

Quantitative Differential Thermal Analysis as Applied to the Thermal Decomposition of Magnesite

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Differential thermal analysis offers a technique by which the enthalpic changes that accompany thermally induced chemical and physical transformations can be estimated. In certain instances the results from d. t. a. agree with those from conventional calorimetry; in other instances the agreement is quite poor (4). This investigation uses differential thermographs of the decomposition of magnesite to test the validity of the Vold-Speil equation (8, 5). The basic equation is

$$\frac{d y}{d t} = -A y + B + \frac{\Delta H}{C_s} \frac{d f}{d t} + \frac{(C_s - C_r)}{C_s} \frac{d T_r}{d t}. \quad (1)$$

A and B are parameters dependent upon furnace construction and geometry, ΔH the total enthalpic change of the active material during the transformation, C_s and C_r the heat capacities of the sample and reference materials, f the fraction of the sample transformed after time, t , and y the differential temperature between reference and sample materials, $T_r - T_s$.

Under the experimental conditions that there is a constant rate of heating of the sample block, symmetric positioning of the reference and sample materials within the furnace, sample dilution with an inert reference material of comparable heat capacity to that of the reference material, and no thermal transformation is occurring, the solution to equation (1) is

$$y = y_s \left\{ 1 - \exp \left[-A (t - t_1) \right] \right\} + y_1 \exp \left[-A (t - t_1) \right]. \quad (2)$$

y_s represents the steady state value for the differential temperature, and y_1 the value of the differential temperature at the arbitrary time t_1 . During the time in which a transformation takes place the solution is

$$A \int (y - y_s) d t = \frac{\Delta H}{C_s} \quad (3)$$

Integration is performed from the point at which the endotherm begins to the point where the reference and the sample have again attained the steady state temperature difference. The term $\int (y - y_s) d t$, is the area under the curve. The parameter A can be evaluated from a plot of $\log (y - y_s)$ versus t . The region of the thermograph from its maximum to the point at which the steady state temperature difference is again realized is used to evaluate A.

Experimental

The d. t. a. apparatus consisted of the furnace and the stainless steel sample block used in the Aminco Thermoanalyzer (American Instrument Co., Inc., Silver Spring, Maryland). The block temperature and the differential temperature were monitored using chromel-alumel, inconel sheathed thermocouples (Thermocouple Products Co., Villa Park, Illinois). The thermocouple output was amplified by a factor of 114 and recorded using the Sargent recorder, model S. R. The heating rate of the furnace was programmed such that the sample block temperature increased 20° C per minute within the temperature range of 150° to 1000° C. Since symmetric thermographs were realized for magnesite decomposition with a dynamic atmosphere of CO₂, a gas flow rate of 1 c. c. per minute at S. T. P. of CO₂ was maintained through both the reference and the sample compartments.

Thermographs were made on a series of mixtures of magnesite-calcium carbonate, dolomite-calcium carbonate, and magnesite-dolomite-calcium carbonate. The MgCO₃ content of the magnesite was 98.95 per cent and that of the dolomite was 40.21 percent as determined by the E. D. T. A. titrimetric method (3). To make the individual mixtures known weights of each material—particle size 100 mesh or less—were thoroughly mixed by tumbling in a closed container. The thermographs of weighed samples, 0.2 to 0.3 grams, were determined; reagent grade, ignited alumina served as the thermally inert reference material.

Results and Discussion

In any sample that contained both dolomite and magnesite, the endotherm due to the magnesitic MgCO₃ and the endotherm due to the

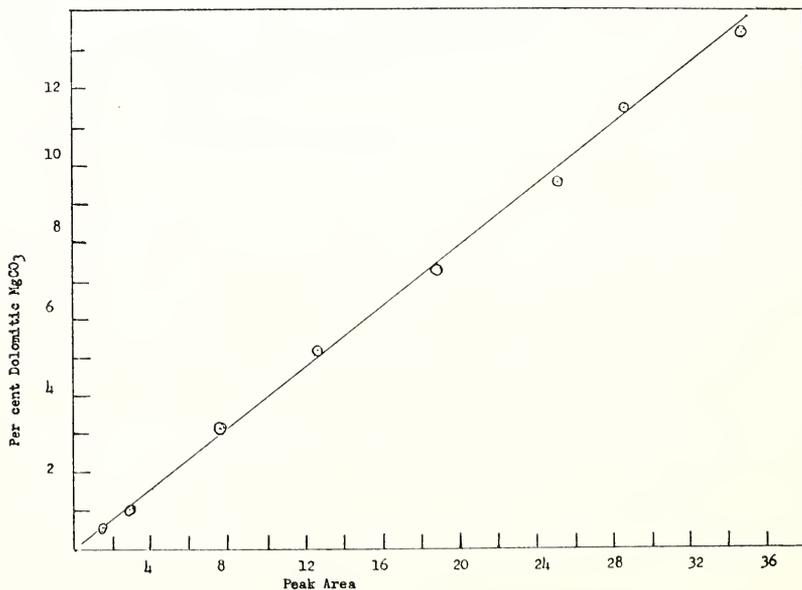


Figure 1. Percent Dolomitic MgCO₃ versus Peak Area

dolomitic MgCO_3 were at the same temperatures as the endotherms for samples of the pure substances. The decomposition temperatures in this work (peak temperature: dolomite 790°C .; magnesite 640°C .) agree with those in the literature (6, 7). The Vold-Speil equation predicts that the peak area should be a linear function of the percent MgCO_3 in the sample. The expected linear relationship was obtained for both magnesite and dolomite. Figure 1 is the curve for dolomitic MgCO_3 . This curve is reproduced since the d. t. a. thermographs of samples of Putnam County, Indiana limestones indicated that MgCO_3 was present in the dolomitic form. It emphasizes that d. t. a. can be used profitably to estimate the magnesium content in limestone.

The enthalpy of decomposition of magnesite can be calculated by the following relationship:

$$\Delta H = \frac{(C_s)(A)(\text{Endotherm area})(0.402)(84.32)(100)}{(\text{Percent MgCO}_3)} \quad (4)$$

C_s is expressed in calories per gram; ΔH has the units of calories per mole; and the factor 0.402 converts the product (A) (Endotherm area) to calories. The apparatus parameter A can be evaluated using the individual thermograph; the slope of the linear portion of a plot of

$\log(y - y_s)$ versus time equals $\frac{-A}{2.303}$. The average value obtained

for a series of eight determinations of the enthalpy of decomposition of magnesite was $15.7 \text{ kcal. mole}^{-1}$. Stone (6) reports the value of $10.1 \text{ kcal. mole}^{-1}$ for its decomposition. His value was calculated by measuring its temperature of decomposition as a function of the CO_2 pressure above the sample. Ellis (1) reports the value of $28.3 \text{ kcal. mole}^{-1}$ which was obtained through area comparison of the magnesite thermograph with the thermograph of a substance of known heat of decomposition. The most precise calorimetric value is $28.27 \text{ kcal. mole}^{-1}$ (2).

The results of this investigation indicate that for magnesite and dolomite the predictions of the Vold-Speil equation are qualitatively observed; however, the calculated heat of decomposition for magnesite is low. Although d. t. a. may not be useful as an absolute micro-calorimetric tool in the study of carbonate decomposition, it is demonstrated that the technique is quite applicable to the determination of the magnesium content of limestones.

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