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DIFFERENTIAL THERMAL PYROSYNTHESIS

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ABSTRACT

Differential thermal pyrosynthesis may be considered a modification of differential thermal analysis which allows investigation under closed system conditions. A record is obtained of thermal reactions which occur during synthesis by heating elemental constituents to the fusion point. The equipment provides a continuous curve which records exothermic and endothermic reactions during formation; at higher temperatures, up to and above the fusion point; and subsequent cooling of synthetic compounds. The relative kinetics of the reactions are readily observable providing information applicable to other types of thermal study.

Modifications of the equipment design, changes in the technique, and alteration of physical parameters combine to provide sensitive thermal data. Pyrosynthesis curves of several synthetic minerals demonstrate the range of the method.

INTRODUCTION

Pyrosynthesis has been utilized in the studies of the differential thermal analysis of the system PbS–PbSe (Dunne and Kerr, 1961) to obtain supplemental data on this system. Rapid fusion of elemental constituents in a Bunsen burner or hotter flame (Earley, 1949, 1950) is undesirable since there is little control of the environment of synthesis and the thermal shock of rapidly applied heat and the rapid increase in the internal pressure produced by some reactions causes the failure of glass vials. Fixed temperature equilibrium synthesis studies used by the majority of the investigators of synthetic systems is similarly restricted by the length of time and the number of syntheses required for a complete determination of equilibria. Neither of the previous methods readily provides information concerning the relative kinetics of the reactions.

In this study, the thermal environment during synthesis is controlled by an electric furnace adjusted to a reproducible linear heating rate, and differential thermal analysis (D.T.A.) equipment is employed to indicate the temperatures at which reactions occur within the system.

Elemental constituents are confined in an evacuated glass vial with a molded depression at one end, which forms the contact with reacting products and a thermocouple. A similar vial filled with thermally inert material and a second thermocouple completes the pair of differential elements. An envelope of granular aluminum oxide holds the vials in a massive metal head. This arrangement provides a stabilized temperature distribution from the furnace to the sample and reference vials.

The technique is well adapted to the investigation of previously synthesized materials and naturally occuring minerals. The method is nondestructive for compounds with thermally reversible reactions and repeated analyses of the same sample are possible. Trial syntheses have shown that the method is capable of recording reactions within vials with sufficient sensitivity to justify refinement and standardization of the technique (Bollin, Dunne, and Kerr, 1960).

Differential thermal pyrosynthesis (D.T.P.) is a highly flexible and reasonably accurate method for the investigation of a large number of minerals. Anhydrous synthesis of the majority of naturally occurring sulfide minerals directly from their elemental constituents and the observation of the kinetics of the reactions is possible. The method is not only adapted to synthesis studies, but also furnishes a sensitive method of investigation of reactions such as melting and transition relations which are not readily observable by other means. As a reconnaissance investigation preliminary to fixed temperature equilibrium studies of a system, or to furnish specific or comparative data on specific minerals, the method is rapid, easily implemented, and is a necessary corollary to the investigation of many systems.

INSTRUMENTATION AND TECHNIQUE

Instrumentation

The recording and heating units are largely the same whether used for D.T.A. or D.T.P. Modification of D.T.A. facilities for D.T.P. merely requires a fast response time in the recording equipment. However, continuous recording is essential and multiple point recorders, such as used by Kerr and Kulp (1948), are unsatisfactory because of the rapid rate of some reactions.

One Leeds and Northrup Speedomax H, model S recorder is used to record the amplified potential of a differential pair of chromel-alumel thermocouples, while another similar unit is used to record the temperature of one of these thermocouples. The potential recorder has a scale range of -5, 0, $+5$ mv, and the temperature recorder has a scale of 0 to 1200° C. The potential recorder is modified to allow variable suppression of the range at any position along the scale by replacing the (E) fixed resistor of the emf bridge* with a variable potentiometer of 4 ohms. This allows the recorder to be offset if either drift or a large thermal peak tends to drive it offscale. A chart speed of six inches per hour is normally used for both recorders. The response time of the potential recorder is one second, while the temperature recorder has a response time of five seconds.

Preamplification of the differential pair of thermocouples is provided

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* Leeds and Northrup Manual #077990, p. N-2.

by a Leeds and Northrup No. 9835 B microvolt preamplifier. Two of the available ranges of preamplification may be used with the present configuration of thermal head and thermocouples. Low sensitivity results in a 5 mv deflection of the recorder with a 0.5 mv input (10X) while high sensitivity produces a 5 mv deflection with 0.25 mv input (20X).

The response time of the preamplifier appears rapid enough to record D.T.P. reactions, and is slow enough to suppress the electrical pulses applied to the furnace by the on-off controller. Use of the extremely fast response direct current amplifiers now commercially available necessitates a proportional type control of furnace input or a reduction of their response by capacitive loading. A Beckman Model 14 breaker amplifier has been modified for fast response by using 60 cycle choppers and direct current feedback. The configuration and magnitude of the D.T.P. curves are not affected during a fast deflection, although the baseline is considerably broadened by current pulses of the furnace controller.

The program controller provides a linear heating rate of 12.5° C. per minute from room temperature to 1200° C. A linear cooling rate at the same speed is also provided. The program controller consists of a Leeds and Northrup Micromax recorder-controller and a M.E.C. two position time-proportional anticipation unit. The control point is driven upscale or downscale by a synchronous motor. Contact pitting, noise, and maintenance associated with standard heavy duty control relays have been eliminated by the use of an Ebert mercury plunger relay to control the current supplied to the furnace.

The furnaces are constructed of internally wound cores supplied by the Hevi-Duty Electric Co., Milwaukee, Wisconsin (type MK-3712, 3″ bore, 12″ long, 1205° C. maximum continuous operating temperature). These cores have a 1900 watt rating when operated on 230 volt alternating current. One-half inch thick transite discs at each end of a five gallon drum constitute the external shell of the furnace. Fiberfrax, ceramic fiber (Carborundum Co., Niagara Falls, New York), packed 6 lbs./cu. ft., is used for insulation.

Four two-inch water pipe vertical supports attached to $\frac{1}{4}$ inch thick boiler plate, above and below, form a substantial frame within which the furnaces are suspended by a pulley mounted sash cord and counter weight. Standard, threaded water pipe floor flanges are used to attach the pipe to the boiler plate.

The power input of the furnace is considerably above that necessary to maintain a 1200° C. terminal temperature;* however, the high input provides a useful excess of available heat. This is highly desirable since other-

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* Norton Company Catalog No. 485, The Construction of Laboratory Electric Furnaces, p. 9.

wise furnace limitations may affect the linearity of the program controller. Continuous input to the furnace yields a heating rate of approximately 28° C. per minute with sufficient linearity of the program throughout most of the range to allow rapid reconnaissance investigations.

Low resistance, high current furnaces, such as the Hoskins 305 previously used by Kerr and Kulp (1948) produce a higher heating rate at lower temperatures than the furnaces now in use; however, linearity is poor above 800° C. Heating rate curves exhibit a high temperature nonlinearity when insufficient insulation is provided for these temperatures. Such furnaces, however, have a considerable advantage for investigations in the low temperature range since their rapid low temperature heating rate allows the program controller to establish a linear heating rate earlier in the cycle. The furnaces now in use have a low initial heat, which does not allow a completely linear curve to be established below approximately 100° C. with the size of the thermal head now in use. Since most of the critical reactions are above this temperature in the present study, the slight deviation from linearity in this range is not considered critical.

Thermal Head

The thermal head (Fig. 1) is constructed of 18-8 chrome-nickel stainless steel, which is essentially as heat resistant as the nickel used in some equipment.* Stainless steel produces no curie effect, is more easily machined, and is more readily obtainable than nickel. A further consideration in the selection of the stainless steel is its oxidizing properties. A uniform dull black oxide film is formed by heating in excess of 1000° C. and subsequent heating to 1050° C. under normal conditions of analysis does not produce appreciable scaling.

