

FURNACE ATMOSPHERE CONTROL IN DIFFERENTIAL THERMAL ANALYSIS

RICHARDS A. ROWLAND AND DONALD R. LEWIS*

ABSTRACT

The usefulness of differential thermal analysis can be extended considerably by controlling the composition of the furnace atmosphere. The method described for securing atmosphere control is applicable to most existing differential thermal analysis furnaces. Examples are given which show the effect of a furnace atmosphere of nitrogen on differential thermal curves of clays containing organic matter and pyrite. Other curves show the effect of CO_2 on differential thermal curves of siderite, magnesite, dolomite and calcite. One curve follows the alternate dissociation-reconstitution of the CaCO_3 part of dolomite in an atmosphere of CO_2 . The effect, on the differential thermal analysis curve, of filling the furnace with a gas which is a participant in the reaction is explained by the relation of the partial pressure to the equilibrium constant and the heat of reaction.

INTRODUCTION

The method of differential thermal analysis consists of simultaneously heating in a furnace two substances, one of which is an inert material which undergoes no phase change or chemical reaction in the temperature range to be covered, while the other is the sample to be analyzed. As the furnace temperature is raised, the temperature difference between the two substances is measured by a dual hot-junction thermocouple, and the thermocouple *EMF* is recorded. If the unknown substance undergoes no phase changes or chemical reactions its temperature will follow that of the inert material. If a change does occur, the temperature of the substance being analyzed will lag behind, or gain over that of the inert material, and deflections of the recorded line will be produced. Conventionally, the recorded curves are oriented for study and interpretation so that endothermic reactions, during which the sample is cooler than the inert material, are shown as downward deflections, and exothermic reactions as upward deflections. The apparatus used here is similar in furnace design to that described by Grim and Rowland (1944), but with the addition of a copper tube cemented into the back plug so that a selected gas may be introduced into the furnace.

The ambient atmosphere in a differential thermal analysis furnace may be controlled in several ways depending on what the control is expected to do. First, an inert gas such as nitrogen or argon may be introduced into the furnace to eliminate oxygen and prevent oxidation reactions without changing the pressure inside the furnace. Second, an

* Publication No. 10, Exploration & Production Research Division, Shell Oil Company, Houston, Texas.

active gas which will be evolved by the expected reaction, such as CO_2 for the carbonate minerals, may be introduced to maintain at one atmosphere the partial pressure of the gas to be evolved. Third, with the usual method of differential thermal analysis, air at atmospheric pressure may be allowed in the furnace so that oxidation proceeds at will within the limits of access of air to the sample, and the partial pressure of an evolved gas may increase during the heating cycle. Fourth, with a special furnace, equipped for either vacuum or moderate pressures, the effects of pressure changes may be followed in air, an inert gas, or an active gas.

For several years this laboratory has regularly introduced various gases into the furnace in differential thermal analyses of geological materials, and recently Whitehead and Breger (1950) have described vacuum equipment for pressure control below one atmosphere. Different commercially available gases can be introduced into the furnace of most existing differential thermal analysis apparatus with the simple addition of a tube in the porous plug generally used to close the end of the furnace opposite that into which the sample holder is inserted. Some of the results obtainable by this simple technique will be described here.

INERT ATMOSPHERES

The presence of organic matter in the fine fraction of soil and clay materials has long made difficult the identification of the mineral content of these materials. When viewed under the petrographic microscope the organic matter obscures the small particles and often partially dissolves in the immersion oil, changing its refractive index. On x-ray diffraction photographs the effect of organic material in the sample is a general scattering of the beam which produces over-all darkening of the film, especially in the critical region where the Bragg angle is small. In differential thermal analysis the exothermic loop resulting from the oxidation of the organic material is often so large by comparison with the dehydration loops of the minerals that the latter, of prime interest in interpretation, are frequently completely obscured up to at least 650°C .

