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DIFFERENTIAL THERMAL CALORIMETRIC ESTIMATION OF THE KAOLINITE-METAKAOLINITE ENDOTHERMIC ENTHALPY

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June 1969

The 550°C endothermic reaction of kaolinite has received much attention. Many studies of the kinetics of the reaction have been made and activation energies obtained.[1-5] In 1952 Stone[6] studied the effect of varying the partial pressure of water vapor on the decomposition temperature of kaolinite. Utilizing the Van'tHoff equation

$$d \ln K = \frac{\Delta H}{RT^2} dT$$

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where K = the reaction equilibrium constant,

ΔH = the reaction enthalpy and

T = the absolute temperature (°K),

he arrived at an endothermic enthalpy value for the reaction. Stone utilized a differential thermal analysis technique in these studies. The presence of a product-gas phase in the system greatly complicates the mechanisms of heat transfer in a D.T.A. experiment, however, and this tends to introduce errors into the D.T.A. measurements.

Differential thermal calorimetric (D.T.C.) techniques do not suffer from this drawback. The basic principle of D.T.C. is to supply or subtract heat to or from a reacting system so as to maintain the temperature at some point in the system the same as that of a similar point in a physically inert system. By carefully monitoring and controlling the temperature gradients in the D.T.C. system, the detrimental effect of the product-gas phases on the heat transfer characteristics of the system can be avoided. The D.T.C. system design utilized in the investigations reported here is discussed elsewhere.[7]

When a reaction starts in the sample system, the power supplied to the inert system must be altered to maintain the two-system differential temperature at zero. The integrated area under the power-time trace obtained gives the enthalpy of the reaction being measured according to the equation

$$H_T = H_{298} + \int_{298}^{T} C_p \, dT$$

where H_T = the heat content/mole at temperature T,

H_{298} = the heat content at room temperature,

C_p = the heat capacity at constant pressure, and

T = the temperature (°K).

The apparatus was demonstrated to have a ±2% accuracy in heat content estimations conducted on quartz and α-alumina.

The dehydration of kaolinite is not strictly a reversible reaction. The enthalpy involved can be measured with a differential thermal calorimeter. Such measurements were carried out on four kaolinites from different geographical areas of the United States. These kaolins were chosen on the basis of their high purity. The chemical analyses of these clays are given in Table I. The measured enthalpy values associated with the 550°C endotherm are given in Table II. The values obtained are in fairly close agreement.

The demonstrated accuracy of the DTC system when used for thermodynamic estimations on known systems lends weight to the endothermic enthalpy values measured for the four kaolins and these values fall within the range predicted by Vaughan.[2]

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TABLE I

Chemical Analyses of the Kaolinite Samples

(only major components shown)

	API 4[8]	API 9[8]	API 17[8]	DRG
SiO_2	44.8%	46.07%	45.72%	47.24%
Al_2O_3	37.20	38.07	39.82	35.72
Fe_2O_3	0.41	0.33	0.10	0.27
MgO	0.23	0.01	trace	0.47
CaO	0.58	0.38	trace	0.52
Wa_2O	0.40	0.27	0.16	0.36
K_2O	0.43	0.43	0.36	0.49
H_2O	14.68	13.90	14.22	14.82
Location of deposit	Macon, Georgia	Mesa Alta, New Mexico	Montana	Georgia

TABLE II

Differential Thermal Calorimetric Enthalpy Values for the 550° Endotherm of Kaolinite

ΔH in Kcals/mol

API 4	API 9	API 17	DRG	Stone
38	39	39	48	37
44	41	39	47	
			45	

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