The black oxide layer tends to smooth out the transition from the conduction and convection mode of heat transfer to the radiation mode of heat transfer between furnace windings and head by increasing the radiation absorptivity at a lower temperature. The porosity of the oxide also furnishes a bonding surface for cementing thermocouple insulator tubes in the head.

If the metal is purchased in rod form, machining of the head is reduced to cutting to desired length, preferably with a power hack saw, and facing the ends in a lathe. The center hole is drilled, and the center line of the sample and reference wells is scribed while the rod is still centered in the lathe chuck in order to assure accuracy of hole location.

The upper half of the head serves as a heat shield for the exposed tips

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* Publication No. 266, Heat Resistant Castings, Corrosion Resistant Castings, Their Engineering Properties and Applications: International Nickel Co., Inc., 60 p.

of the vials which protrude from the lower portion. This two piece construction of the head is of considerable advantage when placing the vials in the head as it allows each vial to be seated firmly on the thermocouples and concentric with the thermal wells. The open space in the lower half of the head is packed with granular aluminum oxide to hold the vials in position before placing the top half in place. The two piece head also allows rapid removal of the vials for quenching. A further advantage of the two piece head is the maintenance of a heat gradient between the top and bottom of the vial during convection cooling of the furnace. The incomplete heat transfer between the two portions of the head under these conditions allows the lower portion of the vial to cool first. This gradient is sufficient to cause single crystal growth within the vial in the case of a number of compounds.

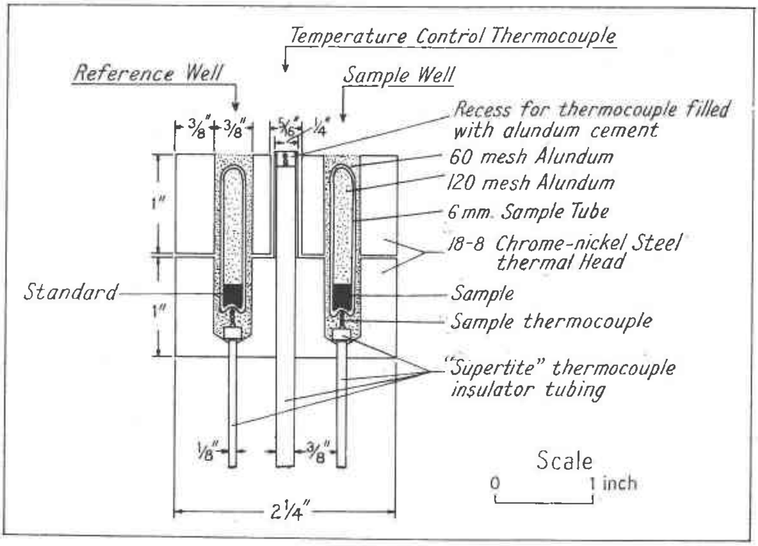

FIG. 1. Cross-section of the thermal head. Sealed, evacuated glass vials are concentrically located in alundum packed apertures in a stainless steel head. Thermocouples fit an indented base.

The thermal head is mounted on a Norton RA 98 alundum tube two inches in diameter with a $\frac{1}{4}$ inch wall thickness. The length of the tube is such that the head is located at the center of the furnace and concentric with the vertical axis of the furnace. When the furnace is lowered over the thermal head, the whole assembly is aligned automatically by the enclosing furnace frame, which restricts horizontal displacement to maintain exact concentricity of the thermal unit with the axis of the furnace.

Much importance is attached to the alignment and the vertical arrangement of the furnace to assure symmetrical convection distribution of heat in the thermal head. Convection currents are reduced to a minimum by a plug on the top of the furnace, and a mechanical seal is provided at the bottom by the insulation in which the thermal head support tube is mounted.

The head should be brought to the exact thermal center of the furnace by a simple procedure. The transite discs at the bottom of the furnace support frame are drilled slightly oversize so that the alundum head support tube may be slightly tilted. The thermal wells are filled with granular alundum, and the furnace is brought to approximately 600° C. The alundum support tube is tilted slightly in different directions and the furnace lowered so that the system comes to an equilibrium condition. Experimental tilting is continued until a minimum base line offset on the differential potential recorder is obtained. This places the head in the exact thermal center of the furnace windings. Base line offset may now be reduced to zero by rotating the alundum support around its vertical axis so that both thermal wells are symmetrically disposed with respect to the vertical furnace windings. The support tube is next cemented permanently in this position. This procedure results in a minimum overall base line drift throughout the heating cycle.

During controlled cooling cycles, convection cooling is accomplished by removing the top plug closure of the furnace and raising the furnace approximately two inches. The temperature controller is left at the highest temperature until a convection equilibrium is established with the thermal head. This is indicated by a return of the base line of the differential record to a normal position. As the convection current cools the furnace at a rate faster than 12.5° C. per minute, the program controller is able to maintain a linear cooling rate by adding heat.

Preparation of Thermocouples

The thermocouples are prepared from B & S No. 22 gauge chromel-alumel wires. A simple arc welding process allows rapid and uniform fabrication without the equipment and skill necessary in gas-oxygen torch welding. The thermocouple welder is shown in Fig. 2. Construction dimensions are not critical, and a considerable modification is possible without affecting results appreciably. The current during the arcing process may be controlled by either a series resistor as shown, or by a Variac. The series resistor of 5 ohms in the present unit is wound with furnace resistance wire on a $\frac{1}{4}$ inch ceramic thermocouple insulator tube and covered with Insalute No. 1 cement. Considerable heat is dissipated by the resistor if welding is prolonged, and ventilation should be provided or the construction should be open. The mercury cup may be made of plastic sheet and tubing. Size is of minor importance as long as sufficient depth is provided to maintain at least a minimum layer one inch thick of mineral oil over the mercury. The cover should have a hole just sufficient to admit the thermocouple wires in order to reduce splattering of oil during welding.

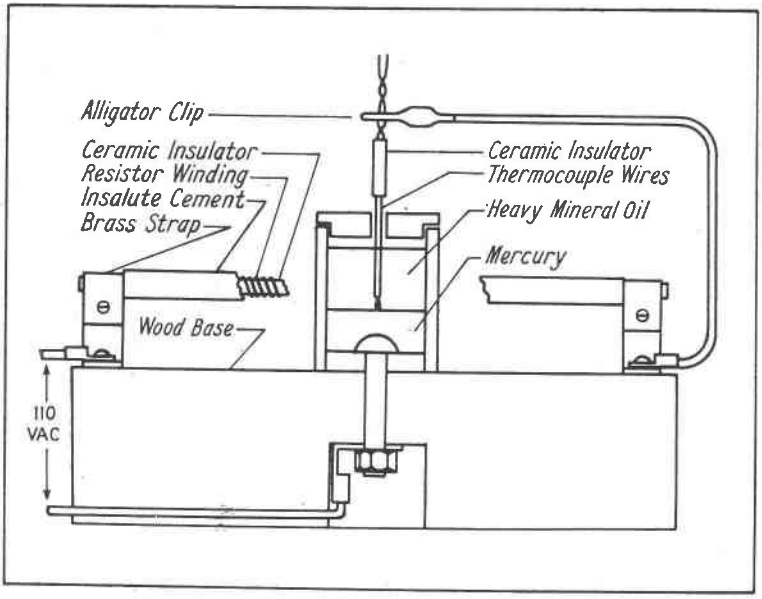

FIG. 2. Thermocouple arc-welding device. A cup containing mercury covered with oil forms one 110 volt A.C. terminal. The thermocouple wires form the other. On contact, the two wires are fused to form a small sphere.

