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DTA STUDY OF KINETICS OF TRANSFORMATION OF SILICA GEL TO CRISTOBALITE

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The activation energy for the transformation of silica gel to cristobalite, a partial reaction of first order, was determined from a single DTA curve by the methods available in the literature. The values obtained were not in agreement with those obtained by the isothermal method. This suggested that the methods were not applicable to reactions which are partial. A modified equation was derived which could be utilized for the determination of the activation energy of first-order reactions from a single DTA curve, if the fraction transformed during the reaction was known.

A number of equations [1–4] have been proposed for the study of the kinetics of chemical reactions by DTA. The evaluation of kinetic parameters by DTA or TG has sometimes been found to lead to very poor agreement in results. This has given rise to a flurry of controversy concerning the validity of the non-isothermal methods of kinetic analysis [5–18]. The assumptions which are involved in such equations are subject to many theoretical and experimental objections. It has been revealed that the present concepts of both isothermal and non-isothermal kinetics have many deficiencies.

Verduch [19] studied the kinetics of transformation of silica gel to cristobalite by the isothermal method. In the present communication attempts have been made to study the kinetics of this transformation by DTA. The limitations of some of the DTA methods, as detected during the investigation, are discussed in the light of the present controversy.

Experimental

A Netzsch thermoanalyser 404 was used for DTA investigations. The apparatus consisted of a vertical furnace and calibrated [20] Pt–PtRh 10% thermocouples.

Silica gel samples used in the investigation were: 1. Column chromatographic grade silica gel, BDH, UK. 2. Silica gel prepared in the laboratory. After drying at 140°, the gel contained 4.2 per cent water, 0.72 per cent alumina and 0.13 per cent other impurities.

Calcined alumina (BDH) was used as both diluent and reference material. The sample holders were platinum sleeves (dia 8 mm, height 25 mm) mounted on top of the thermocouple sheaths and were separated from each other. Reaction temperatures were monitored from an inert sample. In all the DTA runs 150–200 mg of silica gel (particle size 200–325 mesh) was packed in the platinum sleeve between two layers of alumina.

Results and discussion

Subramanian et al. [1] proposed a method for determination of the activation energy E of first-order reactions from a single DTA curve. The isothermal rate equation for first-order reactions is given by

$$K_{i'} = \frac{1}{t} \ln \frac{1}{1 - x} \tag{1}$$

where K_T is the reaction rate constant at temperature T and x is the fraction of the reactant transformed in time t. They also considered Eq. (1) to be valid under dynamic conditions of DTA where both time and temperature are varying. Eq. (1) was then transformed into

$$K_T = \frac{1}{t} \ln \frac{A}{A - a} \tag{2}$$

by substituting a/A for x, where A is the total peak area and a the area swept in time t. E was then calculated from the slope of the line obtained by plotting $\log \left(\frac{1}{t} \log \frac{A}{A - a} \right)$ against $1/T$.

In the derivation of Eq. (2), the fraction transformed in time t has been assumed equal to a/A. This could be true only when the peak area A represented the heat of reaction for complete transformation of the reactant.

Many chemical reactions of first order are known to cease or become asymptotic after a fraction of the reactant is transformed. For such reactions rate Eq. (1) is valid in the range $0 \leq x \leq 1$. In such reactions the DTA peak area A represents the heat of reaction for only a fraction of the transformation of the reactant. In Eq. (2), therefore, x of Eq. (1) should correspond to fa/A, where f is the fraction of the total mass transformed during the reaction. Eq. (2) may therefore be written in the generalized form

$$K_T = \frac{1}{t} \ln \frac{A}{A - fa} \tag{3}$$

When $f = 1$, Eq. (3) reduces to Eq. (2). E can be calculated from Eq. (3) by plotting $\log \left(\frac{1}{t} \log \frac{A}{A - fa} \right)$ against $1/T$ and equating the slope of the line to $-E/2.303\,R$ if the value of f is known.

