DTA OF KAOLINITE AND MONTMORILLONITE UNDER WATER VAPOR PRESSURES UP TO SIX ATMOSPHERES *

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ABSTRACT

Thermograms of kaolinite and montmorillonite were obtained at water-vapor pressures varying from approximately 0.0001 to 4,500 mm. of Hg with a variable pressure, dynamic gas, differential thermal analysis apparatus. The beginning of the kaolinite endotherm is shifted to a higher temperature with increasing water-vapor pressure. The sharp kaolinite exotherm is shifted to a lower temperature until at six atmospheres water-vapor pressure it makes a small broad peak at approximately 900° C. The dehydroxylation endotherm of montmorillonite is almost unaffected. The 900° C endotherm and the recrystallization exotherm are shifted to a lower temperature with increasing water-vapor pressure. The temperatures of the start of the endothermic peaks associated with exchange cations are shifted upward by increased gas (N_2) pressure.

INTRODUCTION

The effect of water vapor at pressures up to one atmosphere on the thermograms of several kaolinites and montmorillonites was reported by Stone (1951), who used the temperatures of the beginning of the dehydroxylation endotherms to obtain the heat of dehydroxylation. Results with the apparatus employed indicated that equilibrium temperatures could not be obtained at pressures below about 500 mm. of Hg. Several effects of water vapor on kaolinite were not anticipated: (1) At very low partial pressures of water vapor the kaolinite exotherm peaked at 1,000° C, but at 1 atm. pressure of water vapor, the exotherm peaked at 970° C; (2) the intensity of the exotherm was decreased by increasing the water-vapor pressure; and (3) the return-to-zero side of the dehydroxylation endotherm became steeper as the partial pressure of water vapor was increased.

Thermogram data for the montmorillonites were not as complete, but the effects of water-vapor pressure appeared to parallel those observed for kaolinite. These effects were: (1) The temperature of the 700° C endotherm was raised; (2) the temperature of the 900° C endotherm was lowered; and (3) the temperatures of the exothermic reactions were lowered. No attempt was made to explain these effects.

In the present study, thermograms were made at pressures up to six atmospheres to extend the range previously observed.

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PROCEDURE AND RAW MATERIALS

The heating rate of the variable-pressure and controlled-atmosphere DTA apparatus used in this study was 10° C to 12° C per minute. The sample holder cavities were 0.375 inch diameter by 0.375 inch deep and the sample weights were 0.50 gm. of kaolinite or 0.65 gm. of montmorillonite. Alcoa A-10 alumina was used as the inert material. Two of the kaolinites, Kaolex WW and Kaolex SC were wetted to a stiff plastic consistency, dried for 15 hours at 60° C, and crushed to pass through a $\frac{1}{2}$ mm. sieve. The other materials were received in lump form, dried at 60° C and crushed to pass through the $\frac{1}{2}$ mm. sieve. The samples were stored in screw-cap bottles immediately after crushing.

Four runs were made on each material: (1) In a vacuum of approximately 2.5 mm. of Hg with N_2 as the dynamic gas which provided a partial pressure of water vapor of about 0.0001 mm. of Hg; (2) at one atmosphere total pressure with dynamic water vapor; (3) at three atmospheres; and (4) at six atmospheres. In the first run, the vacuum was created (with N_2 as the dynamic gas) before the temperature rise was started; these conditions were maintained throughout the run. In the one-atmosphere run, oil-pumped nitrogen was used as the dynamic gas up to approximately 300° C and above this temperature the N_2 was replaced with steam (*i.e.,* water vapor). In the three- and six-atmosphere runs, the pressure of the system was raised to these pressure values with N_2 as the dynamic gas before the temperature rise was started; at about 300° C the dynamic N_2 was replaced with water vapor.

Three kaolinites, Kaolex WW, Kaolex SC, and New Mexico flint clay were used. Kaolex WW is a water-washed kaolin from Macon, Georgia, produced by J. M. Huber, Inc. Kaolex SC is an air-floated unrefined kaolin from near Bath, South Carolina, also marketed by Huber. The sample of the N.M. flint clay was obtained from the Filtrol Corp. Chemical analyses are given in Table I.