The thermocouple wires are threaded through a short piece of ceramic insulator tubing and the ends uniformly twisted together. An alligator clip is then attached to the wires protruding through the other end of the insulator, and the twisted end is lowered through the mineral oil allowing momentary contact with the mercury. The thermocouple is immediately raised very slightly allowing an arc to form for a second or two; then the contact is broken by lifting the thermocouple slightly higher into the overlying mineral oil. The thermocouple is removed from the mineral oil after approximately ten seconds so that the temperature is low enough to prevent oxidation. The mineral oil serves to reduce the amount of mer-

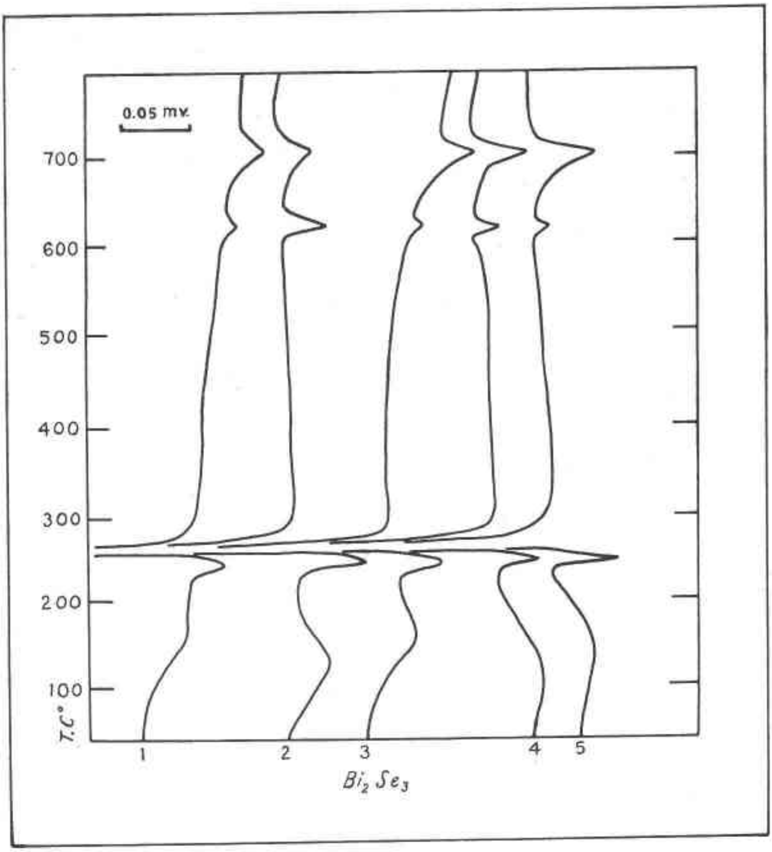

FIG. 3. Pyrosynthesis curves for Bi_2Se_3 for vials with different basal configuration for thermocouple contact. (1) A round bottom with a point thermocouple contact. (2) A flat bottom with a point thermocouple contact. (3) Base indented $\frac{1}{8}$ inch. (4) Base indented $\frac{3}{16}$ inch. (5) Base indented $\frac{1}{4}$ inch.

cury vapor produced during the welding and allows the surface tension of the molten thermocouple to produce a spherical shape. The size of the thermocouple junction can be readily controlled by the amount of arc time, and after a few experiments uniform couples may be produced with little difficulty. A sphere approximately twice the size of the wire diameter is used to provide a good contact with the sample vials. In standard D.T.A. investigation, where thermal contact is provided by the sample completely surrounding the junction, a weld which shows no increase or decrease in size at the junction is desired to obtain optimum response time commensurate with longevity.

Preparation of Sample and Reference Vials

A somewhat similar thermal technique has been used by Jensen (1942) and Kracek (1946). However, the construction of the double re-entrant vials, used by these workers to allow placement of the thermocouples in the center of the reactants, requires considerable glass blowing technique and provides less strength than the vials used in this study. The increased thermal transfer by placing the thermocouple in the center of the reactants is of doubtful value, and may be even less effective than in the present construction. In the present design the thermocouple recess is molded around the end of the thermocouple junction, providing intimate physical contact. The complexity of fabrication of the double re-entrant vials and the associated multiple seals of the previous designs has probably prevented wide adoption of the method. The effect of thermocouple penetration into the reactants, as shown for Bi_2Se_3 (Fig. 3) demonstrates that reactions may be observed in simplified vials with excellent results.

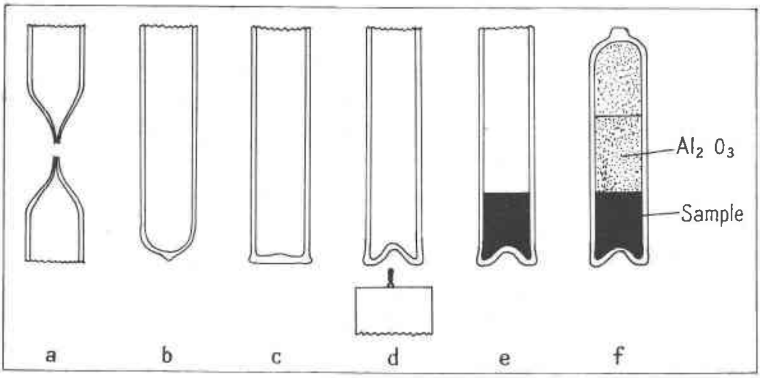

FIG. 4. Successive steps in the preparation, filling, and sealing of a sample vial.

The sample vials may be constructed of Pyrex, Vycor, or fused quartz tubing 6 mm. in diameter, depending upon the highest temperature to which the tubing is to be subjected. A tube wall 1 mm. thick is normally used where internal pressures are not excessive. Pyrex tubing remains rigid to 600° C. and is easily worked with a gas-air torch. Vycor and fused quartz tubes require the use of an oxygen torch for fabrication and are usable to at least 1200° for short periods.

A tube twice as long (8 inches) as the final length is heated and pulled into a fine capillary in the middle, providing two tubes (Fig. 4*a*). The capillary is necessary, as fusion of a tube with a normal diameter often produces an imperfect vacuum seal. The capillary is fused, and, as the tubing approaches a spherical shape, caused by surface tension (Fig. 4*b*), it is flattened against a heat resistant surface (Fig. 4*c*). The closure is reheated to softening temperature, and a cold thermocouple is pushed into the bottom of the tube until approximately a $\frac{1}{8}$ inch re-entrant is formed (Fig. 4d). A thermocouple is used as a mold and is mounted in a large diameter ceramic tubing from which it extends the required $\frac{1}{8}$ inch. This procedure results in a uniform thermocouple recess depth which conforms to the size and shape of the thermocouple used in analysis. The vials are thoroughly heated at a temperature below softening to anneal the seal and drive off any entrapped moisture, then are cooled in a desiccator and kept until ready for use.

A measured volume or weight (1–2 mg.) of reactants is placed in the bottom of a vial (Fig. 4*e*) and tapped on a solid surface until no further compaction is noted in order to reduce the pore space to a minimum without mechanical pressure. A uniform volume of 120 mesh granular aluminum oxide is placed on top of the sample to fill the open space in the vial and to protect the sample during the sealing operation. The aluminum oxide filling of the tubes may be omitted if a pure sample is desired for *x*-ray analysis. The alundum filler is likewise omitted where cooling curves are to be examined to prevent reactants from being trapped in the pore space or on the surface area of the alundum. Closely fitting glass rods may be used where volume considerations are more important than base line drift.

