

DEHYDROXYLATION OF KAOLINITE, DICKITE AND HALLOYSITE: HEATS OF REACTION AND KINETICS OF DEHYDRATION AT

$$P_{H_2O} = 15 \text{ psi}$$

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ABSTRACT

Values of the enthalpy of dehydration determined by differential thermal analysis are 151, 156 and 160 cal/gm for kaolinite, dickite and halloysite respectively. Activation energies for dehydration at a water pressure of 15 psi are considerably greater than published activation energies determined at much lower water vapor pressures. Kinetic data obtained from the DTA curves suggest that the order of reaction for the dehydration of kaolinite, dickite and halloysite is somewhat greater than one.

INTRODUCTION

Published determinations of the heat required to dehydrate the clay minerals have generally been in poor accord. Values of  $\Delta H$  for unidentified brick clays (Ramachandran and Majumdar 1961) have ranged as low as 9 cal/gm, while values as high as 253 cal/gm for kaolinite (Barshad 1952) have been reported. In this paper, the results of 51  $\Delta H$  determinations of 9 samples of kaolinite, 5 samples of halloysite and 1 specimen of dickite dehydrated at  $P_{H_2O} = 15$  psi are given. Data concerning the reaction kinetics were derived from the same differential thermal analysis (DTA) curves.

EXPERIMENTAL

The DTA apparatus described by Herold and Planje (1948), in which the sample containers themselves serve as the differential thermocouple, has been modified and incorporated in a  $\frac{1}{2}$ " I.D., 2" O.D. stellite pressure vessel. The differential thermocouple comprises a sealed platinum "reference" capsule about 15 mm long and 2.5 mm in diameter containing  $Al_2O_3$ , and an unsealed capsule of similar dimensions in which approximately 80 mg of sample are packed. Connecting the two capsules to each other and to the potentiometric recorder are Platinel noble-metal thermocouple wires (Accinno and Schneider 1960) which provide an emf comparable with chromel-alumel. Amplification is provided by a solid state Acromag d.c. amplifier with a long term drift of 5 microvolts and a noise level of 1 microvolt.

After a weighed amount of sample crushed to -325 mesh particle size is packed into the sample capsule, fiberfrax for electrical insulation is wound around the differential couple and the temperature measuring

thermocouple, and the apparatus is inserted in the pressure vessel of the cold seal type.

Several advantages accrue from the use of such apparatus:

(1) very small samples permit rapid equilization of temperature differences within the sample, (2) high sensitivity is achieved with Platinel thermocouple alloys and the solid-state d.c. amplifier permitting better measurement of the time and temperature at which the reaction begins, and (3) the thick metal walls of the pressure vessel reduce small temperature fluctuations of the furnace, and in addition, effectively serve as electrostatic and magnetic shielding.

Theoretical analysis of the heat transfer by Sewell (1955) indicates that with this type of apparatus, the DTA peak area is to a first approximation independent of the thermal conductivity of the sample. Moreover, Sewell (1952) and others have shown that the peak area is proportional to the heat of reaction per unit mass of reacting material, and that the peak area is independent of the heating rate provided it is linear, the rate at which the reaction takes place, and the specific heat of the sample.

The area under the DTA curve produced by endothermic dehydration of the clay minerals can be related to the heat involved in the reaction after calibration of the DTA apparatus. The technique has been utilized by Barshad (1952) and by Ellis and Mortland (1962). Plotting peak area against calorie measurements obtained by differential thermal analysis of a variety of compounds with known heats of fusion or inversion, a calibration curve was constructed for the apparatus. Precision (reproducibility), evaluated by replicate analysis, is indicated by the calculated standard deviation of 5.9 cal/gm.

