

## DEHYDRATION KINETICS OF SOME SMECTITES: A THERMOGRAVIMETRIC STUDY

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### ABSTRACT

Weight-loss experiments for eight smectite samples, from various international localities, were followed by dynamic thermogravimetry. Analysis of the curves was achieved by plotting  $\log g(\alpha)$  vs.  $1/T$ , according to Satava (1971), or by applying the methods of Coats and Redfern (1964). The estimated activation energies of dehydration ( $E_d$  below  $300^\circ\text{C}$ ) were 10-17 and 8-14 kcal mol<sup>-1</sup>, respectively. In the former method, the  $F_1$  function (random nucleation mechanism) fits better to dehydration, whereas the first-order kinetics apply in the latter method. Nontronites do not show different  $E_d$  values compared to montmorillonites. The different values of  $E_d$  seem to be correlated with the water content lost through the dehydration region.

### INTRODUCTION

Thermal methods are often used to study the kinetics and mechanisms of solid state reactions under isothermal and non-isothermal conditions. The non-isothermal methods are considered more popular for several reasons: (a) they are rapid and their results easier to evaluate, (b) they can be used in a wide temperature range and allow the reaction to be followed over the entire range, (c) several decomposition steps can be studied by means of one curve, (d) the theory and methods of evaluation have already been developed for the interpretation of curves obtained at linearly increasing heating rate.

The differential equation describing reactions proceeding under non-isothermal conditions is [1]

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{Rq} \int_X^\infty \frac{e^{-X}}{X^2} dX \quad (1)$$

where  $\alpha$  is the fraction reacted,  $g$ ,  $f$  are function symbols,  $A$  is the pre-exponential term,  $R$  is the gas constant,  $q$  is the heating rate,  $E$  the activation energy;  $X = E/RT$ ; and  $T$  is the temperature at which the solid has the fraction  $\alpha$ ;

$$\int_\alpha^\infty \frac{e^{-X}}{X^2} = p(X) \quad (2)$$

The left hand side of eqn. (1) is called by MacCallum and Tanner [2], the "weight integral", and the right hand side of the same equation is similarly called the "temperature integral",  $f(\alpha)$  function denotes a certain function of the weight or a term proportional to the weight. In practice the values of  $\alpha$  are, in most cases, obtained from the thermogravimetric or differential thermoanalytical curves. The forms and number of equations used by different authors as kinetic functions or rate-controlling processes are quite different. Šatava and Škvára [3] gave tables for nine equations for the value  $g(\alpha)$ , whereas Gallagher and Johnson [4,5] used 18 equations.

Since the differential equation for  $p(X)$ , eqn. (2), cannot be integrated in its infinite form, a number of methods have been introduced to approximate the function. Approximation formulae were given by Ozawa [6], MacCallum and Tanner [2], Šatava [7] and Flynn and Wall [8].

The expressions of MacCallum and Tanner [2], as well as that of Šatava [7], as given by Sesták [9], are

$$E = - \left( \frac{449 + tg\beta/2.303}{217} \right) \times 10^3 \text{ (cal mol}^{-1}\text{)} \quad (3)$$

and

$$E = \frac{1.987}{2} \left( -tg\beta + \sqrt{tg^2\beta + 8 tg\beta T} \right) \text{ (cal mol}^{-1}\text{)} \quad (4)$$

where  $tg\beta$  is the slope of the straight line approximation of the plot of  $\ln g(\alpha)$  vs.  $1/T$ , and  $T$  is the average temperature on the thermogram.

In the present study, eight smectites from widely different international localities were analyzed by dynamic thermogravimetry. Two methods were employed for the kinetic analysis of the dehydration region (below 300°C). This was carried out for the purpose of investigating the effect of the origin of smectites on the prevailing dehydration mechanism as well as on the associated activation energy.

## EXPERIMENTAL

### *Materials*

Thermal analysis was performed on eight smectites from varying international localities. These are: I. Manito (U.S.A.), II. Sampor (U.S.S.R.) nontronites, III. Polkville (U.S.A.), IV. Arizona (U.S.A.), V. Ginovec (Yugoslavia), VI. Askangel (U.S.S.R.), VII. Pyzevsky (U.S.S.R.) and VIII. Jelsovy Potok (Czechoslovakia) Montmorillonites.