The activation energy E for the transformation of silica gel to cristobalite was determined from a single DTA curve (heating rate 10°/min), utilizing Eq. (3)

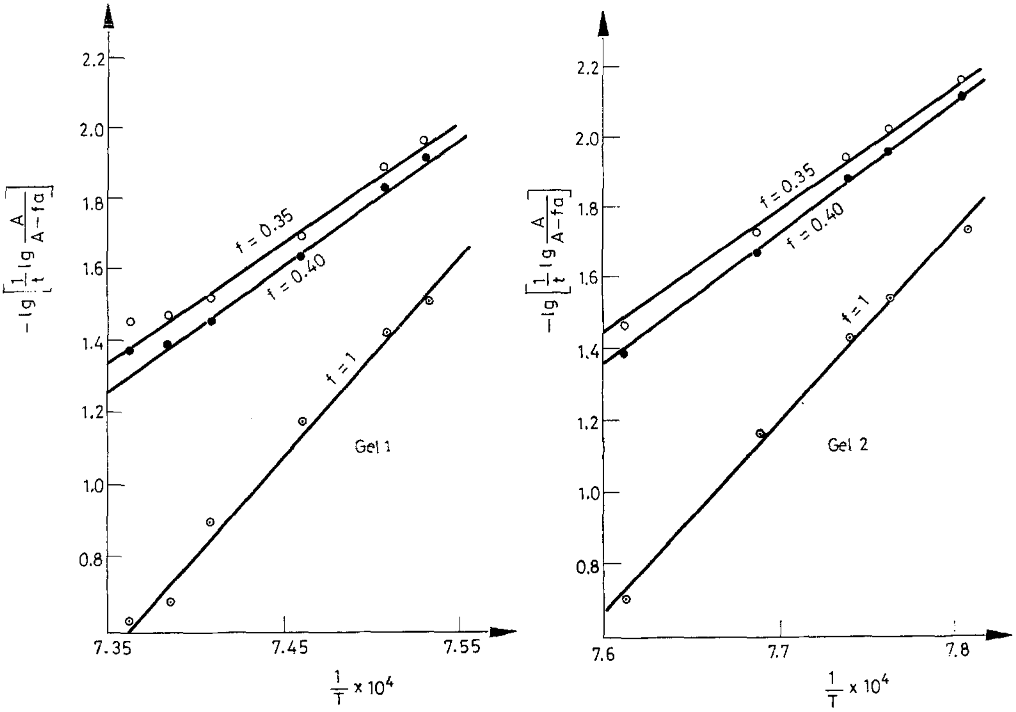

Fig. 1. Arrhenius plots for the silica gel—cristobalite transformation following Eq. (3)

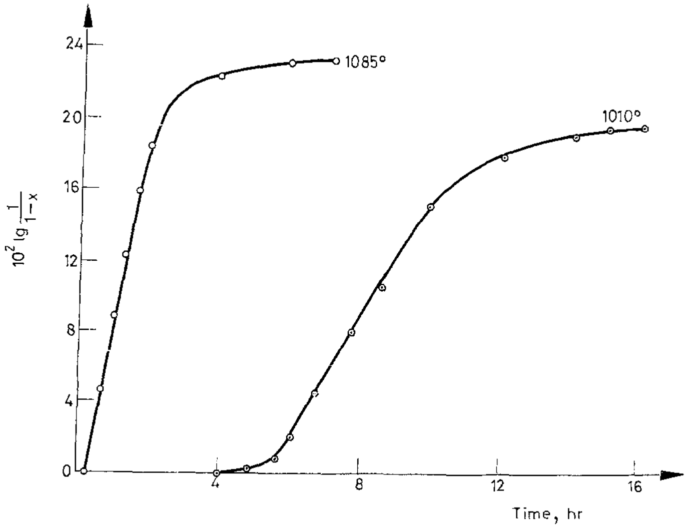

Fig. 2. Plot of log 1/1 — x vs. time t for the isothermal transformation of silicic acid to cristobalite; from the rate curves of Verduch [19]

(Fig. 1). From the isothermal rate curves of transformation of silica gel to cristobalite, given by Verduch [19], a plot of $\log 1/t - x$ against time t was made. The rectilinearity of the plot (Fig. 2) showed that the transformation followed the Arrhenius law for a first-order reaction. The plot of $\log \left(\frac{1}{t} \log \frac{A}{A - fa}\right)$ against $1/T$ (Fig. 1) also showed that the transformation was a first-order reaction. In using Eq. (3), the values of f were taken to be 0.35 and 0.40 on the basis of Verduch's [19] investigation. Verduch reported that the transformation of silica gel to cristobalite ceased when it had reached about 35 to 40 per cent. Activation energy values obtained by utilizing Eq. (3) were in agreement with that obtained by Verduch [19] from isothermal rate curves (Table 1). For $f = 1$, the plot yielded much higher values of E (Table 1).

Eq. (3) can also be utilized [21] to find out the fraction of the total mass transformed during a reaction, if the value of E is known. In a reaction where f is not known, the plot of $\log \left(\frac{1}{t} \log \frac{A}{A - fa}\right)$ against $1/T$ yields different values of E, if different values of f are assumed. The value of f that yields an activation energy value similar to the known value of E gives the fraction of the total mass transformed during the reaction.