The vial is evacuated to approximately 50 microns of mercury pressure with a Cenco Megavac vacuum pump. While under vacuum the vial is heated and sealed by rapidly twisting the plastic portion of the vial. Any open space above the aluminum oxide is eliminated by continued twisting while the seal is still plastic. The seal is then drawn out to separate the tube from the pump and flattened against a heat resistant surface (Fig. 4*f*). The aluminum oxide filler in the vial not only serves to mark a consistent length for the seal, but also protects the sample from coming into contact with the heated portion of the vial in handling. When sealing Vycor or fused quartz vials there is a tendency for the vacuum trapped with the reactants to bulge the tubing inward at the seal. Until facility is gained in the sealing process, failure of the vials may result unless the inward bulging is prevented by contact with the aluminum oxide filler or glass rods.

Internal standards may be used in the reference vial to provide check points on curves by which the emf record may be indexed over the temperature record and traced on a light table. From the differential standpoint, it is of no consequence which vial contains the standard. From the chemical standpoint, the standard in the reference vial removes a source of possible sample contamination and spurious reactions from interaction between the sample and the standard.

Electrical Wiring of the Thermal Head

In wiring the thermal head, the reference thermocouple of the differential pair also serves as the temperature recording thermocouple. A further reduction in the number of thermocouples may be made by using this thermocouple to activate the program controller. However, the program control thermocouple is located in the center of the head and serves to maintain alignment of the two halves. In this position it does not disturb the thermal symmetry of the head.

If the thermocouples are reduced to two, the temperature of the reference vial is controlled and not the furnace. Because of the thermal inertia of the head surrounding the reference vial, some difficulty caused by control overshoot may be expected unless the temperature controller has sufficient latitude of adjustment, or a very small thermal head is used.

The reference thermocouple of the differential pair is used as the temperature recording thermocouple for several reasons.

(1) The addition of another thermocouple mounting for a separate head temperature thermocouple, as used in some D.T.A. arrangements, would disturb the thermal symmetry of the head.

(2) Maintaining an exactly symmetrical heat flow distribution for a third thermocouple increases the number of uncontrolled variables in the system and increases the difficulty of construction.

(3) The temperature of the head is of no significance, since there is a slight difference in the head temperature and the actual sample temperature caused by the imperfect heat transfer through the aluminum oxide surrounding the sample and the reference vials.

(4) The reference thermocouple has a more nearly linear heat rise than the sample thermocouple, as there is a slight deviation of linearity in the sample well caused by the reactions produced. It may be argued that the temperature in the two wells is not exactly the same because of differing rates of heat absorption of the reactants in the sample well and the aluminum oxide or the reference in the reference well. However, the amounts of reactants used are so small that this effect is negligible. The actual temperature difference between the two vials may be computed from the displacement of the base line of the emf recorder from zero by dividing actual displacement by the preamplifier gain. In properly designed and aligned thermal heads and furnace configurations, the distinction concerning which thermocouple is the valid temperature recording couple is not significant. The temperature difference between the two vials in the present instrumentation, when a reaction is not in progress, is in the range of 0° to 0.25° C., which is too small to be resolved on the temperature record.

(5) Thermal deviations from linearity produced by some reactants during a reaction are large enough to slightly distort the temperature curve and give anomalous temperatures of reaction when the sample thermocouple is used to record temperature. Self heating or self cooling during strong reactions may cause the actual sample temperature to be slightly different from that recorded in the reference well. Since relative temperatures based

upon a specific linear heating rate are a basic assumption in this method of analysis, the temperatures as expressed by the reference vial more nearly approach a valid figure for comparison. An otherwise linear temperature curve, which is distorted at the point of measurement, is not susceptible to interpolation of small differences in temperature.

(6) The presence of a standard in the reference vial does not interfere with the temperature record because the amount may be regulated to avoid affecting the temperature curve. The difference in the sensitivity of the temperature and the differential recorders makes this procedure possible.

Physical Factors in Thermal Methods

The control of environmental variables encountered in differential thermal analysis applied to the study of clay minerals (Kerr and Kulp, 1948); thermal analysis applied to the study of metallurgical problems (Jensen, 1942); and the utilization of fixed temperatures held until equilibrium is attained (Kullerud and Yoder, 1959), all involve factors which must be considered in applying the D.T.P. method. The technique for the standardization of D.T.A. has been treated extensively by Mackenzie (1957) and is applicable for most methods in which an open sample is in contact with the thermocouple. A number of parameters which affect D.T.A. also affect D.T.P., and only those with characteristics which are essentially changed by D.T.P. procedures need be discussed.

The major modifications which occur in D.T.P. involve the enclosure of the sample within a sealed vial and the method of heat transfer to the thermocouples. Also, extension of investigations to include the liquid and vapor state requires control of pressure influence and a thermal head design which must enclose the sample and reference vials.

Effect of Grain Size

The components should be as finely divided as possible, although the particle size employed depends upon the physical and chemical nature of the elemental constituents of the mineral under investigation. Several factors determine grain size, other than the complete physical homogenization obtainable with extremely fine-grained powdered mixtures. The optimum grain size for any single combination of elemental constituents should be experimentally determined for each system.

The initial reaction temperature in forming a specific chemical compound may influence tke choice of grain size. Three basic types of reactions predominate (Fig. 12): (1) reaction in the solid state (Ag+S or Cu+S); (2) reaction with one component in the solid state and the other component in the liquid state (majority of the compounds studied); (3) reaction with both components in the liquid state (Zn+S). All three of these types of reactions may occur to a greater or lesser degree in any system. As the temperature increases, the vapor state reaction enters into all three divisions to an increasing degree. The effect of the vapor state is easily demonstrated, even for condition (1) above, by the marked increase in the reaction of Cu+S at room temperature in evacuated vials compared with vials at normal pressure. Considerable reaction takes place in a week at one atmosphere pressure; whereas the same grain size material produces an equivalent amount of reaction overnight when sealed in evacuated vials. However, the slowness of the reaction rate in the unsealed vials may be in part due to the presence of oxygen which substitutes for sulfur in the lattice sites and decreases the diffusion rate within the structure (Hannay, 1959, p. 281). Grain size has little influence on those components which become liquid before reaction occurs.

The extremely fine grain size, which is important in obtaining homogeneity of the constituents, presents several specific problems. A decreasing accuracy of chemical composition is caused by increased weighing and transfer losses, especially with elements which develop a static charge which causes adherence to weighing instruments, vials, etc. These difficulties may be eliminated by weighing the constituents directly into the vials; however, the problem of removing portions of the constituents which adhere to the walls of the vial still remains. Care must be exercised to prevent these particles from being removed from the vial during the sealing of the vial.

Difficulty is also encountered in evacuating vials since trapped air pockets expel constituents by their rapid escape. This problem can be alleviated to some extent by including an adjustable air bleed to allow gradual application of the vacuum or by placing a relatively large container in the vacuum line. This container may also be used as a trap to prevent foreign particles from entering the pump. Tightly packed glass fiber may also be used between the vial and the pump to act as a trap and to allow gradual application of the vacuum. An electromagnetic or ultrasonic vibrator coupled to the vial is also helpful in preventing air pocket "explosions" during pumping.

Compaction of the constituents is desirable if glass rods are inserted into the vials before sealing to reduce the volume of the vapor space. However, incomplete compaction is less desirable than a loosely packed mixture because the escape of the air pockets through partially compacted material becomes violent during pumping.

The study of inversions of previously synthesized or naturally occurring minerals may be enhanced by the use of a single grain of material to avoid the effects of multiple nucleation of the transition.

Fine grain size is important because the heating rate limits the time available to attain equilibrium during any specific temperature interval. Thus the state of division of the constituents is more important in D.T.P.

than in fixed temperature equilibrium studies. Effects such as mobility of reacting ions; the chemical gradient toward reaction as a function of the relative chemical activity of the constituents; or the tendency of the reactants to form partial reaction barriers around the individual grains, must be evaluated in relation to grain size.