Preparation of pure montmorillonites from the above-mentioned natural deposits was carried out by repeated dispersion in distilled water, sedimentation and decantation and final drying. X-ray analysis of the separated samples showed them to be free from any other minerals.

TABLE 1

Structural Formulae of pure smectite samples

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I. Manito: $(\text{Si}_{6.90}\text{Al}_{1.10})(\text{Al}_{0.08}\text{Fe}_{3.83}\text{Mg}_{0.09})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.52}\text{Mg}_{0.07}$
II. Sampor: $(\text{Si}_{6.93}\text{Al}_{1.07})(\text{Al}_{0.06}\text{Fe}_{3.98}\text{Ti}_{0.02})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.54}\text{Mg}_{0.02}$
III. Polkville: $(\text{Si}_{7.54}\text{Al}_{0.46})(\text{Al}_{2.69}\text{Fe}_{0.68}\text{Mg}_{0.61}\text{Ti}_{0.02})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.54}\text{Na}_{0.02}$
IV. Arizona: $(\text{Si}_{7.67}\text{Al}_{0.33})(\text{Al}_{2.59}\text{Fe}_{0.43}\text{Mg}_{0.90}\text{Ti}_{0.08})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.58}$
V. Ginovec: $(\text{Si}_{7.67}\text{Al}_{0.33})(\text{Al}_{2.72}\text{Fe}_{0.42}\text{Mg}_{0.86})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.93}$
VI. Askangel: $(\text{Si}_{7.79}\text{Al}_{0.21})(\text{Al}_{2.72}\text{Fe}_{0.40}\text{Mg}_{0.88})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.51}\text{Mg}_{0.04}$
VII. Pyzevsky: $(\text{Si}_{7.66}\text{Al}_{0.34})(\text{Al}_{2.74}\text{Fe}_{0.19}\text{Mg}_{1.06})\text{O}_{20}(\text{OH})_4 - \text{Ca}_{0.83}$
VIII. Jelsovy Potok: $(\text{Si}_{7.78}\text{Al}_{0.22})(\text{Al}_{2.98}\text{Fe}_{0.26}\text{Mg}_{0.73}\text{Ti}_{0.03})\text{O}_{20}(\text{OH})_4$ $- \text{Ca}_{0.38}\text{Mg}_{0.06}\text{Na}_{0.02}\text{K}_{0.02}$

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Chemical analysis of the eight collected smectites was achieved by conventional silicate analysis. The corresponding structural formulae were calculated by the method described by Kelley [10]. The evaluated chemical formulae are shown in Table 1 [21].

### *Techniques*

Thermal weight loss curves were obtained by the help of an automatic thermobalance, produced by Gebrüder Netzsch, West Germany, at a heating rate of  $10^\circ\text{C min}^{-1}$ .

## RESULTS AND DISCUSSION

### *Thermogravimetry of the smectites*

The thermograms obtained are shown in Fig. 1. Direct analysis of these curves helps in estimating the weight loss associated with the processes of dehydration and dehydroxylation. The former is estimated from weight loss up to  $300^\circ\text{C}$ , and the latter from weight loss between 300 and  $800^\circ\text{C}$ . Dehydration is usually exhibited in a single wave whereas dehydroxylation appears, in many cases, in the form of overlapping waves.

The data in Table 2 indicate that the weight lost through the dehydroxylation region is generally in good concordance with the loss of two water molecules (corresponding to  $4\text{OH}$ ). Nevertheless, three montmorillonites (IV, V and VII) show higher loss than the respective values calculated from the chemical formulae. The excess loss amounts roughly to two more OH groups which could be attached to the exchangeable cations in the octahedral layer, or superficially to Si atoms in the tetrahedral layer. An apparent correlation seems to relate the excess water loss to the presence of