Chemical treatment to remove the organic material either by solution in appropriate solvents or by oxidation has met with only partial success. When various organic solvents are used the liquid sometimes dissolves the unwanted organic material, but as frequently as not it simply displaces the organic matter and is itself held by the clay. The various oxidizing agents are generally ineffective until their concentration is such that the action is vigorous enough to disrupt the clay mineral lattice.

This problem is especially critical in differential thermal analysis and can be partly solved by the rather obvious technique of controlling the composition of the ambient furnace atmosphere so that oxidation is

either suppressed or allowed to proceed so slowly that the heat effect is negligible. This may be accomplished by allowing a stream of nitrogen to flow into the furnace through a porous plug of insulating firebrick inserted in the furnace tube from the end opposite that containing the sample holder. The required rate of nitrogen flow will vary with different apparatus and should be large enough to suppress oxidation but not so large as to affect the heating rate appreciably. For the apparatus here employed the optimum rate is about 0.25 cubic feet per minute.

Although water-pumped nitrogen (usual compressed cylinder nitrogen) contains some oxygen, no exothermic oxidation reactions are recorded when this nitrogen makes up the furnace atmosphere. When the sample is removed from the furnace before cooling, as is standard practice, only the upper crust is oxidized and then only after contact with the air. The bulk of the sample contains black particles of carbon.

Since oxidation of the organic matter is prevented by displacing the oxygen in the furnace atmosphere with nitrogen, the organic material may pyrolyze or vaporize. The process of pyrolysis involves the breaking up of large unsaturated molecules into smaller molecules which then vaporize. Both of these reactions are endothermic. They are not recorded, however, because the organic matter contains only a very small amount of many different molecules which undergo pyrolysis over a wide temperature range. Furthermore, the heat of vaporization of the products is only about $\frac{1}{6}$ to $\frac{1}{10}$ that of water, and is not sufficient to change the sample temperature relative to the inert material.

EFFECT ON ORGANIC MATTER

In Fig. 1 are four curves of the same clay from near Brenham, Texas. The first curve was obtained from the raw sample ground to pass 100 mesh and exhibits no recognizable clay characteristics. Its outstanding feature is a broad exothermic deflection starting at 200° C. and ceasing abruptly at 800° C. The second curve was made from the same material with nitrogen streaming through the furnace. This curve resembles kaolinite except for the endothermic loop between 50° C. and 200° C. The abrupt break at 800° C. has disappeared. It is thought that this break coincides with the completion of burning of an organic constituent. The third curve was made from the minus-two-micron fraction of the same sample. As is generally the case, the minus-two-micron fraction contains more clay mineral and a concentration of some of the organic matter. That the organic constituent responsible for the abrupt endothermic break in the first curve has been eliminated suggests that it is associated with particles larger than two microns. The fourth curve represents the minus-two-micron fraction when heated in an atmosphere

of nitrogen. This curve indicates that the clay mineral is chiefly kaolinite mixed with a small amount of a three-layer lattice clay. The x-ray diffraction pattern indicates kaolinite with about 15 per cent illite.

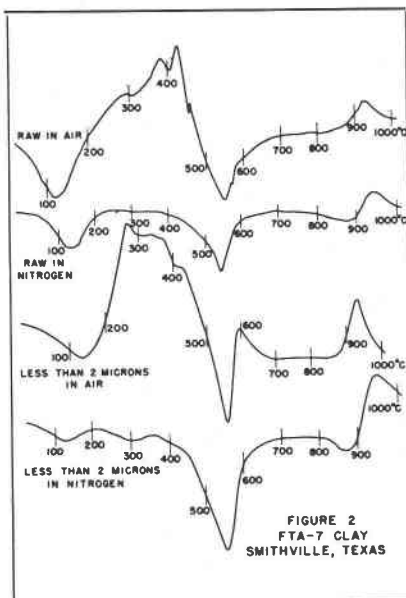
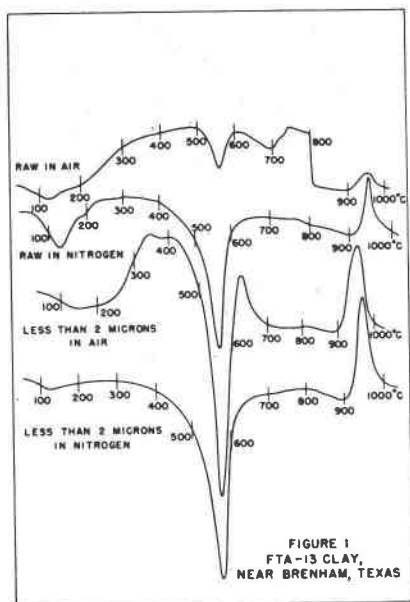