Information concerning the reaction kinetics was derived from the DTA curves assuming a relationship between the rate of reaction and the concentration of the remaining reactant:  $-dc/dt = kc^n$ , where  $dc/dt$  is the change in concentration of the reactant with time,  $c$  is the concentration of the unreacted sample,  $k$  is the specific reaction rate or rate constant, and  $n$  is the order of reaction. The value of  $k$  can be determined if  $n$  is known and if measurements of  $dc/dt$  and  $c$  can be made. The latter are obtained from measurements of the area under a number of sections of the DTA curve. Using measurements of  $dc/dt$  and  $c$  at as many as 20 points distributed over the interval between the beginning and the completion of the reaction, sets of values of  $k$  are computed for arbitrary values of  $n$  ranging from 0 to 4.0 at 0.2 increments. Each set of  $k$  values and associated values of the temperature of the sample<sup>1</sup> corresponding to

<sup>1</sup> The temperature of the sample is obtained by subtracting the temperature difference between the reference and sample capsules (proportional to the distance between the DTA curve and the base line) from the temperature indicated by the temperature measuring thermocouple.

one of the 21 arbitrary values assigned to  $n$  is fitted to the Arrhenius equation,  $k = Ae^{-E/RT}$ , where  $E$  is the energy of activation,  $A$  is a constant,  $R$  is the gas constant, and  $T$  is the absolute temperature. The value of  $n$  for the set of  $k$  and  $T$  values which best fits this equation is selected as the observed order of the reaction.<sup>2</sup>

Inherent in this method are the assumptions that:

(1) the rate of reaction is very small at the lowest temperature obtainable and the reaction is essentially complete below the highest temperature attained, (2) heat is transferred to the sample and reference capsules uniformly, and heat loss by radiation or by conduction along the thermocouple wires is small and uniform, (3) the temperature of the reactant is uniform, that is, there is no temperature gradient in the sample capsule, (4) the area under any appreciable portion of the DTA curve is proportional to the heat absorbed during the time interval in which that portion of the DTA curve was recorded, and this quantity of heat is in turn proportional to the mass of the sample which reacted during this time, (5) the kinetics of the reaction can be described by a single rate constant, and (6) the activation energy does not vary with temperature during the reaction.

## RESULTS

*Heats of reaction.* Measured heats of reaction (Table 1, col. 7) constitute the heat transfer during dehydration divided by the weight of the sample. Because of sample impurity, the observed  $\Delta H$  will always be less than the heat of reaction to be associated with the pure kandite. For this reason, considerable variation in measured  $\Delta H$  is evident, for example 118 to 159 cal/gm in the case of kaolinite. It is necessary, therefore, to adjust the measured heats of reaction according to the purity of the sample. Although  $x$ -ray diffraction and microscopic examination might be used to estimate the kandite content of the clay samples in this study, it is probable that data of greater accuracy are obtained by chemical analysis. Accordingly,  $Al_2O_3$  analyses by replicate  $x$ -ray fluorescence were used to calculate the percentages of kaolinite, dickite, and halloysite (Table 1, col. 8) on the basis that all of the observed aluminum was present in these minerals. Corrected values of  $\Delta H$  are relatively concordant, and appear in col. 9.

For kaolinite, the mean heat of reaction is 151 cal/gm, in good agreement with 154 and 157 cal/gm reported by Ellis and Mortland (1962)

<sup>2</sup> In practice, for each of up to 20 points selected along the DTA curve, measurements of area, time, temperature and height above base line are input to a digital computer program which calculates sets of  $\log k$  and  $1/T$  values for each selected value of  $n$ . Since the transform of the Arrhenius equation,  $\log K = \log A - E/2.303 RT$ , is linear, least squares or linear regression is used to construct the best fit straight line through each of the 21 sets of data associated with one DTA curve. The correlation coefficient,  $r$ , is computed and the value of  $n$  associated with the highest value of  $r$  is selected as the order of reaction. Plots of  $\log k$  against  $1/T$  are automatically printed by the same computer program for verification and visual inspection of the data.

and obtained by DTA and by calculation using the Clausius-Clapeyron equation respectively. Variation among samples (standard deviation 8.5 cal/gm) is little greater than that expected from experimental error (standard deviation 5.9).  $\Delta H$  for dickite is within the range of values

TABLE 1. HEATS OF REACTION AND REACTION KINETIC DATA FOR KAOLINITE, DICKITE, AND HALLOYSITE, DEHYDRATION AT  $P_{H_2O} = 15$  psi