TABLE I. — TYPICAL CHEMICAL ANALYSES OF TEST CLAYS [1]

	Kaolex WW	Kaolex SC	N.M. Flint	Wyoming Montmo- rillonite	Apache Montmo- rillonite
SiO_2	45.64	45.01	48.48	64.32	59.23
TiO_2	1.27	1.42	—	.14	.26
Al_2O_3	38.53	38.95	37.50	20.74	17.58
Fe_2O_3	.53	.50	tr.	3.03	1.99
FeO	—	—	—	.46	—
MgO	.01	.03	.02	2.30	6.19
CaO	.13	.13	.06	.52	2.84
Na_2O	.002	.004	—	2.59	.16
K_2O	.008	.008	—	.39	.75
H_2O	13.85	13.89	13.97	5.14	11.03
Total	99.97	99.94	100.03	99.63	100.03

[1] All analyses through the courtesy of the producers.

The kaolinite materials represent (1) a coarse-grained, well-crystallized kaolinite, (2) a fine-grained, poorly crystallized kaolinite of sedimentary origin, and (3) a very fine-grained kaolinite of the flint clay type. All three are extremely pure kaolinites.

The two montmorillonites are Wyoming bentonite, marketed as Volclay, and a calcium montmorillonite from Apache County, Arizona, known as Cheto bentonite. Chemical analyses are given in Table I. These two montmorillonites were selected because of their high-temperature exotherm. The Wyoming material has the exotherm immediately following the 900° C endotherm while the Arizona material has the delayed exotherm peaking above 1000° C.

RESULTS AND DISCUSSION
A. — Kaolinite

The thermograms for the four pressures of each kaolinite (Figs. 1, 2, and 3) have been transposed to the same chart to facilitate comparison.
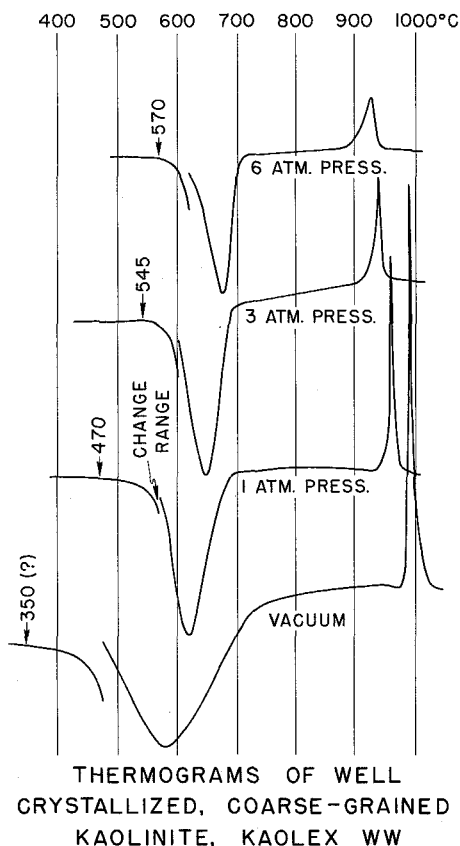

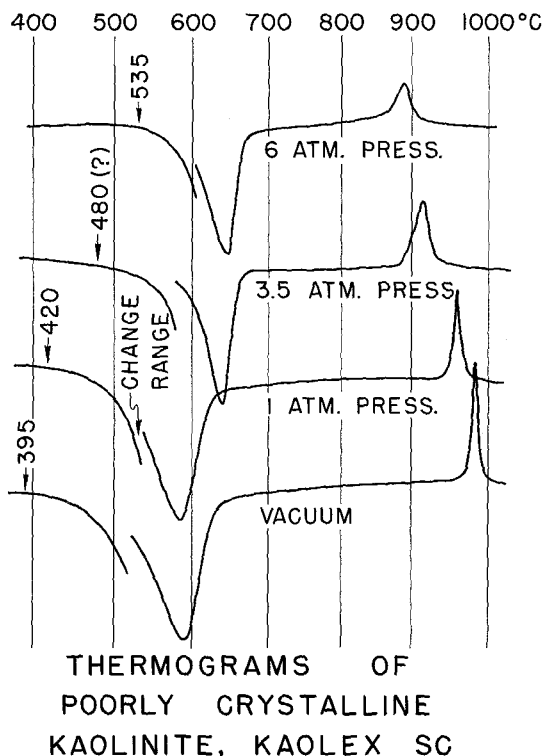FIGURE 1. — Thermograms of well crystallized, coarse-grained kaolinite Kaolex WW.