Figure 2 presents a similar series for a clay sample from a bentonite horizon exposed under the bridge where State Highway 71 crosses the Colorado River at Smithville, Texas. The clay portion of the curve for the raw clay and the minus-two-micron fraction heated in air are partially obscured by the exothermic deflections accompanying the burning of organic matter. In an atmosphere of nitrogen, however, both the raw and minus-two-micron fractions produce curves with identifiable clay mineral loops. The curve for the minus-two-micron fraction in nitrogen is similar to curves obtained from montmorillonites of sedimentary origin. X-ray diffraction identification shows the clay mineral to be a well organized montmorillonite, which can be expanded with ethylene glycol.

A series of four curves for the well-known Kentucky Ball Clay is presented in Fig. 3. The curve for the raw clay exhibits a large exothermic deflection on which is superimposed the dehydration loop of kaolinite. This is followed by an endothermic deflection between 700° C. and 800° C., and finally at 950° C. the exothermic loop associated with mullitization

appears. When the same material is heated in an atmosphere of nitrogen, the exothermic effect between 200° C. and 500° C. is eliminated as is the endothermic deflection between 700° C. and 800° C. The minus-two-micron fraction heated in air shows that some of the organic matter and the clay mineral have been concentrated. When the minus-two-micron material is heated in nitrogen a typical, uninterrupted kaolinite curve is obtained.

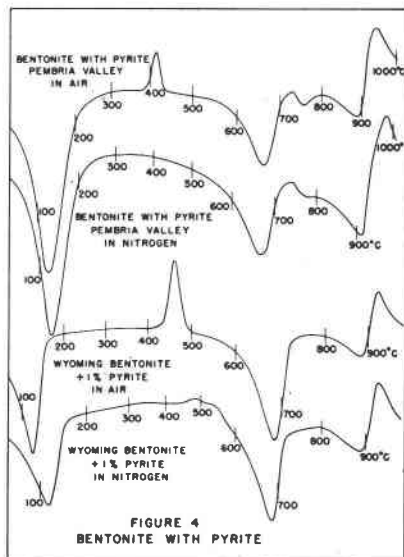
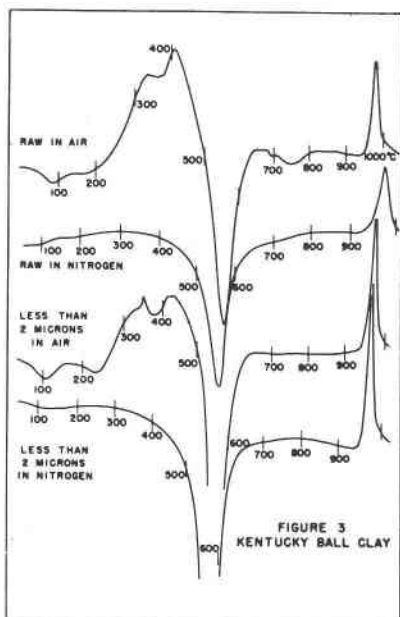
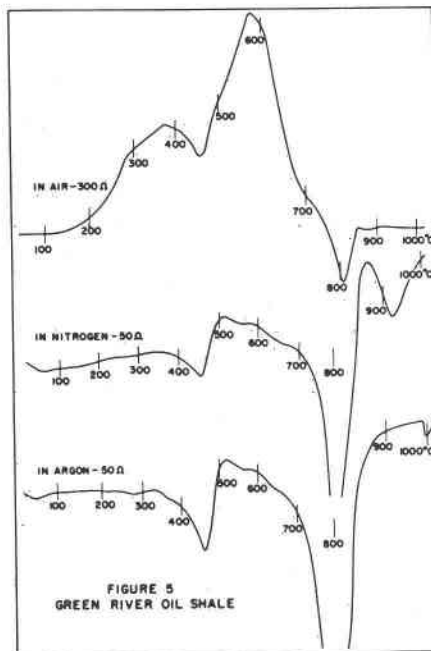