Partial reaction products, which may occur at grain boundary interfaces and tend to prevent further reaction, depend in many respects upon the physical characteristics of the reaction product and of the host grain. The tenacity, porosity, relative thermal coefficient of expansion of the host and its rim, film adherence between rim and host, and the ductility of the film affect the duration of the reaction rim as the temperature increases. The ductility of the film, in a large measure, determines the tolerance of a relatively large difference in thermal expansion properties of the film and host before rupture occurs allowing further reaction.

The effect of reaction rim or barrier development may be observed in Figure 5. Here, and in other compounds, reaction rim development tends to break down in a stepwise manner as the temperature increases. The composition range from CuS to Cu_2S was made with coarse grains of copper and sulfur to eliminate weighing and transfer losses and to provide as much accuracy in chemical composition as possible. Some combination occurred during sealing and storage of the vials before heating; also, the time during which constituents were in contact was not controlled as the dissociation and melting relations were of major interest in this experiment. The series was synthesized, starting with the CuS end where a major development of exothermic peaks is shown accompanied by the endothermic melting of sulfur at 115° C. The decrease in intensity of these peaks is a function of the time the constituents were in contact, as all vials were sealed at the same time. The similarity of the stepwise exothermic peaks indicates that a characteristic development of reaction rim breakdown occurs. Analysis of this appears feasible under controlled conditions of sample preparation.

Limited conclusions concerning some of the reactions indicated by Fig. 5 appear justified. The endothermic peak at 505° C. is the incongruent melting point of covellite to digenite+liquid+vapor, which as determined by Kullerud (1956) occurs at $507° \pm 3°$ C. at about 880 mm. Hg pressure. The temperatures obtained by D.T.P. are within the limits of error of reading the temperature scale and thermocouple variations ($\pm 5°$ C.). The magnitude of the endothermic peak decreases toward extinction at a composition of $Cu_{1.8}S$, which is the composition of digenite. The decrease results as less and less covellite becomes present. The temperature of the reaction is constant up to a copper to sulfur ratio of 1.6:1, which indicates that the volume of the vapor space in the vials is such that liquid sulfur is always present at this temperature. The reac-

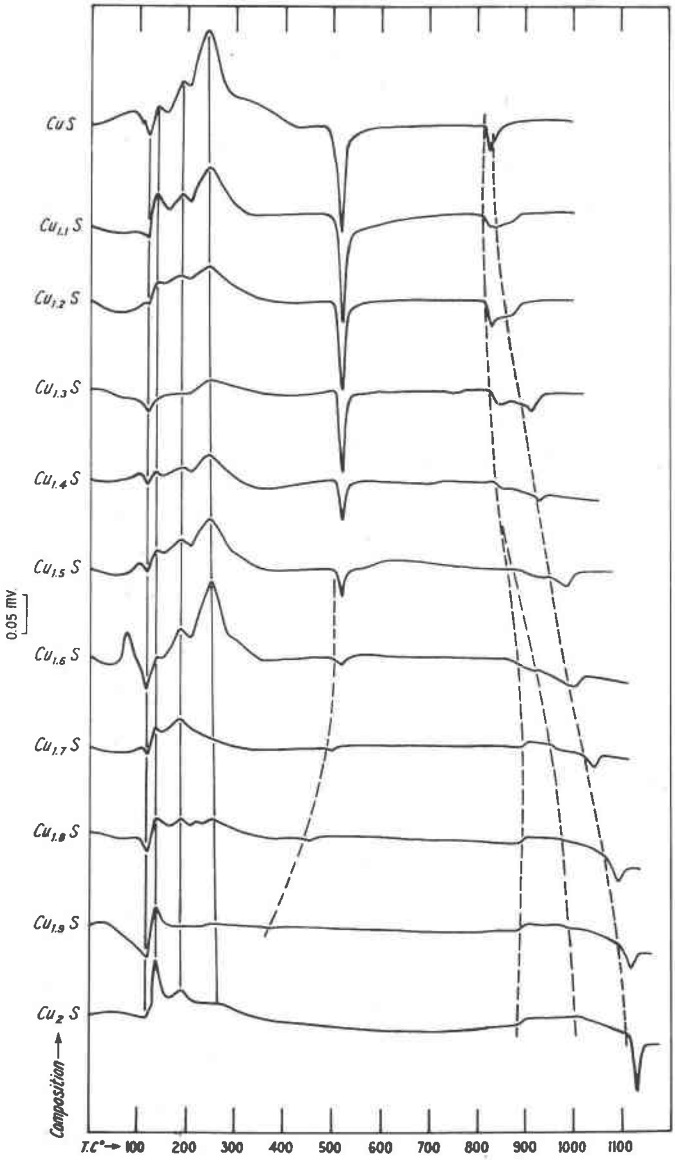

FIG. 5. Pyrosynthesis curves for the system CuS-Cu_2S.

tion is observable to a copper to sulfur ratio of 1.9:1. The peaks at the composition of $Cu_{1.8}S$ and the copper to sulfur ratio of 1.9:1 are attributed to non-equilibrium formation of a small amount of covellite during synthesis. The decrease in the temperature of dissociation from the copper to sulfur ratios of 1.6:1 to 1.9:1 graphically demonstrates that the vapor pressure was less than that over liquid sulfur, and that the effects of changes of sulfur pressure within the vials are observable.

The dissociation of covellite to digenite+sulfur at vapor pressures less than that of liquid sulfur is extremely sensitive to bulk composition and the relative proportions of covellite, digenite, and chalcocite which may be formed during synthesis under non-equilibrium conditions. Factors such as grain size, degree of homogenization of the sample during mixing, partial reaction during sealing and storage, and the heating rate all contribute to the degree of equilibrium attained during analysis. Therefore, these peaks are non-reproducible from sample to sample and the smooth curve drawn through the peaks in Fig. 5 from $Cu_{1.6}S$ to $Cu_{1.9}S$ merely indicates that the majority of the steps in the sample preparation of this series were closely controlled.

Exothermic peaks of copper and sulfur using extremely finely divided constituents, not mixed until immediately before heating, show an abrupt single peak immediately following the melting of sulfur. The copper used in this case was electrolytic dust. The exothermic peak using this material appears much like the exothermic peak of Cu_2S in Fig. 12. The electrolytic dust has not been used in composition dependent reactions because of the difficulty experienced in removing it from weighing instruments, vial walls, etc.

Each of the previously mentioned factors of reaction rim development may become significant under special circumstances of chemical composition, but in other compositions may be of little consequence. The precise interpretation of the range and significance of each of these factors has not been attempted. However, in the detailed study of a particular system the effect of non-equilibrium reaction rim development must be considered and procedures to minimize its occurrence should be evaluated.

In some systems, the formation of reaction rims, with the attendant suppression of a reaction at the true initial temperature of combination, may be a source of trouble in fixed temperature equilibrium studies. Where a reaction rim develops which is thermally and chemically metastable, repeated grinding and reheating may be necessary to achieve complete reaction. Such repeated handling increases the possibility of changing bulk composition.

In numerous studies of the formation of double sulfides, difficulty has been encountered in achieving the reaction of the second molecule of sulfur with the cation. This has caused some investigators to form the monosulfide by reaction for long periods of time with repeated grinding and reheating. The disulfide is usually formed by adding sulfur in excess, and reheating. The present study has encountered little difficulty in the synthesis of disulfides directly, using stoichiometric bulk compositions, and avoids the above procedure by using fine-grained, well mixed, non-oxidized elemental constituents. It is believed that many of the obstacles in difficult syntheses may be eliminated by thorough precautions to eliminate substitution of oxygen in the sulfur lattice sites. Some reaction rims may be dissipated more readily by a cyclic temperature program rather than fixed temperature equilibria programs by differential expansion and contraction of the reaction rim and unreacted material.