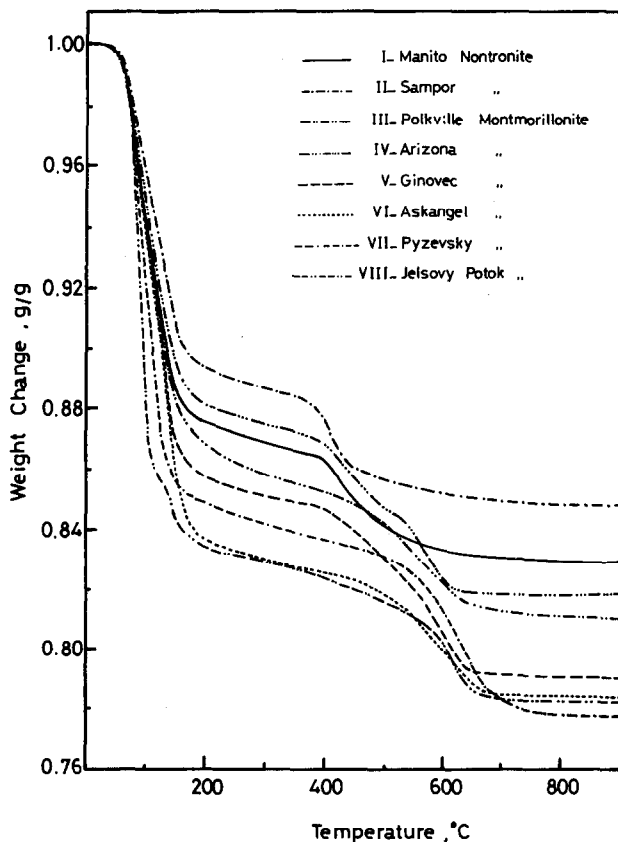


Fig. 1. TGA curves of the pure smectite samples.

a higher content of calcium oxide, or to the sum of both CaO and MgO. The loss of water in this case may be exhibited in a multi TG wave in the dehydroxylation temperature range as seen in Fig. 1.

TABLE 2

Weight loss in the dehydration and dehydroxylation regions of TG (%)

Sample	Total loss < 800°C	Dehydration < 300°C	Dehydroxy- lation 300-800°C	Dehydroxy- lation d.w.	Dehydroxy- lation chem. formula
I. Manito	16.92	13.01	3.91	4.49	4.22
II. Sampor	15.16	11.20	3.96	4.46	4.19
III. Polkville	18.95	14.27	4.68	5.46	4.73
IV. Arizona	18.19	12.25	5.94	6.77	4.77
V. Ginovec	20.97	15.06	5.91	6.98	4.69
VI. Askangel	21.47	17.18	4.29	5.18	4.79
VII. Pyzevsky	22.23	16.04	6.19	7.37	4.76
VIII. J.P.	21.85	17.31	4.54	5.49	4.87