FIGURE 2. — Thermograms of poorly crystalline kaolinite, Kaolex SC.

Only those portions of the thermograms involving features to be discussed are given in the figures.

All three kaolinites show the same general effects of water-vapor pressure, but there are distinct differences among the three which may be attributable more to crystallinity than to particle or crystal size.

In general the effects are as follows: (1) The *starting* temperature of the dehydroxylation loop is moved to a higher temperature by increasing the water-vapor pressure. (2) The return-to-zero point and the peak of the dehydroxylation loop are almost unaffected. (3) The peak temperature and the intensity of the recrystallization exotherm are lowered by increasing the water-vapor pressure. These data are given in Table II and are plotted in Figure 4.

1. *The Dehydroxylation Endotherm.* — In the plot of the data on the start of the dehydroxylation endotherm the points for pressures below one atmosphere do not fall on a straight line with those of one atmosphere and above. This is because of insensitivity of DTA apparatus — for the machine to show deflection, as at the start of a loop, the reaction must be proceeding at a minimum rate. At low pressures, the temperature interval above equi-
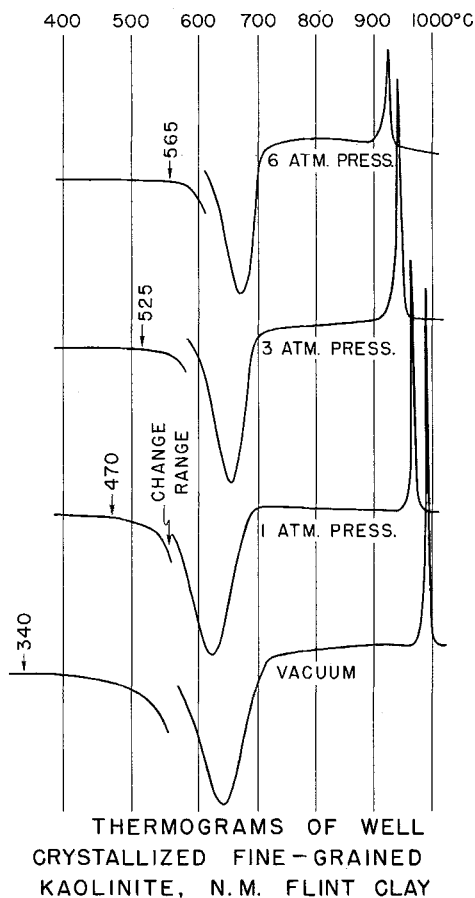
FIGURE 3. — Thermograms of well crystallized fine-grained kaolinite, N.M. flint clay.

librium to cause this minimum rate is considerable, but rapidly decreases as the pressure of the active gas increases so that at approximately one atmosphere the temperature interval closely approaches zero. The fact that this point is about one atmosphere is purely coincidental.

Theoretically, increasing the sensitivity of the machine might produce accurate data at lower pressures, but this is limited by practical aspects of design. Drift of the zero level due to inhomogeneity of the wires in the differential couple and to differences in thermal conductivities and heat capacities of the standard and unknown must be overcome and a nearly perfect temperature-rate controller must be built. The values reported herein are commensurate with present designs of apparatus.

The data on the start of the endotherm are shown in Figure 4 as the line having a slope to the left. If the decomposition proceeds according to

Table II. — Data on the Endotherms and Exotherms

Material	p_{H_2O} (in. Hg)	Dehydrox. Endo (°C)			Destruct. Endo (°C)		Exotherm (°C)	
		Start	Peak	Return	Start	Peak	Start	Peak
Kaolex WW	1.5	380	600	750±			985	995
	29.5	470	620	700			930	960
	88.0	545	655	700			895	940
	177.0	570	675	705			870	925
Kaolex SC	0.3	395	590	650±			950	980
	29.5	420	590	630			930	950
	88.0	480	640	670			880	910
	177.0	535	645	675			860	890
N.M. Flint	<.01	340	640	730±			960	985
	29.5	470	625	695			940	965
	88.00	525	650	705			900	940
	177.0	565	670	710			895	925
Wyoming Mont.	<.01	520±	705	760	810	915	——	955
	29.5	560±	705	750	775	875	——	915
	88.0	625	750	780	——	810	——	885
	177.0	660	770	810	Merged		——	865
Apache Mont.	<.01	425	655	790	810	880	930±	1010
	29.5	590	715	765	795	850	935	980
	88.0	600(?)	745	780	795	840	925	970
	177.0	600(?)	765	785	790	815	890	950

equation (1), the $\triangle H$, or heat of dehydroxylation, can be calculated by equation (2).