Extremely pure metals may now be obtained in the form of refined rods intended for use in the semi-conductor industry. The synthesis of compounds from these highly purified materials is highly desirable if precision determination of any parameter is contemplated. The reduction of these materials to a fine grain size without contamination is readily achieved by the method described by Van der Lann and Nicholls (1960). A spray of molten metal from a nozzle is forced into a free falling column under the pressure of nitrogen or hydrogen gas. Relatively perfect spheres of 10 to 100 microns in diameter may be formed by this method. The possibility of rapid oxidation of these fine-grained materials may be overcome if the free falling column is constructed so that the metal freezes in an oxygen free atmosphere derived from the nozzle. The materials should be immediately transferred to, and held in, evacuated vials until used. The original apparatus was constructed of metal, limiting its use to low melting point metals. The apparatus may be readily adapted to higher temperatures by cementing nozzles and gas lines of fused quartz to the rod of metal with ceramic cement and enclosing the assembly in castible ceramic. This procedure also reduces possible contamination from metallic parts of the apparatus.

Effect of Heating Rate

The heating rate has a pronounced effect upon the thermal curve. The intensity of the peaks is altered and the temperature at which the reactions occur is affected by a rate change. Two examples were used to show their relative effect upon the D.T.P. curves. The compositions FeS to FeS_2 first were synthesized in ten per cent mol increments at the standard D.T.A. rate of 12.5° C. per minute, and then at a continuous furnace input which yielded a semi-linear heating rate of approximately 28° C. per minute. The family of curves for the slower heating rate is shown in Fig. 6. The faster heating rate curve is as reproducible as the slower heating rate curve and the comparison of the two heating rates for the bulk composition $FeS_{1.5}$ (Fig. 7) is valid for all compositions of both heating rates. The faster heating rate curve shows an increase in resolution above

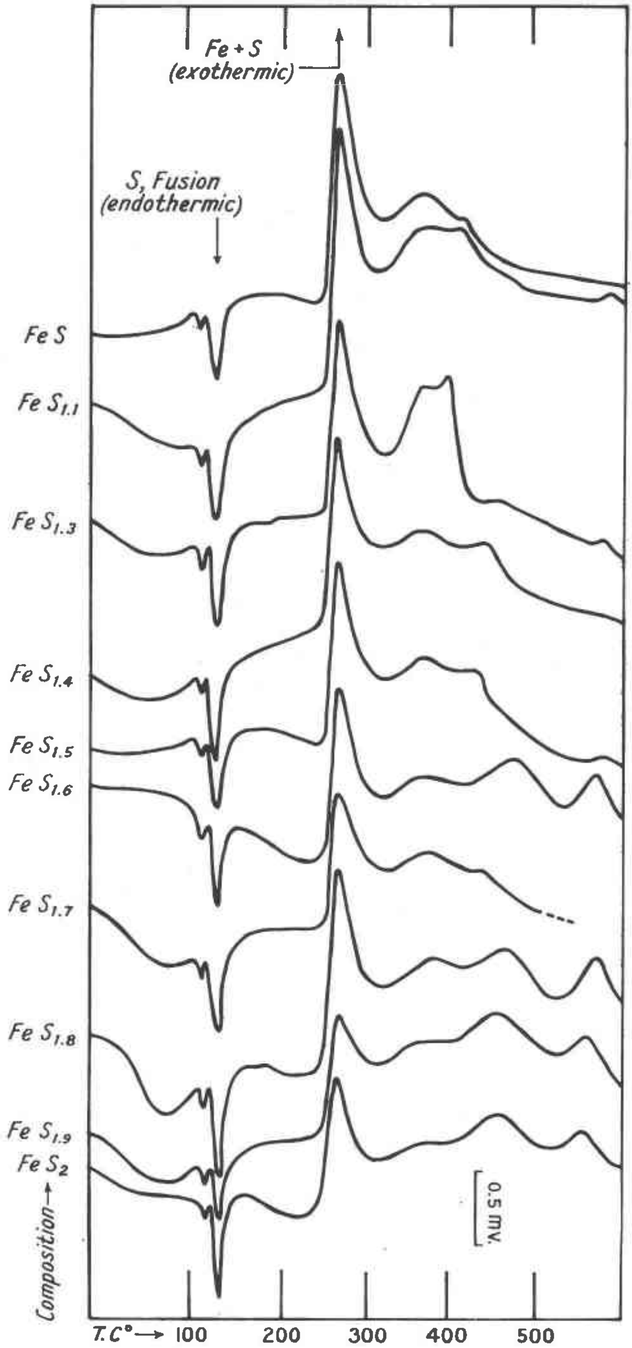

FIG. 6. Pyrosynthesis curves for the system FeS-FeS_2.

275° C. where a single broad peak in the slower heating rate curve is resolved into three distinct peaks. The intensity of the peaks is not only increased, but also the deflection at the initial point is considerably sharper, The possibility exists that the three peaks represent a rapid removal of reaction rims which are gradually broken down in the broad peak of the slower heating rate curve.

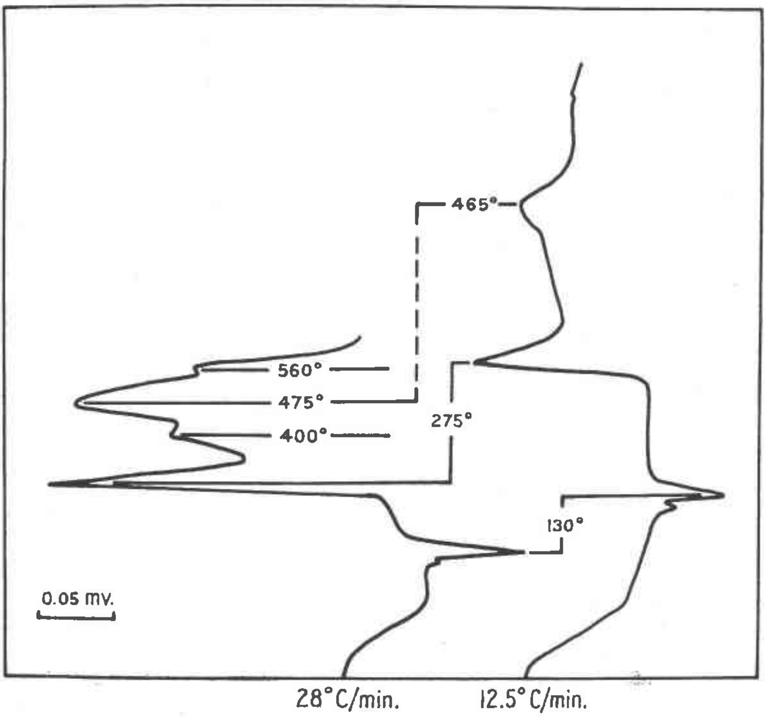

Fig. 7. Change in configuration of pyrosynthesis curves of $FeS_{1.5}$ with differing heating rates.

High heating rates yield an increased intensity of temperature dependent reactions, and are most likely to produce temperature differentials within the samples, cause an upscale shift of true reaction temperatures, and a compression of the temperature scale reducing accuracy. Kingery (1959, p. 284) also points out the existence of " . . . nonequilibrium temperature indications for phase changes, such as undercooling or possible complete suppression of solid state transformations." High heating rates also impose stringent requirements upon furnace capacity and furnace insulation. They also require a small thermal head, which in turn reduces reproducibility and increases base line drift. A higher rate of sealed vial failure occurs with the faster heating rate which may be caused by the thermal shock or the increased rate of pressure produced within the vials because of faster reactions. However, the heating rate of 28° C. per minute is of interest in a preliminary study of a system or in the study of decompositions and similar rate dependent reactions which tend to be broad and undifferentiated from the base line when slower heating rates are used.

A slow heating rate, in the range of 0.5° to 5° C. per minute, is preferable for the study of liquidus-solidus relations and with powdered samples to increase the precision of temperature determination. The slow rates are necessary in the study of some samples to prevent the overlap of two successive peaks (Fig. 5) for nonequilibrium conditions, such as undercooling or the suppression of solid state reactions.