Serial Number	No. Anal.	$^1T_c$ °C	$^1T_p$ °C	n	E Kcal/ mole	Meas. $\Delta H$ cal/gm	% kan- dite	Corrected $\Delta H$ cal/gm	
(1) <i>Kaolinite</i>									
1	Rio Grande, Sao Paulo, Brazil	3	575	633	2.7	111	134	93.8	143
2	Zettlitz, Germany	3	568	615	3.0	147	133	93.8	142
3	Cape Province, South Africa	3	559	603	1.3	106	118	83.3	142
4	Pugu, Tanganyika	3	557	600	1.3	102	118	79.6	148
5	Heystrek, South Africa	3	572	614	3.0	152	133	91.3	146
6	Bath, South Carolina	3	555	603	1.1	92.8	144	94.6	152
7	Mesa Alta, New Mexico	3	571	620	3.0	134	159	98.2	162
8	Lewistown, Montana	3	582	635	1.9	107	153	97.4	157
9	Spruce Pine, North Carolina	3	555	607	1.9	99.7	141	86.3	163.5
	Mean		566	614	2.1	117			151
	Standard deviation		9.8	12.9	0.8	21.7			8.5
(2) <i>Dickite</i>									
1	Chihuahua, Mexico	5	575	688	1.1	52.5	149	95.6	156
(3) <i>Halloysite</i>									
1	Eureka, Utah	5	544	592	1.4	94.5	167	93.9	178
2	Democrat, North Carolina	3	545	599	0.9	85.2	128	92.5	138.5
3	Wagon Wheel Gap, Colorado	3	546	604	1.0	79.0	163	100	163
4	Alexander, North Carolina	5	549	604	1.0	94.2	164	99.6	165
5	Sheba, Transvaal	3	549	603	0.4	72.5	133	86.3	154
	Mean		547	600	0.94	85.1			160
	standard deviation		2.3	5.1	0.36	9.58			14.6

<sup>1</sup>  $T_c$ —DTA characteristic temperature.

$T_p$ —DTA peak temperature.

determined for kaolinite. Halloysite, however, exhibits a greater range of  $\Delta H$  as shown by the standard deviation for 5 samples of 14.6 cal/gm. Three of the halloysites (Eureka, Wagon Wheel Gap, and Alexander) provided  $\Delta H$  measurements between 10 and 27 cal/gm greater than the mean of the kaolinite group, and the average  $\Delta H$  of the halloysites studied is 9 cal/gm above that of the kaolinites. These observations are in accord with reliable chemical analyses assembled by Bates (1959), which

demonstrate both a higher average  $\text{H}_2\text{O}^+$  content and greater variation in the  $\text{H}_2\text{O}^+$  content of halloysite.

*Reaction kinetics.* There is general agreement that differential thermal analysis is inferior to weight loss techniques for the determination of kinetic data for three reasons:

(1) the temperature is changing while the reaction is taking place, whereas ideally, isothermal dehydration methods provide more reliable and precise information, and may contribute to the understanding of reaction mechanisms, (2) the concentrations of the reactant and products at any given time are determined indirectly by temperature differences (between the sample and a reference) resulting from heat transfer during the reaction; since heat transfer is not instantaneous, precise determination of concentrations is not possible, (3) it is necessary to assume that an equation relating the rate of change in concentration of the reactant to the concentration of the remaining reactant is a reasonable description of reality, and such factors as the shape of the reactant particles are not taken into account.

In an attempt to evaluate the reliability of kinetic data derived from DTA, Tsuzuki and Nagasawa (1957) obtained both weight loss and DTA curves for the same samples. Theoretical DTA curves constructed from kinetic parameters derived from weight loss data were shown to agree with DTA curves determined experimentally except for a slight displacement of the peak temperature.

Kinetic data were obtained from the same DTA curves used for determination of heats of reaction. The results are shown in Table 1. Except for halloysite, all observed values of the order of reaction are greater than the value of 1.0 usually obtained or in some cases assumed in previous studies (Shlykov 1960, Murray and White 1955, Allison 1954, Jacobs 1958 and others). Activation energies calculated from these data are by a factor of two (with the exception of dickite) greater than values obtained by Sabatier (1954) (44 Kcal/mole), Allison (1954) (37–58), Murray and White (1955) (37–45), Jacobs (1958) (38), Holt *et al.* (1962) (43.5), Brindley and Nakahira (1959) (65), Toussaint *et al.* (1963) (25), and Tsuzuki and Nagasawa (1957) (27 to 57).