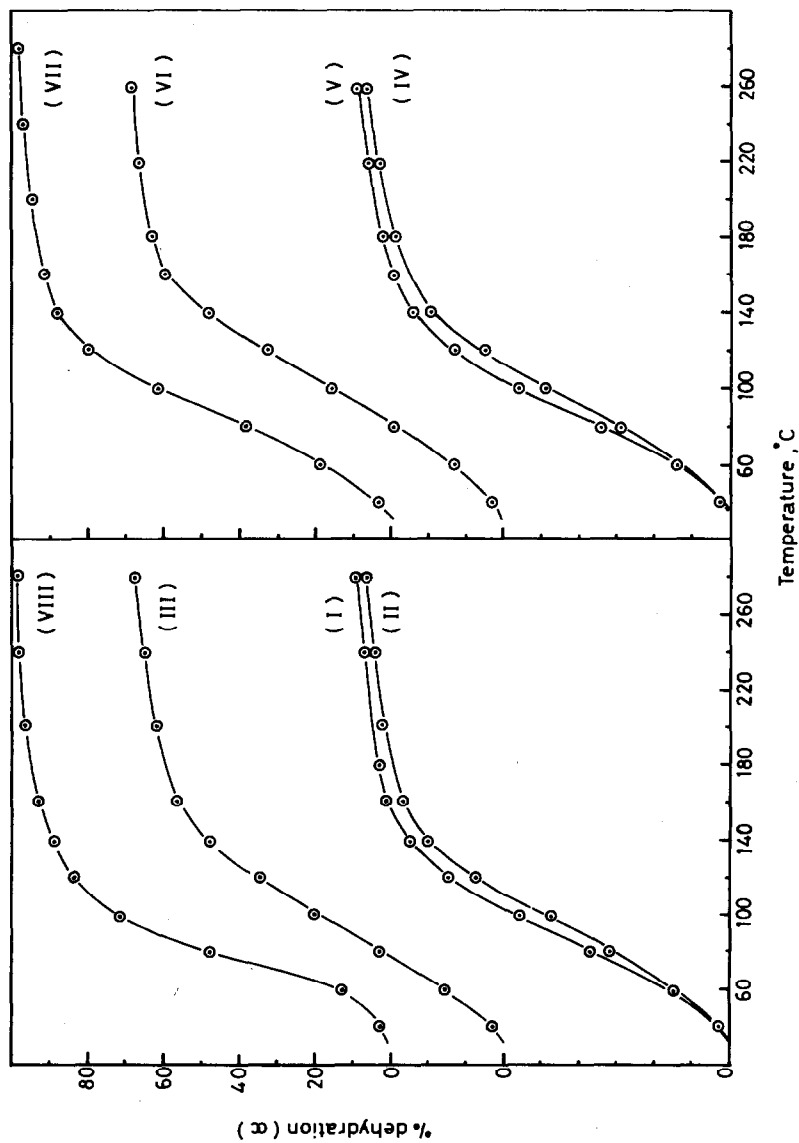


Fig. 2. Fractional decomposition curves of pure smectites in the dehydration region.

*Dehydration kinetics of the smectites*

The TG curves in Fig. 1 were segmented into two parts: the first covering the range up to 350°C and the second covering the range from 350 up to 800°C. The former was transformed into decomposition curves plotted in the form of fraction decomposed as a function of temperature (Fig. 2).

For the analysis of the dehydration curves two methods were employed.

