Mining and Metallurgical Engineers convention, San Francisco, February 1959.
3. A. Deniges, *Compt. rend.* **188**, 654 (1920).
4. Publication of this report as paper No. 2410 of the journal series of the Pennsylvania Agricultural Experiment Station, University Park, Pa., was authorized 9 Oct. 1959. We are indebted to R. B. Booth of the American Cyanamid Company for supplying the polymers (Superfloc 16 and Aerofloc 3171) used in this study. These polymers are polyacrylamides prepared by polymerization of the monomer acrylamide.
5. The statistical data were prepared by Leon Johnson.

20 October 1959

## Differential Thermal Study of Pyrosynthesis

*Abstract.* Equipment is described which provides a thermal record of the synthesis of sulfides and related minerals contained in easily constructed tubular glass vials. As an example, a temperature curve for the synthesis of galena (PbS) is given. Similarly derived temperatures of formation for eight other synthetic sulfides and selenides are reported.

The differential thermal analysis technique may be modified to provide information concerning the temperature at which crystallization takes place and at which other fundamental heat changes occur during mineral synthesis. A modification of equipment has been developed which provides a continuous differential record of exothermic and endothermic reactions as the temperature of a mixture of the components of a desired synthetic compound is increased at a linear rate. A record is obtained of the temperature, the magnitude, and the relative reaction rate of those physical-chemical processes which tend to give off or absorb heat. Among these processes are fusion, crystallization, chemical combination, dissociation, and the inversion of one structure to another. The equipment yields a continuous observable record during heating as well as cooling; this makes it possible to interrupt the cycle at any desired point for quenching, in order to study particular phases.

The apparatus (Fig. 1) consists of a thermal head containing Chromel-Alumel thermocouples and thermal wells which will accept sealed specimen vials of glass tubing 6 mm in diameter. A thermocouple is placed in a recess at one end of a tube, as shown in the sectional drawing. The recess is formed in the tube while one end still remains open and before the constituents are inserted. A dummy thermocouple is pressed against the end of the heated tube, forming a small depression into which an active thermocouple may be inserted.

The tubular sample vials are made of Pyrex, Vycor, or fused quartz, depending upon the terminal temperature required for the experiment. Each vial is evacuated by a mechanical vacuum pump during final sealing in order to guard against oxidation of the components. The space between the vials and the head metal is filled with 60-mesh Alundum in order to improve the thermal contact between the walls and the material in the vials. In this way, an attempt is made to provide an even, but still slightly incomplete, temperature flow between the thermal head and the constituents in the vial. Since the thermal conductivity of the Alundum is less than that of the metal head, the Alundum serves to prevent the mass of the head from masking the temperature effects produced in the vial. Although the thermal contact at the end of the tube between the thermocouple and the sample is relatively small, it has proved adequate to produce effective differential thermal records.

A similar thermal technique was described by Jensen (*1*) for the study of fusion points. However, the double tubes required in his work were found unnecessary in this study, and the fabrication of vials was simplified.

The instrumentation adopted was developed from differential thermal analysis equipment described by Kerr and Kulp (*2*) for work with clay minerals and related species. The major components consist of a 4000-watt electrical furnace; a program controller capable of maintaining a linear heating or cooling rate; a direct-current preamplifier for the differential thermocouples; and recorders for electromotive force and temperature.

The program controller has a two-position proportional section which provides a linear heating or cooling rate of 12.5°C/min from room temperature to 1050°C. A continuous furnace input produces a heating rate of approximately 28°C/min, with sufficient linearity for rapid testing of a sample.

Two ranges of preamplification provide a 5-mv deflection of the potential recorder, which has sensitivities of −5, 0, +5 mv. A low sensitivity of 0.5 mv is used on samples which have a large thermal reaction, and a high sensitivity of 0.25 mv is used on samples with a smaller reaction.