Figure 5 presents three curves from the Green River Oil Shale which contains more than 25 per cent organic matter. The first is in air, the second in nitrogen, and the third in argon. The first is recorded on a scale which represents temperature differences at about $\frac{1}{3}$ the scale for the second and third. On the first curve the oxidation of organic material is represented by a broad exothermic deflection between 150° C. and 700° C. This deflection is interrupted by endothermic loops between 400° C. and 500° C. and between 700° C. and 800° C. These two loops remain when the sample is heated in an inert atmosphere. The minor difference between the nitrogen and argon curves is attributed to a small amount of oxygen in the nitrogen, since water-pumped nitrogen contains about 4

per cent air. The significance of the two endothermic loops is not known and the curves are presented to show the effectiveness of the method even when large quantities of organic matter are present.

EFFECT ON PYRITE

Figure 4 presents two bentonites containing pyrite. The one from Pembria Valley is a natural mixture. The other is a prepared mixture of 1 per cent pyrite in Wyoming bentonite. As can be seen from the



curves, heating in a furnace atmosphere of nitrogen eliminates the exothermic effect beginning at 390° C. in the Pembria Valley sample, and at 450° C. in the prepared mixture, and spreads out the approach to the endothermic loop at 900° C. The inert atmosphere has little effect on the endothermic deflection between 700° C. and 800° C. on the curve for the Pembria Valley sample. It is thought that in each case both the sulfur and the iron are oxidized, since the final product proves to be hematite. When the sample is heated in air this oxidation takes place between the temperatures indicated by the exothermic loop. In a nitrogen atmosphere

the sulfur is vaporized and removed from the furnace by the stream of nitrogen, and the iron is oxidized only when, after the run is finished, the hot sample is withdrawn and exposed to the air.

CARBON DIOXIDE ATMOSPHERE

In addition to the use of inert gases to suppress the oxidation reaction of materials associated with clays, differential thermal curves of the carbonate minerals can be improved by introducing an atmosphere of CO_2 in the furnace. When calcite is heated in air in the differential thermal apparatus, its dissociation begins to be registered at about 650°C . and the reaction progressively becomes more vigorous until a peak is reached at about 925°C . When the reaction starts, the CO_2 content of the air surrounding the CaCO_3 is very low but progressively increases as CO_2 is evolved from the sample. If the furnace is filled with CO_2 at approximately one atmosphere pressure, the reaction does not begin until a temperature of 925°C . is reached, whereupon it proceeds vigorously until completion.

These phenomena may be interpreted in terms of the basic thermodynamics of the calcium carbonate-calcium oxide-carbon dioxide system. For the reaction:



the equilibrium constant may be written as

$$K_p = \frac{p_{\text{CO}_2} \times p_{\text{CaO}}}{p_{\text{CaCO}_3}}$$

The general case of a gas reacting with a solid is treated by MacDougall (1939). Since the partial pressure of the solid phase is constant, this can be written as

$$K_p = p_{\text{CO}_2}$$

The equilibrium constant at a given temperature is determined only by a function of the partial pressure of the carbon dioxide evolved, which will, in turn, depend on the pressure of the CO_2 in the surrounding atmosphere. The pressure of a mixture of gases is equal to the sum of the partial pressure of each of its constituents. In an ideal gas the partial pressure of each constituent is equal to the pressure that constituent would exert if it occupied the entire volume of the mixture or to its mol fraction times the pressure of the mixture. Since the mol fraction of CO_2 in air is about 0.0003, then the partial pressure of CO_2 in air is about 0.0003 atmosphere. According to various investigators, the temperature corresponding to this equilibrium partial pressure should be between 500°C . and 600°C . Before attaining this temperature, CO_2 has not been dis-