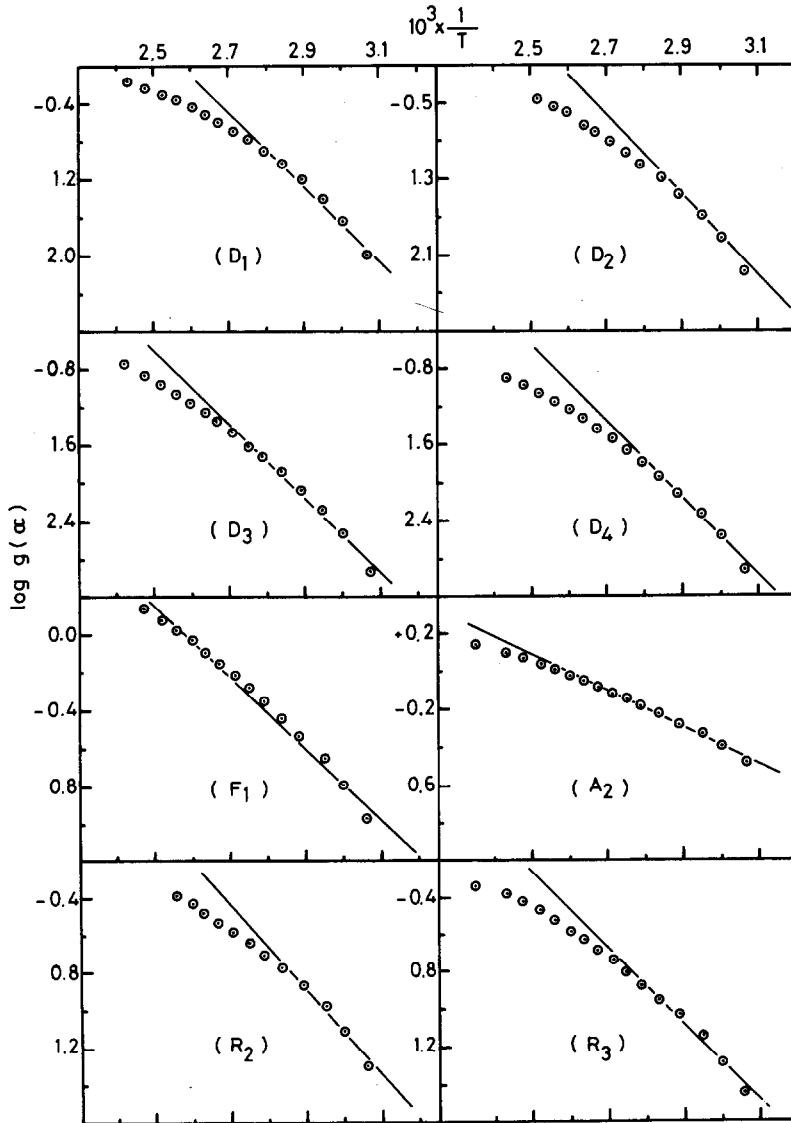


Fig. 3. Plots of  $\log g(\alpha)$  vs.  $1/T$  for the dehydration of Sampor nontronite (sample II), applying the various functions of Šatava.

The one developed by Šatava and Skvára [3] and Šatava [7] and the method of Coats and Redfern [11] as outlined by Johnson and Gallagher [12].

*The method of Šatava*

A number of solid-state reaction mechanisms has been developed and given definite symbols denoting the form of the predominantly occurring

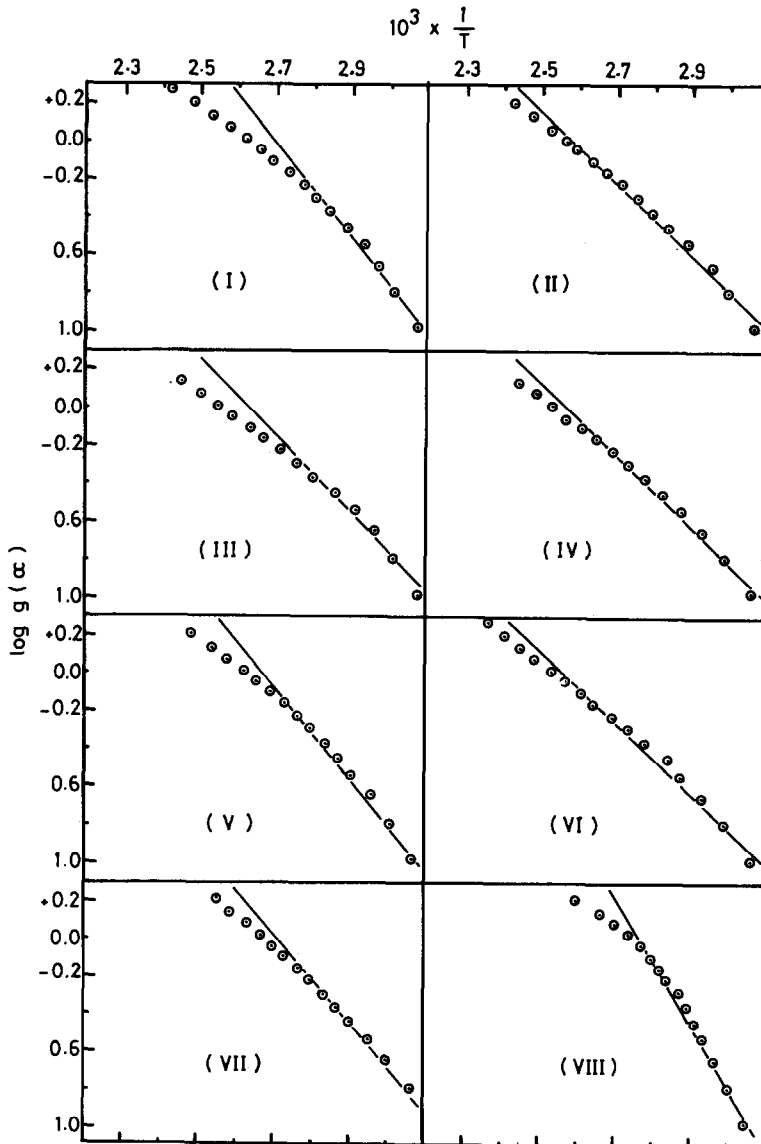


Fig. 4. Plots of  $\log g(\alpha)$  vs.  $1/T$  for  $F_1$  function of Šatava for the eight smectite samples.