Figure 2 shows the formation of galena (PbS) by pyrosynthesis. An endothermic reaction appears at 110°C, which represents the melting point of sulfur, while an exothermic reaction shows initial deflection at 210°C. As the heat of the exothermic reaction is added to the temperature of the sample, the reaction proceeds at a faster rate and culminates in a peak deflection at 300°C. This point apparently represents the complete crystallization of galena, as indicated by supplemental x-ray studies. The return of the curve to the base line represents primarily the decay of the thermal gradient as the reaction is absorbed by the thermal mass of the head. In the synthesis of some minerals, final crystallization occurs during this period and is indicated by a comparatively slow return of the curve to the base line. The area of the curve and its configuration permit investigation of the chemical affinity of the constituents, relative bonding energy, amount of thermal energy released during crystallization, and rela-

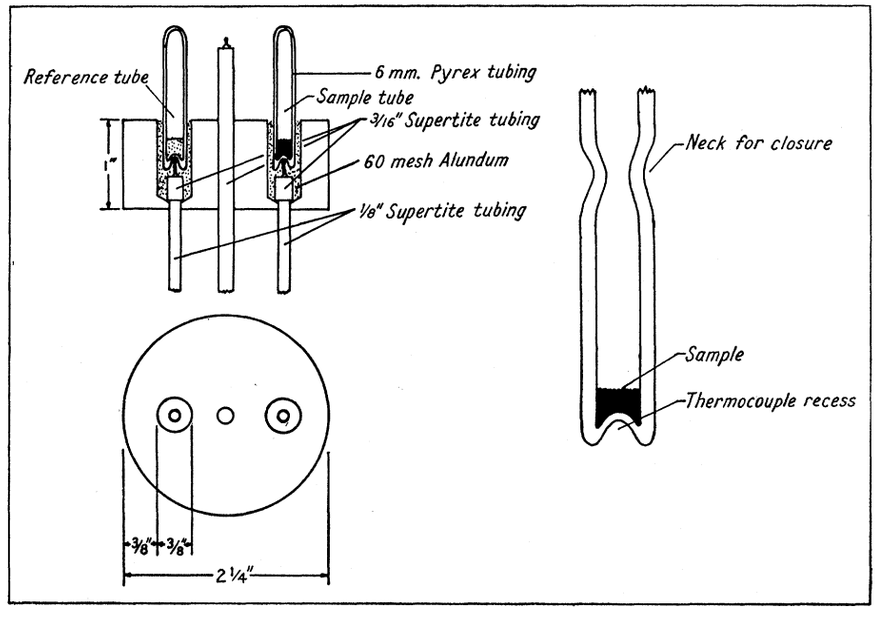


Fig. 1. Thermal head and detail of specimen vial.

tive rate of the reaction throughout the crystallization process.

Similar curves have been derived for other sulfides, selenides, tellurides, arsenides, and antimonides. The technique has been shown to be particularly adaptable to the study of isomorphous minerals. Two series [galena (PbS)—clausthalite (PbSe) and covellite (CuS)—klockmannite (CuSe)] now being investigated show gradational changes of the curves from one end of each series to the other.

Preliminary curves show initial temperatures for several simple metallic sulfides or selenides as follows: covellite (CuS), 115°C; clausthalite (PbSe), 160°C; klockmannite (CuSe), 225°C; Alabandite (MnS), 340°C; greenockite (CdS), 410°C; arsenopyrite (FeAsS), 475°C; and pyrite ($FeS_2$), 505°C. The temperatures indicated are preliminary estimates, since the accompanying x-ray studies for these and more complex compounds are still incomplete.

It appears from preliminary results that differential thermal pyrosynthesis offers a convenient and reasonably exact method for investigating the fundamental properties of a number of sulfides or related minerals during their formation. When used in conjunction with differential thermal analysis and x-ray analysis, a more complete survey of the temperature relations of these minerals may be conducted. Study to date shows that differential thermal analysis is particularly adaptable to studies of mineral sequences which involve cation substitution, whereas differential thermal pyrosynthesis now appears more applicable to sequences involving anion substitution.

Since the method is dynamic and present equipment is limited to the study of dry systems, the results obtained are relative, and the data derived must be applied to natural mineral formation with caution. Present knowledge of temperatures of formation of mineral deposits leaves much to be desired, and the results of this technique, although only relative, may prove of considerable value in estimating such temperatures. The dynamic method readily demonstrates that the assumption frequently made that long periods are necessary for the formation of "sulfide type" minerals may be misleading (*3*).