Table 1

Activation energy for the transformation of silica gel to cristobalite, determined by different DTA methods

Silica gel	E (kcal/mole)						
	a			b	c	d	e
	$f = 0.35$	$f = 0.40$	$f = 1$				
1	154	164	252	494	485	155	154
2	151	160	238	467	453	150	

a — Calculated from Eq. (3),
b — Calculated from Eq. (4),
c — Calculated from Eq. (5),
d — Calculated from Eq. (6),
e — Determined by Verduch [19] from isothermal rate curves.

The kinetics of transformation of silica gel to cristobalite were also studied by applying three other equations

a) *Borchardt and Daniels' equation*

Borchardt and Daniels [2] derived relation (4) for a first-order reaction in a stirred solution:

$$K_T = \frac{\Delta T}{A - a} \tag{4}$$

where K_T is the reaction rate constant at temperature T; ΔT the height of the DTA peak at time t; A the total area of the peak; and a the area swept in time t. E was calculated from the plot of log $\frac{\Delta T}{A - a}$ against $1/T$. Eq. (4) has frequently been applied to solid-state reactions [1, 22–24]. In the present investigation too application of Eq. (4) was made (Fig. 3). The DTA curve at the heating rate of 10°/min was used.

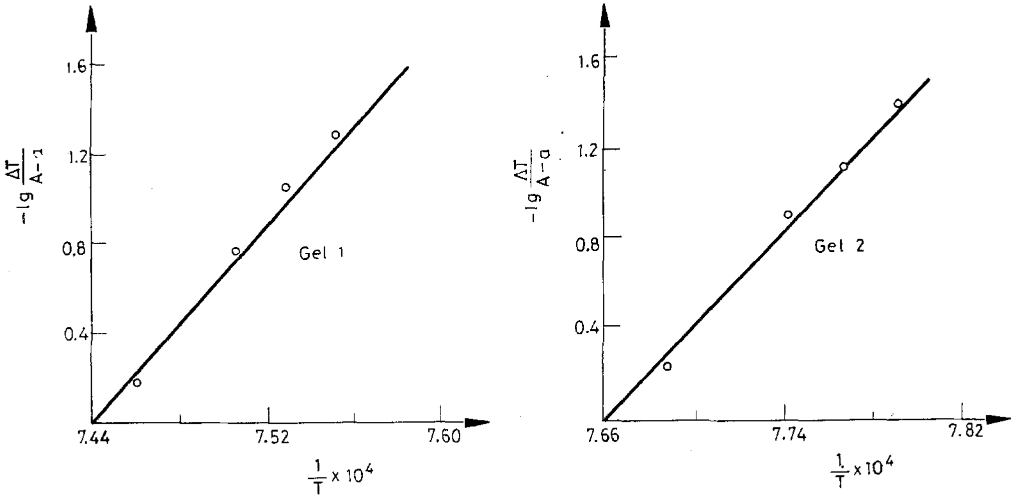

Fig. 3. Arrhenius plots for the silica gel—cristobalite transformation following Eq. (4)

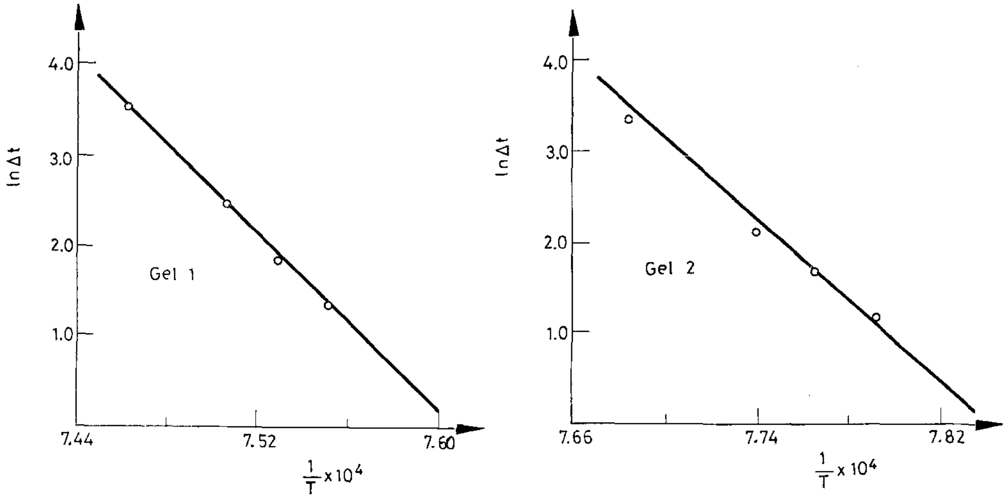

Fig. 4. Arrhenius plots for the silica gel—cristobalite transformation following Eq. (5)