$$Al_2Si_2O_5(OH)_4 = (Al_2O_3 + SiO_2 \text{ complex}) + 2H_2O \qquad (1)$$
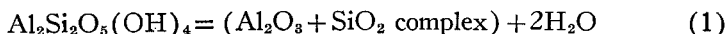
$$\ln p_2 - \ln p_1 = \frac{\triangle H}{2R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (2)$$

In making calculations, the values at $p_2 = 200$ inches of Hg and $p = 30$ inches of Hg are reasonable. $R = 1.9864$ cal. per deg. mole. The value of $\triangle H$ calculated from the data on Kaolex WW and N.M. flint clay is 170 cal. per gram while the $\triangle H$ calculated from the data for the Kaolex SC is 140 cal. per gram.

These data indicate that the poorly crystallized material requires less heat for dehydroxylation. The temperature of the dehydroxylation is lower for the poorly crystallized kaolinite than for the more perfectly crystallized kaolinite. Crystal size does not appear to have an effect. The crystals of the N.M. flint clay are far more minute than are those of the Kaolex SC kaolinite.

2. *The Exotherm.* — The plot of the exotherm data in Figure 4 and the thermograms in Figures 1, 2, and 3 show that the water vapor has a very real effect on the position and shape of the exotherm: the intensity and temperature are lowered materially. The peak of the exotherm of the
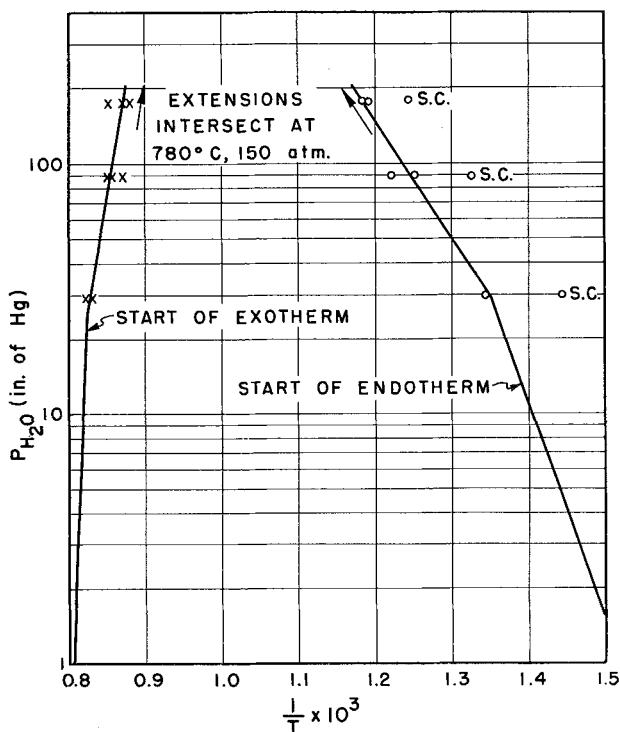
VAN'T HOFF PLOT OF THE KAOLINITE DATA

FIGURE 4. — Van't Hoff plot of the kaolinite data.

vacuum run for Kaolex WW, Figure 1, is shown at 990° C, and similar values are reported for the other kaolinites. One experimental run on Kaolex WW under conditions closely paralleling those which produced the thermograms in Figure 1 gave the exotherm peak at 1,065° C. Repeated runs failed to reproduce this peak temperature although this value when plotted on Figure 4 falls on the line for pressures of one atmosphere and above, indicating that it is a correct temperature.

The effects observed were first thought to be partially a manifestation of the Le Chatelier-Braun law; therefore, Kaolex WW and the N.M. flint clay were tested at the corresponding four pressures using dynamic N_2 throughout the runs. All thermograms were alike, showing that the effects observed were due to water-vapor pressure and not to increased pressure alone.