Despite the low precision of DTA methods, both activation energies and orders of reaction are reproducible for a given sample. The extreme variation in  $n$  and  $E$  from sample to sample was not encountered in a study of the dehydration of brucite with the same apparatus (Weber and Roy 1965). It should be emphasized, however, that the samples were dehydroxylated under  $P_{\text{H}_2\text{O}} = 15$  psi, whereas published activation energies were determined for the dehydration of kaolinite under vacuum or very low water vapor pressure conditions, or in air. If the activation energy for the dehydration of kaolinite varies with water pressure, as it does for the dehydration of gypsum (McAdie 1964) and brucite (Weber and Roy 1965), values of  $E$  greater than the published values quoted

above would be expected. To investigate this possibility, kinetic data were obtained from DTA curves obtained at pressures up to 130 psi. Activation energy, plotted as a function of water pressure in Figure 1, appears to increase with increasing  $P_{H_2O}$ , but the relationship is poorly defined. It is interesting to note, however, that the best fit line through these points extrapolates to an activation energy of about 40 Kcal/mole at water vapor pressures in the range of the ambient  $P_{H_2O}$  in which published experiments were made. Preliminary thermogravimetric experiments by Sharp and Patterson (1964) suggest a pronounced increase in activation energy with increasing water vapor pressure for a Florida

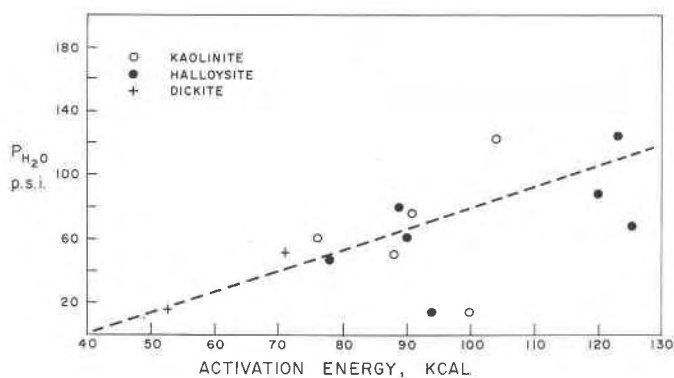


FIG. 1. Pressure dependence of the activation energy for dehydration of kaolinite, dickite, and halloysite at water pressures between 20 and 130 psi.

kaolinite. The observed order of reaction for this kaolinite is greater than one. For kaolinites from Mesa Alta and Mikawa, Tsuzuki and Nagasawa (1957) found  $n$  equal to 1.5 and 2.0 respectively.

Further evidence for the pressure dependence of the activation energy is found by inspection of the DTA curves of well crystallized kaolinite (Kaalex WW) provided by Stone and Rowland (1955). Under vacuum dehydration, the DTA curve is relatively broad. With increasing water pressure, up to the maximum of 6 atm attained by these authors, the endothermic curve becomes better defined and sharper (of higher kurtosis). As Tsuzuki and Nagasawa (1957) have demonstrated, the effect of increasing activation energy on the shape of the DTA curve is to sharpen the peak considerably.

#### SUMMARY

Heats of reaction, corrected for sample impurity, have been determined as 151, 156 and 160 cal/gm for kaolinite, dickite and halloysite

respectively. Greater variation in  $\Delta H$  for halloysite is attributed to greater  $H_2O^+$  variation in this mineral. There is some evidence that the heat of dehydration (intralayer water) of halloysite is greater than  $\Delta H$  for kaolinite and dickite, corresponding with the somewhat greater  $H_2O^+$  content of halloysite with respect to kaolinite and dickite.

Activation energies for dehydration at a water pressure of 15 psi are two to three times greater than published values obtained at very low water vapor pressures, and evidence is presented to demonstrate that the activation energy increases with increasing water pressure. Despite the low precision of differential thermal analytical methods, the data suggest that dehydration of the kandites at water pressures of 15 psi and above follows a reaction law somewhat above first order.

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