sociated from the solid CaCO_3 . In this temperature range and at higher temperatures, the system in which all three phases CaO , CaCO_3 and CO_2 are present continuously attempts to adjust to equilibrium conditions by releasing more CO_2 and forming more CaO at the expense of CaCO_3 . As the furnace temperature increases, the partial pressure of CO_2 continues to rise until it approaches atmospheric pressure, which it cannot exceed since the sample is not enclosed. At this point the rate of dissociation becomes a maximum, and the heat absorbed allows the thermocouple junction in the sample to lag in temperature behind the temperature of the junction in the inert material, which produces a strong endothermic loop on the diagram. When the furnace atmosphere consists entirely of CO_2 at approximately one atmosphere pressure, little or no dissociation takes place until a temperature is reached at which the equilibrium partial pressure becomes equal to that prevailing in the furnace. Delays involving the transfer of heat through the sample to the thermocouple junction and the simultaneous increase, at a regular rate, of the furnace temperature make the recorded endothermic deflection of the D.T.A. curve appear at a higher temperature than the temperature at which the reaction takes place.

A similar explanation applies to the dissociation of all carbonate minerals although the effect may not be as evident as with calcite because the dissociation temperature — p_{CO_2} relation may not extend over so wide a temperature range below one atmosphere. The effect of dissociation in CO_2 rather than in air may be estimated by comparing the heat of reaction with that of calcite. The relation between the equilibrium constant and heat of reaction is stated by the expression

$$\left(\frac{d \ln K_p}{dT} \right)_2 = \frac{\Delta H}{RT^2}$$

in which ΔH is the heat of reaction, T the absolute temperature, and R the gas constant. This equation shows that the effect of the increase in p_{CO_2} on the temperature at which the dissociation loop will occur will be greater for carbonates with ΔH larger than calcite and less for carbonates with ΔH smaller than calcite. An example is afforded by comparing calcite, $\Delta H_{18^\circ\text{C}} = 43.2$ kilocal/mole, and magnesite, $\Delta H_{18^\circ\text{C}} = 27.4$ kilocal/mole. The magnitude of the shift for calcite is considerably greater than for magnesite, Fig. 6.

Figure 6 shows the dissociation of several carbonates the curves for which are reproduced only in the range of dissociation. The upper curves were prepared in an atmosphere of air, while the lower curves represent dissociation in a CO_2 atmosphere. Calcite dissociation is illustrated by the two curves at the right side of the figure.

The dissociation of siderite in air and in CO_2 has been discussed previously (Rowland and Jonas, 1949). Briefly, the curve indicates that between 450°C . and 530°C . the endothermic effect of the dissociation of CO_2 is accompanied by oxidation of FeO , so that the first part of the curve is a compromise. When a temperature of 530°C . is attained, sufficient CO_2 is liberated to prevent the oxidation of the FeO , and a modified endothermic loop is registered. At about 570°C . the evolution of CO_2 decreases enough so that the FeO can oxidize, and an exothermic loop is recorded. The small exothermic mound between 750°C . and 850°C .

