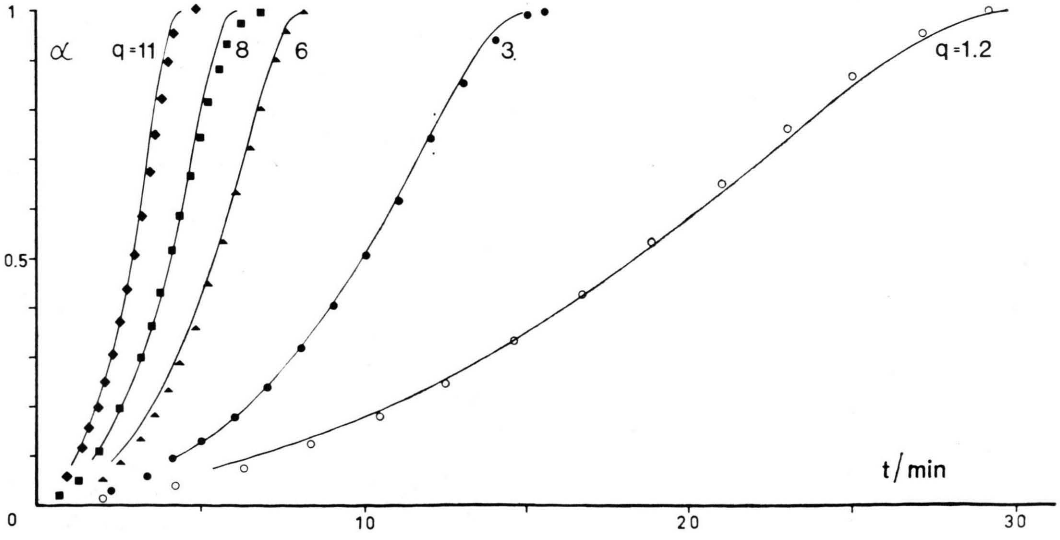

Fig. 2. Reaction (II): comparison between experimental and calculated (full lines) α vs. t curves.

By putting $x = E/RT$ one obtains

$$g(\alpha) = \frac{ZE}{Rq} \int_{x}^{x_0} \frac{e^{-x'}}{x'^2}\,\mathrm{d}x' . \tag{3}$$

By assuming according to Doyle [7]

$$\int_{x}^{x_0} \frac{e^{-x'}}{x'^2}\,\mathrm{d}x' = \left| - \frac{e^{-x'}}{x'^2} \right|_{x}^{x}$$

we get

$$g(\alpha) = \frac{k(T)\,R}{Eq} \left\{ T^2 - \exp\left[-\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] T_0^2 \right\} . \tag{4}$$

As regards reaction (I), the isothermal ($k(T) =$ constant) study [5], employing also direct observations of the process by optical microscopy, allowed to deduce a topochemical mechanism which involved three periods:

An initial acceleration period ($\sqrt{\alpha} = k_1 t$), a main period ($0.1 \leqq \alpha \leqq 0.7$) at a constant rate ($\alpha = k_2 t$) due to the advancement of the reacting interface along a preferential direction, and finally a decay period which followed the "contracting area" law $1 - (1 - \alpha)^{1/2} = k_3\,t$.

As regards reaction (II), it was observed that the experimental data were satisfied, in the range $0.15 \leqq \alpha \leqq 0.90$, by the equation

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

Therefore: for the first period of reaction (I), $g(\alpha) = \sqrt{\alpha}$, for the second period of reaction (I), $g(\alpha) = \alpha$, for the third period of reaction (I) and for the single period of reaction (II), $g(\alpha) = 1 - (1 - \alpha)^{1/2}$.

By substituting these expressions for $g(\alpha)$ in Eq. (4) and solving with respect to α we obtain the equations used in the calculation of the α vs. t curves; in these equations we introduced for T_0 the values experimentally determined* and for the kinetic constants the values obtained through the isothermal investigation**.

Figures 1 and 2 report these curves for the two reactions at different heating rates.

In Fig. 1 the dashed lines represent the calculated trend of the three periods beyond the limits of validity of the pertinent equations, while the full lines are the best graphical interpolations. It can be seen that there is a nearly perfect agreement between calculated and experimental curves for $q = 3\ \mathrm{K\ min^{-1}}$, whereas the agreement, although still satisfactory, becomes less good at increasing heating rates. This can be explained with the growing "weight" of the "thermal lag" at higher heating rates, as already observed by other authors [3, 8].

From Fig. 2 it appears that the calculated and experimental curves are in fair agreement; some divergence, however, is observable for $\alpha < 0.15$. In this connection, it is to be noted that also in the isothermal measurements the "contracting area" law was satisfied only for α values higher than 0.15.

Notheworthy is the fact that the α vs. t experimental curves of reaction (I) are very well reproduced by those calculated on the basis of the three periods. This reaction therefore, also when carried out dynamically, satisfies the same equations and presents the same mechanism as deduced from the isothermal studies.

To reach such a conclusion would have been difficult by only working out the experimental dynamic data through one of the known calculation methods.

Indeed it is to be noted that the methods proposed for evaluating the experimental non-isothermal curves require a "best fitting" procedure which assumes the validity of only one phenomenological equation over the whole range of the reaction; this represents a considerable limit and, along with other potential experimental error sources, can yield results different from the isothermal ones.

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* The following T_0 values were found at different heating rates:

Reaction (I)

q [K min^{-1}]	3	6	8	11
T_0 [K]	332	336	338	340

Reaction (II)

q [K min^{-1}]	1.2	3	6	8	11
T_0 [K]	377.5	380	385	390	395

** $\log k_1 = 12.81 - \dfrac{21{,}300}{4.576\,T}$,

$\log k_2 = 11.42 - \dfrac{19{,}400}{4.576\,T}$

and $\log k_3 = 12.02 - \dfrac{20{,}400}{4.576\,T}$ for reaction (I);

$\log k = 12.35 - \dfrac{25{,}300}{4.576\,T}$ for reaction (II). The k values are in min^{-1}.

Table 1. Activation energy values obtained from the α vs. t non-isothermal curves for reaction (I).

q [K min^{-1}]	E [kcal mole^{-1}]	
	Achar's method [9]	Coats and Redfern's method [10]
3	25.0	32.0
6	23.0	31.1
8	22.1	29.3
11	19.9	26.1

Actually, employing for reaction (I) either the "differential" Achar's [9] method or the "integral" Coats-Redfern's [10] method in the range $0.1 \leqq \alpha \leqq 0.7$, a better fit was obtained for the reaction order $n = 1/2$ than for $n = 0$. Hence, in the range which was proved isothermally to satisfy the $n = 0$ order, the application of the above methods would lead to accept the validity of the "contracting area" law, whereas the isothermal optical observations [5] showed that it holds only for the decay period ($0.7 \leqq \alpha \leqq 0.95$).

As regards the activation energy (see Table 1) the values obtained for reaction (I) are:

a) considerably decreasing with increasing heating rates [11];

b) different according to the mathematical treatment employed;

c) very far (mostly in the case of the Coats-Redfern's method [10]) from the "isothermal" value ($E = 19.4$ kcal mole^{-1}).

Therefore, at least for this reaction which does not present a single mechanism, the methods for the determination of the kinetic parameters from dynamic TG measurements appear not very reliable.

In conclusion, it appears that the dynamic thermogravimetric curve, although potentially containing broader information than the isothermal one, is however not able to yield satisfactory values of the kinetic parameters, owing to the thermal lag, the criteria adopted for the treatment of experimental data and the approximations introduced in the mathematical evaluation.

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