A heating rate of 12.5° C. per minute is used, unless otherwise indicated, since it represents a compromise which has been standardized in D.T.A. as giving the most adequate resolution of all differing types of reactions for a single heating rate and is available in most laboratories engaged in thermal analysis.

The use of a wide range of heating and cooling rates is mandatory if all types of reactions which are observable by the instrumentation are to be analyzed. The optimum heating or cooling rate for a specific reaction in a specific system can be recommended only if the kinetics of the reaction are known. As this type of information is usually not available, experimental variation of the heating rate is the best solution to the problem. In many studies it is of extreme importance to determine if a reaction rate is sufficiently high to allow attainment of equilibrium under dynamic conditions of observation. The degree to which the thermal curves are affected by various heating rates gives considerable information toward this end, and in many cases it is necessary to ascertain these effects in order to allow the correct emphasis to be placed upon the results obtained.

Optimum resolution of the thermal curves for different types of reactions depends to a considerable degree on different heating or cooling rates. High-low displacive transformations tend to be rapid and may be studied at high heating rates. Reconstructive transformations involving the breaking of chemical bonds, and structural rearrangement or diffusion are generally sluggish and require slow heating rates if they are to be observed at all (Buerger, 1951, p. 189).

Similar reactions, such as liquidus-solidus relations, in differing types of materials may proceed at different rates. Bivariant transformations, such as the freezing of solid solutions may result in a shift of the base line rather than a distinct peak. Univariant equilibria, such as the freezing of a eutectic, are isothermal and are therefore not as rate dependent as other liquidus-solidus relations. Hypo- and hyper-eutectic alloys yield curves that have intermediate characteristics of the solid-solution and eutectic type curves. Peritectic alloys produce a sharp deflection of the thermal curve with a gradual return to the base line. Undercooling is usually more pronounced in eutectoid transformations than in eutectic or monotectic reactions and tends to be even more pronounced in peritectic transformations. These reactions and thermal characteristics are described in detail by Rines (1956). Even greater variance in the liquidus-solidus relations is found when comparing metals and alloys to intermetallics and especially to silicates.

The physical state of the material under observation further affects the kinetics of the reaction. Whether the material is in a single crystal, polycrystalline, or in powdered form influences the rate at which equilibrium is attained; thereby necessitating adjustment of the heating rate for proper observations.

Non-equilibration shifts of the true temperature of reaction may be compensated for to some extent by approaching the reaction from both directions, heating and cooling. The observed range in the temperature between the liquidus and the solidus, minimizing the influences of undercooling and overheating can be narrowed by slow heating rates. The magnitude of undercooling and overheating can be estimated by the use of different heating rates in observing these phenomena.

Reactions which change the thermal conductivity or the heat capacity of the sample may be observed by shifts in the base line of the thermal curve, although a distinct peak is not produced. In such reactions the heating rate is important if the reaction is to be observed. The differences in thermal conductivity and heat capacity between the sample and the reference largely regulate the drift of the base line for any specific heating rate. This is especially true if the thermal distribution of the head and the symmetry of the head and furnace are not perfect. A combination of different heating rates, reference materials, and deliberate slight misalignment of the head and furnace can be used to enhance the observation of these reactions.

In addition to the variation of the heating or cooling rates to emphasize a specific reaction, it is necessary to employ extremely non-linear heating programs for some reactions. In determination of some solidus temperatures it is important to equilibrate the sample for long periods of time just below the melting point. In determination of the liquidus of viscous melts it is also necessary to equilibrate just above the freezing point.

Effect of Thermal Head Design

The thermal head design is predicated upon an exact symmetry of disruption of heat flow in the head by the placement of the thermal wells. The dimensions of the head do not appear to be critical if symmetry is maintained. Modifications in the head size depend upon: the size of the furnace available; heat input available; smoothness of program control action; size of sample vials to be enclosed; and the magnitude of the peaks necessary for a particular problem under investigation.

The apparent simplicity of the thermal head is somewhat misleading. Several factors enter into the design which are not obvious and exert a profound influence upon the data obtained.

Examination of the influences on head design has indicated that the original head design (Fig. 1) is not optimum for the complete range of D.T.P. investigations. However, as the design produces a maximum uniformity of results, it has been retained for the remainder of the investigation as a major change would invalidate continuity of the analysis. As a general survey type of head, certain practical advantages are inherent which allow a rather wide margin of control of several parameters without severe distortion of the D.T.P. curves.

The major thermal requirement of optimum head size is a head with sufficient thermal mass to equalize differences in temperature distribution from the furnace windings, and with small enough thermal mass to minimize absorption of temperature differences produced by reaction within the vials. A head with sufficient mass to completely equalize temperature differences within the furnace tends to suppress the magnitude of the reactions and smooth abrupt step-functions of heat change produced in the sample if the thermal conductivity between the sample vial and the thermal head is high. The design (Fig. 1) used in the present study provides a high thermally conductive metal head to smooth out temperature gradients, and a partial barrier of aluminum oxide of much lower thermal conductivity between the sample vial and the head, to reduce dissipation of the heat of reaction in the head.

The decrease in the amplitude of the peaks, by dissipation of heat to the head, may be balanced by preamplifier gain because of the reduced base line offset produced by a high conductive head. However, this procedure is to be avoided because rapid reactions are appreciably broadened, and the curves approach a function which represents a characteristic of the heat capacity of the head rather than of the reaction which is produced in the sample. The initial reaction point becomes a broad gentle

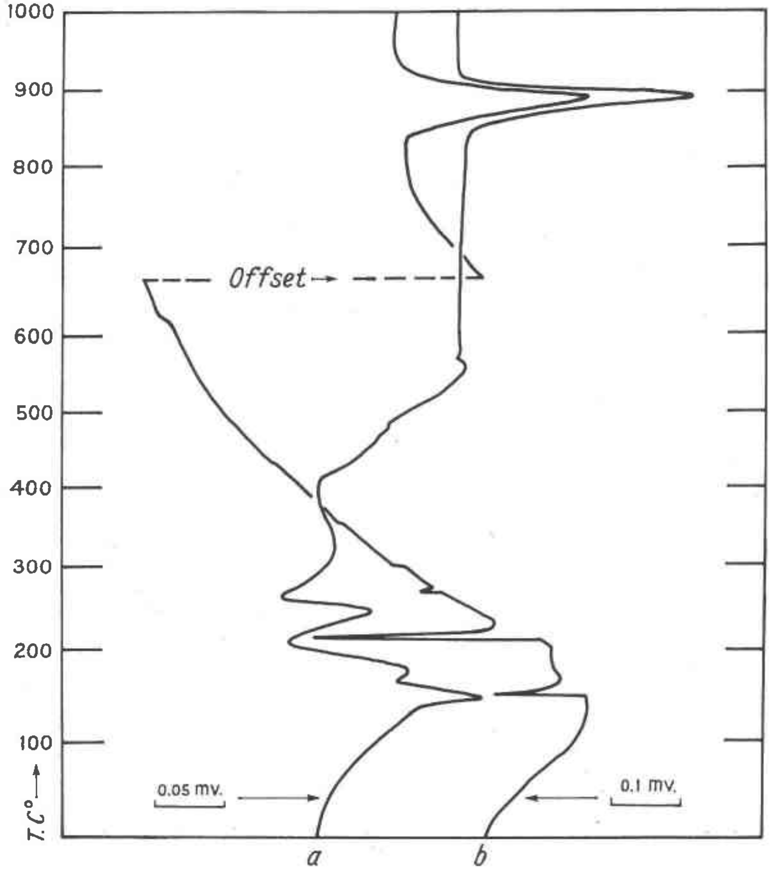

FIG. 8. Pyrosynthesis curves for $CuFeS_2$ (chalcopyrite) showing change in configuration of curves using thermal heads with differing heat capacities: (a) metal head; (b) ceramic head.

slope and not an abrupt deviation from the base line. This results in decreased accuracy of data and has been one of the major factors in the nonreproducibility between differing types of thermal heads in D.T.A. investigations.