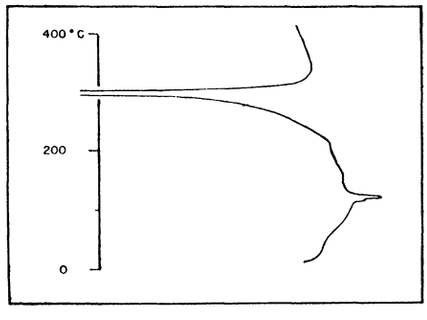


Fig. 2. Thermal record of the formation of galena by pyrosynthesis. The endothermic deflection to the right indicates the melting of sulfur, and the exothermic deflection to the left indicates the crystallization of galena.

EDGAR M. BOLLIN
JAMES A. DUNNE
PAUL F. KERR
*Columbia University, New York*

**References and Notes**

1. E. Jensen, *Am. J. Sci.* **240**, 695 (1942).
2. P. F. Kerr and J. L. Kulp, *Am. Mineralogist* **33**, 387 (1948).
3. This study was made possible through the assistance of the National Science Foundation.

18 November 1959

## Effect of Lesions in the Septal Forebrain of the Rat on Sleeping Time under Barbiturate

*Abstract.* Rats with electrolytic lesions in the septal forebrain show increased sleeping times after injection with thiopental sodium or barbital, as compared with normal and other control rats and rats with lesions in the cerebral cortex or caudate nucleus.

As part of a program investigating the effects of drugs on the emotional behavior in animals, we have studied the effects of barbiturates on the behavior of rats with lesions in the septal area of the forebrain. Such lesions ordinarily produce marked emotionality or hyperirritability. An earlier study found that meprobamate dramatically offset this irritability (*1*). In fact, rats with septal lesions showed clear sedation in response to doses of the drug that had little or no effect on the behavior of the intact animal.

In subsequent investigations of this phenomenon barbiturates were employed, because more is known about their metabolic fate and pharmacological action. These experiments have included not only rats with septal lesions, but also rats with lesions in the caudate nucleus or in the cortex and underlying white matter. All lesions have been bilateral and have been placed stereotaxically in the brains of 60- to 70-day-old male albino rats at an anteropostero location 2 mm anterior to the bregma, by the passage of a 3-ma direct current for 45 seconds at each needle placement. The septal and cortical lesions were placed 0.5 mm lateral to the mid-line on each side, the septal 6.5 mm and the cortical 2.5 mm below the surface of the skull. The lesions in the caudate nucleus were placed 3.0 mm lateral to the mid-line on each side at a depth of 6.5 mm.

Histological confirmation of the lesions has been completed for all animals. These data have shown that the operative technique produces standard lesions with fairly restricted variability at the loci intended. The septal lesions were found to consistently destroy that area lying beneath the corpus callosum in the rostromedial wall of the hemispheres, bounded laterally by the lateral ventricles and extending from the frontal cortex to the gray of the hippocampal commissure dorsally and from the olfactory tubercle to the preoptic area ventrally. Animals with caudate lesions showed localized destruction beginning in the head of the caudate and extending through the medial aspect of the caudate nucleus with no damage to the septal region. The animals with cortical lesions showed small isocortical lesions lying close to the mid-line above the corpus callosum and extending from the level of the head of the caudate nucleus to the columns of the fornix.

In addition to normal control rats, most of the experiments also have included sham-operated, deaf, and reduced-weight control groups. In the sham operation, the rat was anesthetized, its scalp was incised and retracted, and the skull was drilled at the appropriate point, with the dura spared. The deaf control rats were anesthetized, and their ear drums were punctured by the stereotaxic ear plugs, when the other animals were given lesions, to provide a control for possible effects of incidental damage to the auditory apparatus on sleeping time. The reduced-weight control rats had their food and water intake restricted for 4 days prior to the test to control for effects of postoperative weight loss usually found in rats with septal and caudate lesions.

In the experiments with thiopental sodium, the drug was injected into the femoral vein after the skin had been incised and the vein exposed to permit viewing of the site. After the injection, each animal was placed on its back and left undisturbed until it turned over. Sleeping time served as the behavioral indicator of drug effect, defined as the number of minutes elapsing between the termination of the injection and the time when the rat righted itself spontaneously.

Figure 1 presents data for a representative experiment in which 20 mg of thiopental sodium per kilogram was injected intravenously at either 21 or 22 days postoperatively. In this experiment the rats with septal lesions showed a mean sleeping time between two and three times the mean sleeping time of any other group. The difference in sleeping time between the group with septal lesions and the com-