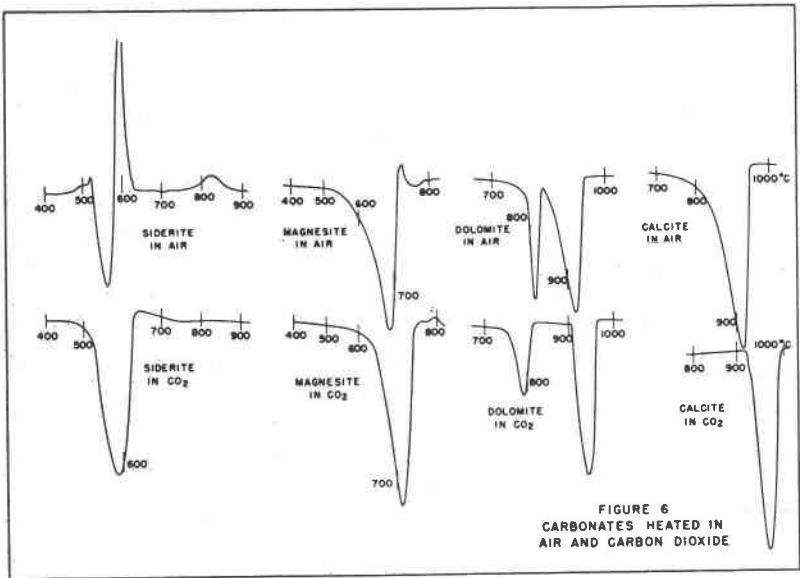


FIGURE 6
CARBONATES HEATED IN
AIR AND CARBON DIOXIDE

is registered when the iron oxide becomes hematite. In a CO_2 atmosphere the iron is not oxidized and a larger, uninterrupted endothermic loop is obtained.

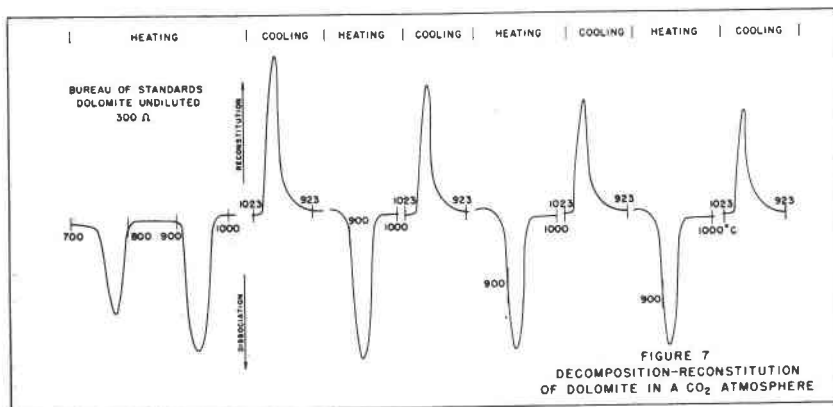
Differential thermal curves for magnesite from Stevens Co., Washington, also showed a marked difference between dissociation in air and in CO_2 . The endothermic deflection, when the sample is heated in air, begins at about 380°C . and becomes quite sharp at 515°C . The peak is reached at 690°C . after which there is a light exothermic deflection. When the sample is heated in CO_2 , the endothermic deflection also begins at about 380°C . but does not bend sharply until about 650°C . It peaks at 710°C . and returns to the base line without an exothermic loop. The endothermic loop in CO_2 encloses a larger area than that enclosed by the

curve obtained in air. The absence of the exothermic loop in CO_2 suggests that an oxidation takes place towards the end of the dissociation when the sample is heated in air. X-ray diffraction and spectrochemical analyses indicate that the sample contains a small quantity of iron (2% Fe) as siderite (FeCO_3). Oxidation of the FeO dissociated from the CO_2 would account for the small exothermic loop and the subsequent wiggles at about 800°C . Beck (1950) has shown that a sample of bruenerite from Gustine, California, produces a curve of the same character, and Gruver (1950) discusses a similar curve obtained from magnesite from Chewelah, Washington. According to Dana, magnesite and siderite form a continuous series without definite intermediate compounds.

Perhaps the differential thermal curve of dolomite (Fig. 6) is benefited more by a furnace atmosphere of CO_2 than is any other carbonate. When this mineral is heated in air, the endothermic loop which accompanies the loss of CO_2 by the MgCO_3 begins its sharp deflection at about 780°C ., more than two hundred and fifty degrees higher than the beginning of the sharp deflection for magnesite alone. The peak occurs at 820°C . and before the loop is completed it is interrupted by an endothermic deflection accompanying the loss of CO_2 by the CaCO_3 portion of the mineral. Frequently this interruption takes place considerably before the first loop is completed. When the same material is heated in an atmosphere of CO_2 , the MgCO_3 part of the curve begins at 750°C ., peaks at about 790°C ., and is complete at 820°C . The CaCO_3 part does not start until 910°C . and is clearly separated from the MgCO_3 loop.