3. *General Interpretation.* — If the lines in Figure 4 are extended they will intersect at approximately 150 atmospheres and 780° C, which would correspond to a quintuple point. This extrapolation of the lines certainly will not produce extremely reliable figures, but the significance is not lost. At

pressures below the quintuple point, the stability temperature for kaolinite is increased by increasing the pressure of water vapor, and at the dehydroxylation temperature it decomposes into the familiar alumina-silica complex which recrystallizes at a higher temperature. The fact that the endo and exo lines of Figure 4 intersect means that at the intersection the existence interval of this anhydrous alumina-silica complex is zero and the decomposition products are not water plus the complex. Above the quintuple point, the decomposition products are probably boehmite and pyrophyllite as indicated by Roy (1954). Furthermore, it is probable that the kaolinite stability line changes slope at the quintuple point so that the stable temperature of the kaolinite is decreased as the pressure is further increased. And, indeed, kaolinite may disappear entirely as a stable phase at higher pressures.

In vacuum runs, the return-to-zero side is very gradual, and the break at the zero level is indistinct for Kaolex WW and for the flint clay. In both cases, the return is complete at approximately 720° C. An increase of the water-vapor pressure to one atmosphere sharpens the return point and lowers the temperature to about 695° C. At higher pressures this point moves to slightly higher temperatures. Kaolex SC, the less perfectly crystallized kaolinite, shows a sharp return-to-zero even in vacuum run in which it reaches the zero level at about 620° C as compared to 720° C for Kaolex WW.

The increase of the starting temperature of the dehydroxylation loop and the rather stationary return-to-zero point would cause the intensity of the loop to be increased if the area under the curve remained constant. But the intensity of the loop remains constant or decreases slightly with increased water-vapor pressure and the area under the curve decreases. According to Spiel *et al.* (1945) the area under the curve is proportional to the heat absorbed. If this is true then the heat absorbed during the time-temperature interval of the loop decreases with increasing water-vapor pressure.

The heat of dehydroxylation data as determined by the starting temperature did not show a decline with increased pressure; hence the decrease in area must be attributed to another cause. Coincidental with the decrease in the area under the endothermic loop there is a decreased intensity of the exothermic loop.

It is postulated here that the dehydroxylation loop is the composite of at least two reactions. The first is the endothermic dehydroxylation, or OH release reaction; the second is an exothermic reorientation (perhaps recrystallization) reaction involving the solid products of dehydroxylation. The very fact that the starting temperature of the endothermic loop moves upward when the pressure of the active gas is increased means that the reaction occurring at that instant is reversible, yet rehydration of the resulting complex is extremely difficult. This may be explained on the assumption that the solid products of the dehydroxylation reaction exist only transitorily — they convert as fast as they are formed into products which do not hydrate readily to form kaolinite.

The conversion of the transitory phases would be the factor controlling the position and shape of the return-to-zero side of the endothermic loop. Water vapor and perfection, or type, of crystallinity have an effect on this conversion reaction. In vacuum (*i.e.,* in the absence of water vapor) the conversion is slow and the return-to-zero side of the loop is not abrupt. An increase in the water-vapor pressure (hence, concentration of water molecules) or a decrease in the perfection of crystallinity causes the conversion reaction to proceed more rapidly, producing a sharper return-to-zero. Poorly-crystalline kaolinite and halloysite support this observation.

Mullite, which forms at the 980° C exotherm, is a stable alumina-silica phase at the temperature of the dehydroxylation reaction; but it does not form there because the energy level is not sufficient to permit appreciable movement of the aluminum, silicon, and oxygen atoms. These atoms possibly have the tendency, when the kaolinite is decomposed, to move into the stable-mineral positions at that temperature, but their movement is blocked by their very positions in the kaolinite structure. Their energy is not sufficient for this shift until the 980° C exotherm. It is herein proposed that the increase in water-vapor pressure permits greater movement toward the mullite structure, thereby increasing the intensity of the conversion reaction at the 650° C level. It follows from this reasoning that the areas under the dehydroxylation loop and under the 980° C exothermic loop should both decrease with increase in pressure of the water vapor.