b) *Piloyan, Ryabchikov and Novikova's equation*

Piloyan et al. [3] derived Eq. (5) for the determination of E for reactions, irrespective of the order of reaction:

$$\ln \Delta t = C - E/RT \tag{5}$$

where Δt is the deviation of the DTA curve from the base line at temperature T; C a constant; and R the gas constant. E was calculated by plotting $\ln \Delta t$ against $1/T$ and equating the slope of the straight line to $-E/R$.

The activation energy for the transformation of silica gel to cristobalite was determined from a single DTA curve (heating rate 10°/min) utilizing Eq. (5) (Fig. 4).

c) *Kissinger's equation*

Kissinger [4] derived Eq. (6) for the determination of E, irrespective of the order of reaction, from the shift in the DTA peak temperature with heating rate:

$$\frac{\mathrm{d}\left(\ln \frac{\beta}{T_{\mathrm{m}}^2}\right)}{\mathrm{d}\left(\frac{1}{T_{\mathrm{m}}}\right)} = -\frac{E}{R} \tag{6}$$

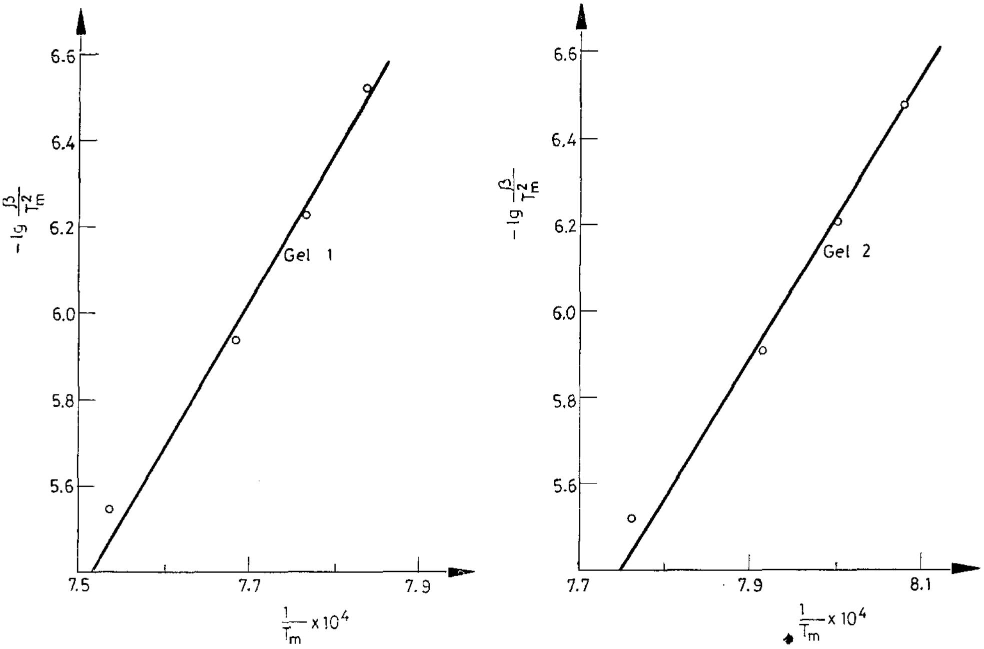

Fig. 5. Arrhenius plots for the silica gel—cristobalite transformation following Eq. (6)

where β is the rate of heating and T_m the peak temperature. E was calculated from the plot of log β/T_m^2 against $1/T_m$.

The activation energy for the transformation of silica gel to cristobalite was determined from the DTA curves at the heating rates of 0.5, 1.2 and 5° per minute, utilizing Eq. (6) (Fig. 5).

The values of E obtained by utilizing the three equations are given in Table 1. The values of E obtained by utilizing Eq. (6) were similar to that obtained by the isothermal method. Eqs (4) and (5) yielded much higher values of E.

In DTA or TG, transformation is considered to be a function of time and temperature only. Thus:

$$x = F(t, T) \tag{7}$$

Differentiating Eq. (7):

$$\mathrm{d}x = \left(\frac{\delta x}{\delta t}\right)_T \cdot \mathrm{d}t + \left(\frac{\delta x}{\delta T}\right)_t \cdot \mathrm{d}T$$

i.e.