TABLE 3

Activation energy of dehydration of smectites evaluated from the methods of Šatava and Coats and Redfern ( $\text{kcal mol}^{-1}$ )

Sample No.	Parameter	Šatava ( $F_1$ ) mechanism	Coats and Redfern $n=1$
I	$E_d$	12.87	9.62
	$\alpha$ range	0.10–0.40	0.10–0.50
II	$E_d$	10.48	8.24
	$\alpha$ range	0.10–0.80	0.10–0.45
III	$E_d$	11.19	9.08
	$\alpha$ range	0.10–0.45	0.1–0.4
IV	$E_d$	9.61	7.83
	$\alpha$ range	0.10–0.80	0.10–0.55
V	$E_d$	11.89	9.77
	$\alpha$ range	0.10–0.60	0.1–0.50
VI	$E_d$	16.89	8.46
	$\alpha$ range	0.10–0.55	0.1–0.55
VII	$E_d$	11.86	9.21
	$\alpha$ range	0.10–0.60	0.1–0.55
VIII	$E_d$	17.35	13.72
	$\alpha$ range	0.05–0.60	0.05–0.60

mechanism [3,7,13–15]. Some of these functions were evaluated and tabulated by Šatava [3,7]. It was proposed that the dynamic thermogram (in the form of fraction  $\alpha$ ) to be plotted according to the various reaction mechanisms, as  $\log g(\alpha)$  vs.  $1/T$ . The most probable kinetic mechanism would be the one that yields a straight line in this plot that covers most of the decomposition reaction.

One sample was tested in this manner by plotting against eight reaction mechanism functions, and are shown in Fig. 3. The random nucleation mechanism, with one nucleus on the individual particle (denoted by  $F_1$ ) seems to hold throughout most of the dehydration range up to  $\alpha = 0.75$ . The equation describing this mechanism is in the form

$$\log\left(\ln \frac{1}{1-\alpha}\right) \text{ vs. } 1/T$$

and was applied to all TG curves of the eight smectites (Fig. 4). The activation energy of dehydration was then evaluated by using the slope of each straight line in eqn. (4) cited above. The activation energies evaluated are given in Table 3.



*The method of Coats and Redfern [11]*

This method, as reviewed by Johnson and Gallagher [12] is an integral method and assumes various orders of reaction and compares the linearity in each case to select the correct order. This orders zero, one-half, two-thirds, and first have been used since each of these correspond to a simple model