MacGee (1926) estimated from specific heat data on kaolinite and meta-kaolinite that the net heat absorbed by the dehydroxylation of kaolinite is in the order of 120 cal. per gm. His experiments were carried out at atmospheric pressure with no control of gas composition; hence his values are used here only as an illustration. His value for $\triangle H$, 120 cal. per gm., would represent the net heat absorbed, *i.e.,* the sum of the endothermic dehydroxylation reaction plus the heat of the proposed exothermic reaction (a negative value). The slope of the van't Hoff line gave a value of 170 cal. per gm. for the dehydroxylation reaction for similar clays. Therefore, 170 cal. minus 120 cal. gives 50 cal. per gm. as the value for the exothermic reaction under the conditions of MacGee's test.

B. — Montmorillonite

The thermograms of the Wyoming bentonite are given in Figure 5 and those of the Arizona bentonite in Figure 6. Only the portions of the thermograms involving the two high-temperature endotherms and the exotherm are shown for the Wyoming material. The entire thermograms are shown for the Arizona material to illustrate the effect of pressure on endotherms associated with base-exchange cations.

The general effects of increasing water-vapor pressure are the same for both montmorillonites: (1) The peak temperature of the dehydroxylation endotherm (*i.e.,* the 700° C endotherm) is moved upward, but the starting point of the endotherm is poorly defined; (2) the temperature of the second
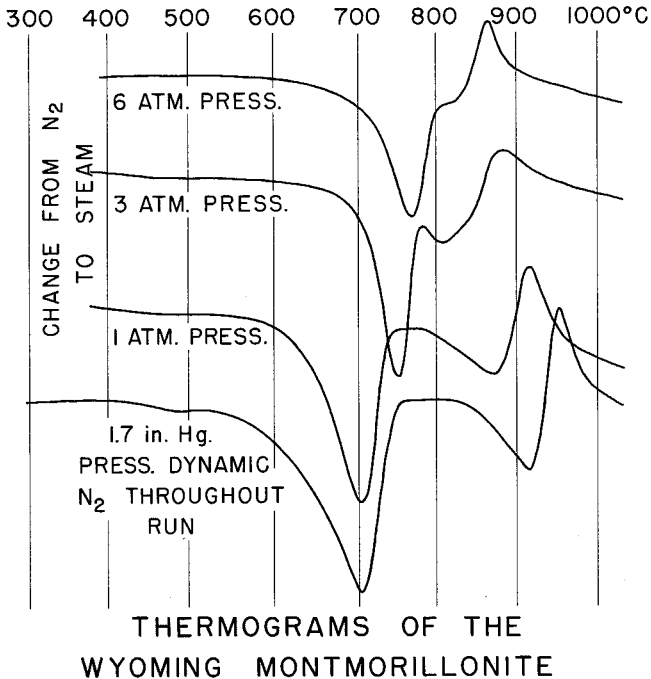
FIGURE 5. — Thermograms of the Wyoming montmorillonite.

or 900° C endotherm is moved downward; and (3) the temperature of the exotherm is moved downward with no marked change in intensity.

1. *The Dehydroxylation Endotherm.* — The behavior of the dehydroxylation endotherm for montmorillonite is somewhat similar to that of the kaolinite, but the differences are significant. For kaolinite, the temperature of the beginning of the endotherm moves upward with increase in steam pressure but for montmorillonite the effect on the starting temperature is not regular throughout the pressure range studied and the break from the zero level is much more distinct for kaolinite than for montmorillonite, where frequently there is some question of which point to choose as the starting temperature. An increase in steam pressure has comparatively little effect on these features of the thermograms, but the peak temperature is more concretely affected.