The use of a CO_2 atmosphere in the furnace likewise affords an opportunity to observe the reversibility of the reaction, $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ by alternately heating and cooling the sample through the temperature range of dissociation-reconstitution. For this purpose a Bureau of Standards sample of dolomite was heated in CO_2 to 1000°C . then cooled to 200°C . and reheated to 1000°C . This cycle occurs four times without removing the sample from the furnace atmosphere of CO_2 . Those parts of the curve on which there was a deflection are reproduced in Fig. 7. On the first heating, the expected dissociation loops for dolomite were obtained. When the sample was cooled, only one loop formed, and successive heating and cooling dissociated and reformed only the compound responsible for this loop. X-ray diffraction patterns indicate the presence of CaO and MgO in the product above 1000°C ., and MgO, calcite, and some CaO in the material after cooling in CO_2 . It should be noted from the position of the 900°C . mark on the dissociation loops that dissociation took place at a progressively lower temperature as the cycle was repeated. Also the size of the reconstitution loops decreased as the cycle was repeated. It is of some interest to compare the areas under the

reconstitution loops with the corresponding dissociation loops since presumably exactly the same amount of material is dissociated as has been previously reconstituted, and the net heat involved in the reaction should be the same. During dissociation, an endothermic reaction, the sample takes up heat and tends to remain at the same temperature until the reaction is complete. While this is happening, the thermocouple in the sample is maintained at a temperature lower than the furnace temperature. When reconstitution takes place, the reaction is exothermic and the sample heats the thermocouple. During this process the thermo-



couple is maintained at a temperature higher than that of the furnace. Since the furnace heating and cooling rates are essentially the same, then a comparison of the areas enclosed by the loops and an extended base line should indicate the relative efficiency with which exothermic and endothermic reactions are recorded. For the four reversals shown here, the ratio of the area under the reconstitution loop to the area under the following dissociation loop lies between 0.68 and 0.72, indicating that the apparatus more faithfully records endothermic effects than exothermic effects.

CONCLUSIONS

It is apparent from the foregoing discussion that the usefulness of existing differential thermal analysis apparatus can be extended considerably by controlling the composition of the furnace atmosphere. Adequate control to take advantage of the method may be obtained by simply passing a gas from commercially available pressure cylinders through the furnace. When it is desirable to suppress the oxidation of organic matter or sulfides, water-pumped nitrogen may be used. If a more completely

inert atmosphere is required, purified nitrogen and argon are available. When it is desired to control the partial pressure of a gas being evolved in the reaction, the participating gas, such as CO_2 in the dissociation of the carbonates, may be introduced into the furnace. In each case confusing aspects of curves obtained in air are eliminated, and inflection points are sharpened considerably.

REFERENCES

- BECK, C. (1950), Differential thermal analysis curves of carbonate minerals: *Am. Mineral.*, **35**, 985-1013.
- GRIM, R. E., AND ROWLAND, R. A. (1944), Differential thermal analyses of clays and shales, a control and prospecting method: *Jour. Am. Ceramic Soc.*, **27**, 65-76.
- GRUVER, R. M. (1950), Characteristic heat effects of some carbonates: *Jour. Am. Ceramic Soc.*, **33**, 96-101.
- MACDOUGALL, F. H. (1939), *Thermodynamics and Chemistry*, John Wiley, N. Y. p. 228 ff.
- ROWLAND, R. A., AND JONAS, E. C. (1949), Variations in differential thermal analysis curves of siderite: *Am. Mineral.*, **34**, 550-558.
- WHITEHEAD, W. L., AND BREGER, I. A. (1950), Vacuum differential thermal analysis: *Science*, **III**, 279-281.

Manuscript received

Aug. 1, 1950