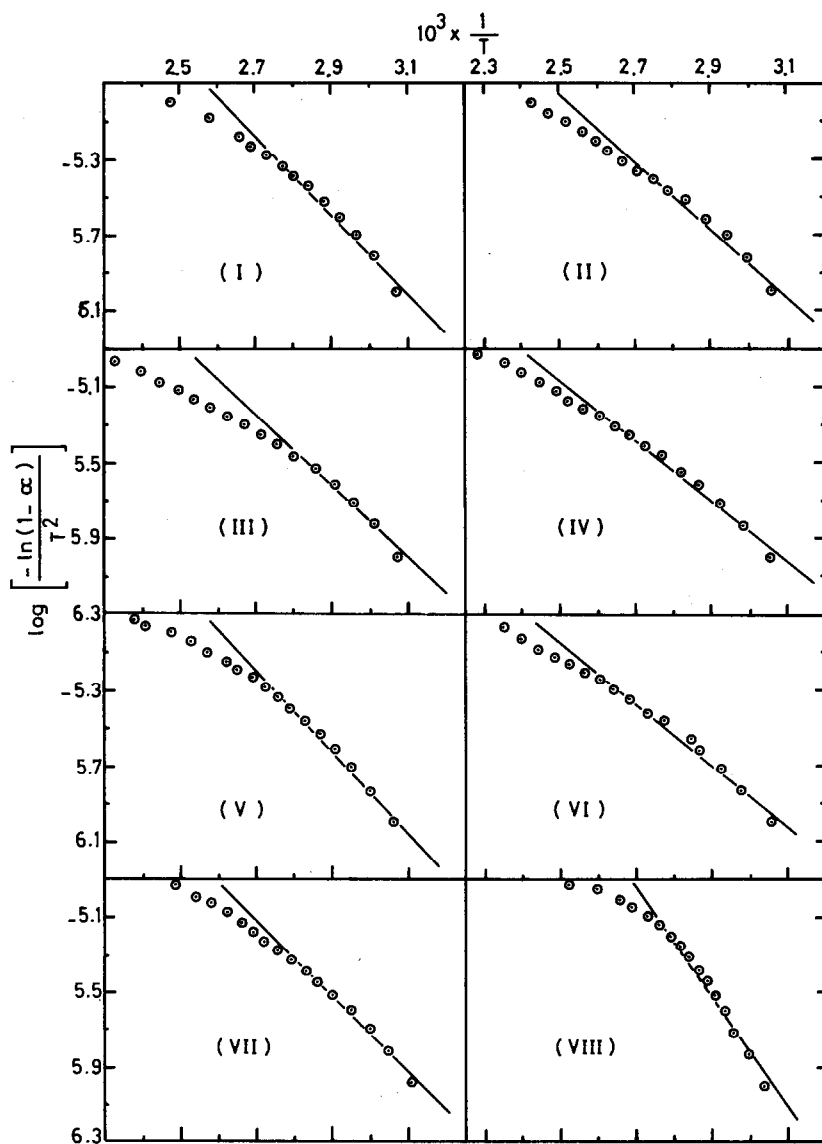


Fig. 5. First-order linear plots of Coats and Redfern for the eight smectite samples.

for solid-state decompositions. Using this, the Coats and Redfern equations become [12]

$$\log \frac{1 - (1 - \alpha)^{1-n}}{T^2} = \log \left[ \frac{AR}{BE} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.3RT} \quad \text{for } n \neq 1$$

and

$$\log \frac{-\ln(1 - \alpha)}{T^2} = \log \left[ \frac{AR}{BE} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{2.3RT} \quad \text{for } n = 1$$

By plotting the appropriate left hand side of the above equations vs.  $1/T$ , the slope equals  $-E/2.3R$ . In testing the present data of dehydration of smectites, the equations expressing the orders 0, 1/2, 2/3 and 1 were plotted accordingly. The first order equation was found to fit better and to extend through a wider range of decomposition. The straight line plots for the eight smectites are given in Fig. 5, and the evaluated energies of activation are cited in Table 3.

## DISCUSSION AND CONCLUSIONS

In general, the  $F_1$  function fits better to the dehydration of the smectites under consideration as it extends to higher fractional decompositions, as compared to the first order equation of Coats and Redfern [11]. Moreover, the former function calculates activation energies that are always higher by about 10% than the latter one. Comparison of the data in Table 3 points to the following remarks.

(1) The mean values for the activation energies ( $E_d$ ) are  $12.0 \pm 2.5$  and  $9.5 \pm 1.6$  kcal mol<sup>-1</sup>, as evaluated from the above-mentioned methods. Only sample VIII shows a significant deviation from these values.

(2) The nontronites, the iron-rich smectite I and II, do not seem to show any characteristically different estimate for  $E_d$ .

(3) The apparent small differences in  $E_d$  are not correlated with the structural formulae of the smectites or to their contents of exchangeable cations (mainly Ca<sup>2+</sup>). However, in general, these values could be correlated with the water content lost through the dehydration region.

(4) The estimated mean values of  $E_d$  are not much different from the values published earlier [16–18].

In conclusion, the eight internationally different smectites seem to show almost similar activation energies. This could be due to the fact that they are almost homoionic, since their predominant exchangeable cation is Ca<sup>2+</sup>. Activation energies of 9.5–12.5 kcal mol<sup>-1</sup> seem reasonable estimates for the dehydration of interlayer physically adsorbed water as well as from the hydration shells of the exchangeable cations. The width or thickness of this adsorbed and shell water usually depends on pretreatment, kind of ex-

changeable cation and locality of the raw material [19,20]. The last of these factors proved to be of no significance.

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