The temperature and shape of the 700° C loop do not correspond to those of any of the hydroxides which could conceivably represent the cation-OH bonds in the octahedral sheet of montmorillonite, such as brucite (Mg) and gibbsite (Al). There is no counterpart among the iron compounds since they all involve hydrogen bonds, *i.e.,* O-H-O bonds. If these cation-OH bonds behaved independently during the decomposition of montmorillonite, there would be separate endothermic loops for each, but such behavior is not apparent in any montmorillonite at any pressure used to date.
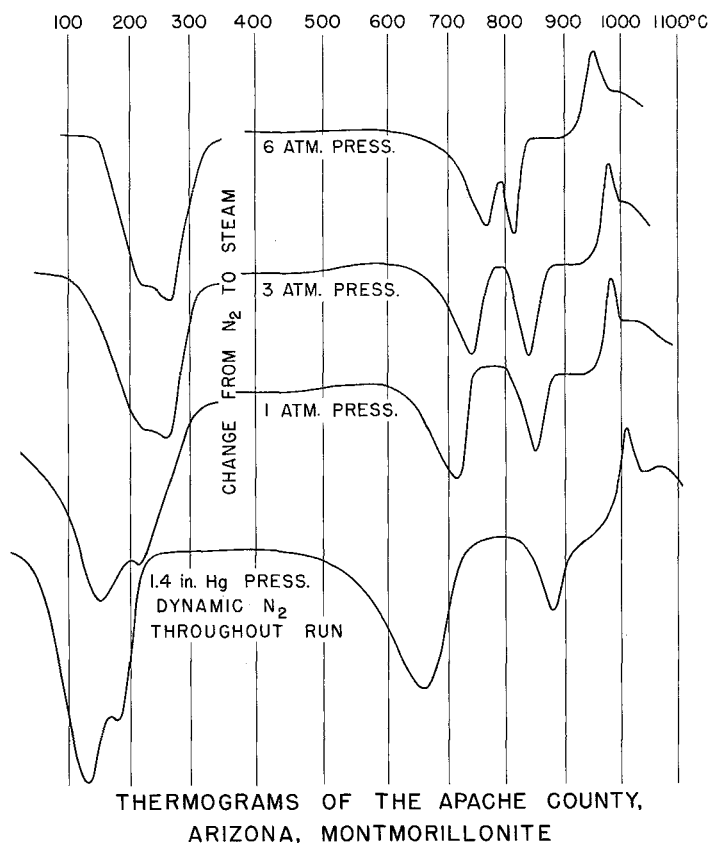
THERMOGRAMS OF THE APACHE COUNTY,
ARIZONA, MONTMORILLONITE

FIGURE 6. — Thermograms of the Apache County, Arizona, montmorillonite.

When the starting temperature of a reaction involving water is moved upward regularly, but in small, distinct increments by increasing increments of water-vapor pressure the van't Hoff plot will show a very high heat of dehydroxylation. When the increments of temperature-increase are large, then the heat of decomposition is correspondingly small. Furthermore, a large $\triangle H$ would produce a large loop, and a small $\triangle H$ a small loop if the rate of reaction is the same. The endothermic loop for montmorillonite is small (compared to kaolinite) indicating a small $\triangle H$; therefore, its starting temperature should be strongly affected by water-vapor pressure, but instead, the starting temperature is relatively unaffected. The peak temperature of the endothermic loop is more affected by the pressure of N_2 (Le Chatelier-Braun principle) than by water-vapor pressures, and the low-temperature side of the endotherm always has a gradual slope. These observations lead to the postulation that the initiating reaction represented in the 700° C loop does not involve OH release and is affected only by pressure and not by water vapor.

It seems feasible to assume that the initiating reaction is a reorientation within the structure, and that the reoriented structure does not involve the original cation-OH bonds. Therefore, simultaneous with formation of new structure, the OH is released and water is evolved, except for new cation-OH bonds that are stable at the temperature of reorientation — these cation-OH bonds would then be affected by the water-vapor pressure. It has been observed in a number of six-atmosphere runs on some mont-morillonites that the low-temperature side of the endothermic loop breaks quite sharply about 50° C preceding the peak. These considerations lead to the conclusion that the 700° C loop represents an algebraic sum of the exothermic and endothermic reactions with the $-\triangle H$ numerically exceeding the $+\triangle H$ so that the net result is in the endothermic direction.

2. *The 900° C Endotherm.* — This endotherm moves to a lower temperature when the water-vapor pressure is increased and therefore the reaction responsible for the loop does not involve a release of water. In case of the Wyoming montmorillonite, the 900° C endotherm is lowered so much at 6 atmospheres that it has completely merged into the 700° C endotherm. The 900° C endotherm of the Apache material is affected to a lesser extent. In vacuum, it peaks at 880° C as compared to 915° C for the Wyoming bentonite, yet it retains its identity in the six-atmosphere run. Undoubtedly, the type of reaction is the same in both montmorillonites, but the Apache material serves better for discussion because of a more distinct appearance of the loop.