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(\frac{\delta x}{\delta t}\right)_T + \left(\frac{\delta x}{\delta T}\right)_t \cdot \frac{\mathrm{d}T}{\mathrm{d}t} = \left(\frac{\delta x}{\delta t}\right)_T + \beta \left(\frac{\delta x}{\delta T}\right)_t$$

where β is the rate of heating.

In non-isothermal kinetics the term $\left(\frac{\delta x}{\delta T}\right)_t$ is considered zero, since fixing the time co-ordinate also fixes the number and positions of the particles constituting the system [4]. Thus, the total reaction rate $\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right)_T$ is found to be equal to the isothermal reaction rate $\left(\frac{\delta x}{\delta t}\right)_T$. The non-isothermal rate equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A(1 - x)^n \exp\left(-\frac{E}{RT}\right) \tag{8}$$

where n is the order of reaction, is then obtained.

MacCallum and Tanner [5] suggested that the assumption $\left(\frac{\delta x}{\delta T}\right)_t = 0$ was incorrect. In reactions for which the DTA or TG methods and the isothermal method yielded similar values of E, the term $\beta\left(\frac{\delta x}{\delta T}\right)_t$ must have been very small in comparison to $\left(\frac{\delta x}{\delta t}\right)_T$ and hence the assumption did not lead to significant error.

Activation energy values obtained by Eqs (5) and (6) for the silica gel–cristobalite transformation do not seem to support the proposition of MacCallum and

Tanner. Though both equations are derived from the same non-isothermal rate Eq. (8), there was disagreement in the case of the values of E obtained by Eq. (5) and agreement in the case of those obtained by Eq. (6). This suggests that the discrepancies in the results might be due to reasons other than that proposed by MacCallum and Tanner.

In solid-state decomposition and dehydration reactions the application of Eqs (2), (4) and (5) has been found to lead to good agreement in the derived values of E. The mechanism of the silica gel – cristobalite transformation is distinctly different from those of solid-state decomposition and dehydration reactions. The gel to cristobalite transformation almost ceases at 35 to 40 per cent, whereas in solid-state decomposition and dehydration reactions the transformations are almost complete. The discrepancies in the values of E for the gel – cristobalite transformation derived by Eqs (2), (4) and (5) therefore suggest that these three equations are not applicable to solid-state reactions which are partial. Eqs (2) and (4) were derived on the assumption that the reaction was complete before the highest temperature of the DTA trace was attained. This in itself puts a limitation on the use of these two equations in reactions which are partial.

The agreement in the values of E for the gel – cristobalite transformation obtained by Eqs (3) and (6) suggests that the two equations might have shortcomings but these do not include the one detected in the case of Eqs (2), (4) and (5).

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RÉSUMÉ — On a déterminé à l'aide d'une seule courbe ATD l'énergie d'activation de la transformation du gel de silice en cristobalite, réaction partiellement du premier ordre, en utilisant les méthodes décrites dans la littérature. Les valeurs obtenues ne sont pas en accord avec celles obtenues par la méthode isotherme. On a déduit que les méthodes utilisées ne sont pas valables dans le cas des réactions partielles. On établit une équation modifiée qui permet de déterminer l'énergie d'activation de réactions du 1er ordre à partir d'une seule courbe ATD si les fractions transformées pendant la réaction sont connues.

ZUSAMMENFASSUNG — Die Aktivierungsenergie der Umwandlung von Kieselgel in Cristobalit, einer Teilreaktion erster Ordnung, wurde aus einer einzigen DTA-Kurve unter Anwendung einer in der Literatur beschriebenen Methode bestimmt. Die erhaltenen Werte standen mit den durch isotherme Methoden ermittelten nicht in Übereinstimmung. Daraus wurde gefolgert, daß die Methoden bei Teilreaktionen nicht einzusetzen sind. Eine modifizierte Gleichung wurde abgeleitet, die sich zur Bestimmung der Aktivierungsenergie von Reaktionen erster Ordnung aus einer einzelnen DTA-Kurve eignet, wenn der während der Reaktion umgewandelte Anteil bekannt ist.

Резюме — Энергия активации превращения силикагеля в кристобалит, частная реакция первого порядка, была определена из единственной кривой ДТА, используя методы, известные в литературе. Полученные значения не согласуются с данными, полученными изотопическим методом. Это доказывает, что эти методы не применимы к реакциям, которые являются частными. Было выведено модифицированное уравнение, которое может быть использовано для определения энергии активации реакций первого порядка из одной кривой ДТА, если известна фракция превращаемая во время реакции.