The effect of water-vapor pressure on relative intensities of the 700° C and the 900° C endotherms was rather unexpected. With the Wyoming bentonite the 700° C endotherm retains nearly the same intensity in vacuum and in the one- and three-atmosphere runs, but at six-atmospheres, where the 900° C endotherm has merged into it, the intensity of the 700° C endotherm decreases markedly. At six atmospheres, therefore, the single loop does not represent a mathematical sum of the two loops. Perhaps the 900° C loop represents an endo-exo combination so that at six atmospheres only the exothermic portion occurs and therefore subtracts from the intensity of the 700° C loop.

In the case of the Apache material, under vacuum the 700° C endotherm is very much larger than the 900° C loop; one atmosphere markedly reduces its intensity, and by six atmospheres the 900° C loop is the larger of the two.

3. *The Exotherm.* — The temperature of the exotherm of both types of montmorillonite is decreased by increasing the water-vapor pressure. For the Wyoming material, the preceding endotherm is decreased in temperature slightly more rapidly than the exotherm so that at three atmospheres there is a slight shoulder between the two loops. At six atmospheres the 900° C endotherm has merged into the 700° C loop so that there is a pronounced shoulder between the endotherm and the exotherm. The intensity of the exotherm is decreased somewhat by the water vapor.

The exotherm of the Apache montmorillonite in vacuum peaks at 1010° C

as compared to 950° C for the Wyoming bentonite. Its temperature is lowered by increasing the water-vapor pressure so that by six atmospheres it peaks at 950° C. The intensity of the peak is not affected appreciably by water-vapor pressure.

The effect of the water vapor on the exotherm seems to be simply that of a mineralizer and is proportional to the concentration of the water molecules.

4. *Effect of Pressure on the Base Exchange Cation Loops.* — In the thermograms of the Apache material given in Figure 6 the doublet of the low-temperature loops indicates that the material is a Ca-montmorillonite. Dry nitrogen was the dynamic gas up to the temperature where the loop returned to zero level; therefore any observed effects are due to pressure alone.

Changes in pressure shift the position (temperature) and relative intensities of the interlayer-water and cation-hydration peaks. In the thermograms of Ca-montmorillonites run at one atmosphere by the static gas method the interlayer-water peak is the predominant one and occurs at about 150° C and the cation-hydration loop appears as a shoulder at about 200° C. This same general contour is shown by the thermograms of Figure 6. In the low-pressure run the interlayer-water peak is at 130° C and the cation-hydration peak is very distinct at 175° C. An increase of pressure (1) raises the temperature of both of these peaks but does not materially affect the spread of 40° C to 45° C between them, and (2) increases the relative intensity of the cation-hydration loop so that in the three-atmosphere run it is the larger of the two. At three atmospheres, the peaks are at 220° C and 260° C; at six atmospheres they show very little increase, being at 225° C and 265° C.

Since pressure is the only variable, it is concluded that the observed effect is simply the manifestation of obedience to the Le Chatelier-Braun principle.

CONCLUSIONS

The following conclusions are based on the effects of water-vapor pressure applied to the specimen during a thermal analysis run:

A. — Kaolinite

1. The dehydroxylation reaction is unaffected by anhydrous gas pressure.

2. The initiating reaction represented in the dehydroxylation loop involves breaking of cation-OH bonds.

3. The solid products of dehydroxylation react immediately to form a new product and this exothermic reaction subtracts from the net area of the 600° C loop.

4. The starting temperatures of the 600° C loop are moved upward regularly with pressure increments above one atmosphere and the heat of decomposition calculated therefrom is 170 cal. per gm. for well-crystallized kaolinite and about 140 cal. per gm. for poorly crystallized kaolinite.

B. — Montmorillonite

1. The temperature of the low-temperature loops (below 250° C) is increased by increasing pressure of inert gas according to the Le Chatelier-Braun principle.

2. At water-vapor pressures of about one atmosphere and above, the initiating reaction of the 700° C loop is unaffected by water-vapor pressure, hence it does not involve breaking the cation-OH bonds.

3. The 900° C endothermic loop does not involve breaking cation-OH bonds since its temperature is lowered by increasing water-vapor pressure.

4. Water vapor has a catalytic or mineralizing effect on the crystallization exotherm and lowers its temperature.

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