The differences produced with a change in the head material are illustrated in Fig. 8, which shows the nature of the reactions produced by the composition $Cu+Fe+S_2$. Figure 8*a* is the normal head used throughout the investigation, and Fig. 8*b* is the ceramic head shown in Fig. 9. The points of initial reaction are not only distinctly resolved in curve 8*b*, but it is also evident that endothermic reactions do not occur on either side of the exothermic peak at approximately 200° C. The differences in the apparent initial temperature of the exothermic reactions are ascribable to reaction development and differences in sample preparation.

In some respects, however, the ceramic head is not as sensitive to small reactions as the metal head. The lowered preamplification necessitated by the increased base line drift is responsible for this loss in sensitivity. The inversion at approximately 565° C. in Fig. 8*a* does not appear on the curve produced by the ceramic head. Thus it becomes apparent, as in the case of variation of heating rates, that different types of reactions are best investigated by thermal heads with differing heat capacities and equalizing characteristics.

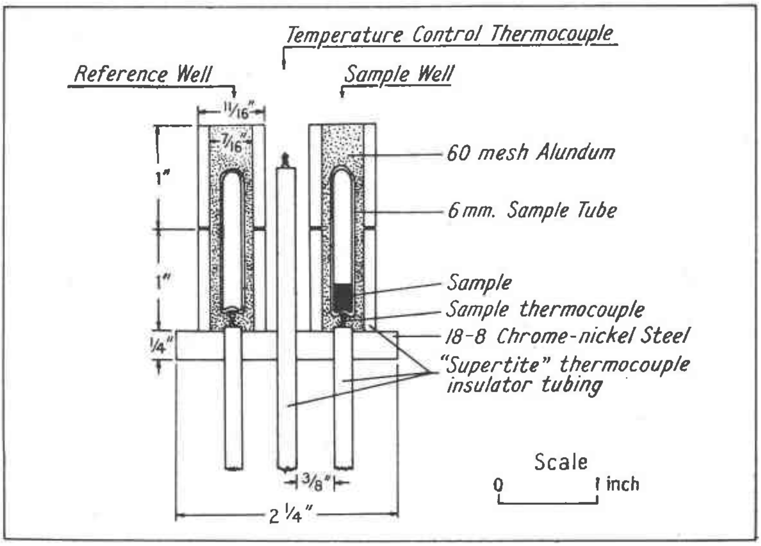

FIG. 9. Cross-section of low thermal mass ceramic head.

Ceramic heads have been considered unsatisfactory by many workers. Kingery (1959, p. 258) states: "Because of its lower thermal conductivity the ceramic holder gives increased sensitivity, but results are less reproducible than with a high thermal conductivity metal block which is preferred." As indicated from the previous discussion, this statement may be modified. A more accurate evaluation of the low thermal conductivity head would be that reactions greater than the threshold limitation imposed by base line drift result in greater sensitivity not only in amplitude of the peaks, but also in increased sensitivity to variations in technique. The high thermal conductivity head tends to make all reactions greater than a certain threshold value, assume the characteristics of the head, which is a fixed quantity. Thus reproducibility appears to be better. Too great a reproducibility is a reflection of the inability to respond to small differences in reactions. Unavoidable differences in sample preparation and technique require a certain amount of non-reproducibility. Complete reproducibility indicates that the instrumentation lacks resolution. Ceramic heads clearly require a much higher order of precision of technique, fabrication, and alignment than metal heads.

The head design in Fig. 1 may be considered to be a composite metal and ceramic head. The alundum filling of the metal thermal wells constitutes the ceramic portion of the head. Characteristics approaching either a metal head or a ceramic head may be achieved by a variation in the diameter of the thermal well. Even greater variation is possible in the head shown in Fig. 9 by replacing the ceramic tubing which forms the thermal wells with stainless steel tubing. The tube wall thickness and diameter may be modified to produce a head with thermal characteristics which are suitable for nearly any type of reaction.

The effect of the thermal mass of the head may be indicated by a series of sample volumes in increments of 0.05 cc of ZnS in a fixed vial length of 1.5 inches. The series was produced to analyze the effect of sample volume on the initial temperature of reaction. Reaction temperatures were identical, and five volumes of ZnS produced only slightly greater amplitude of peak height than a single volume. The thermal head was evidently absorbing the extra heat of reaction produced by the increase of material in the vial. The thermal wells in the present head design are therefore too close to the sample vial for the total amount of heat produced in the sample to be recorded by the thermocouple. The optimum ratio of sample vial diameter to thermal well diameter has not been determined. As a general rule, to reduce excessive heat of reaction dissipation in the thermal head, the distance from any point on the sample to the thermocouple junction should be less than the distance to the thermal head.

Thermocouple Lead Wires

Considerable concern about the dissipation of the heat of reaction by the thermocouple lead wires has been shown by workers in D.T.A. Kingery (1959, p. 259) indicates that total heat dissipation may amount to 75 to 80 per cent for practical configurations. However, if the thermal relations are considered in a normal D.T.A. head, the greatest amount of of heat is dissipated where the walls of the thermal wells are in direct contact with the sample. Since the thermal masses of the thermocouple lead wires are nearly insignificant in comparison to the thermal mass of the head, the amount of heat dissipated in the head is proportionately much greater. The amount of reacting materials in contact with the thermal head is a fixed quantity which does not lend itself to systematic study without changing the head. This usually reduces reproducibility to such an extent that the factor may not be analyzed statistically. Materials such as powdered clay mineral usually studied by D.T.A. are such poor thermal conductors that the reaction of the portion of the sample in contact with the thermal wells is not recorded. The portion of the charge which is recorded is that part immediately surrounding the thermocouple itself.

The lead wires may be considered an extension of the thermal head and, since only the minor portion of the charge in contact with the thermocouple is recorded, this effect is multiplied to such an extent that the assumption of a 75 to 80 per cent loss ascribed to thermocouple wires is understandable. Thus it becomes apparent that the thermal efficiency of the head used in D.T.P., with a single point contact of the thermocouple with the sample, may be nearly equal to standard D.T.A. configurations.

In effect, the standard D.T.A. sample forms its own heat barrier to the dissipation in the thermal wells by poor thermal conductivity. Factors such as sample packing assume magnitudes of importance well beyond their actual validity. The thermal barrier formed by the sample is highly susceptible to a large range in thermal conductivity and is modified greatly by packing and composition of each sample analyzed. The analysis of this problem is beyond the scope of this investigation, but a standardized method of packing normal D.T.A. and corrosive D.T.A. samples is being described separately, which incorporates the alundum heat barrier used in D.T.P. heads (Bollin and Kerr, 1961).

The effect of loss of the heat of reaction by thermocouple wires and their insulator tubes in the D.T.P. arrangement may be illustrated by Fig. 10, which shows the difference in curves obtained by a relatively small change in the path length from the thermocouple junction to the head. The initial deflection of the exothermic reaction of Fe+S at approximately 240° C. is rounded to such an extent by the extra heat capacity of the $\frac{1}{8}$ inch path length that an estimate of initial temperature of reaction is only approximate. The higher temperature portion of the curve, showing the reaction of the additional sulfur to form pyrrhotite +pyrite is similarly of little value. The short path length from the thermocouple junction to the head allows a substantial amount of the heat of reaction to be transferred to the head increasing the heat capacity of the assembly.

The thermal path from the thermocouple junction to the head may be disrupted to a considerable degree by the following factors: (1) the use of thermocouple insulator tubing with a bore considerably larger than the wires, permitting as little physical contact as possible; (2) increase in the

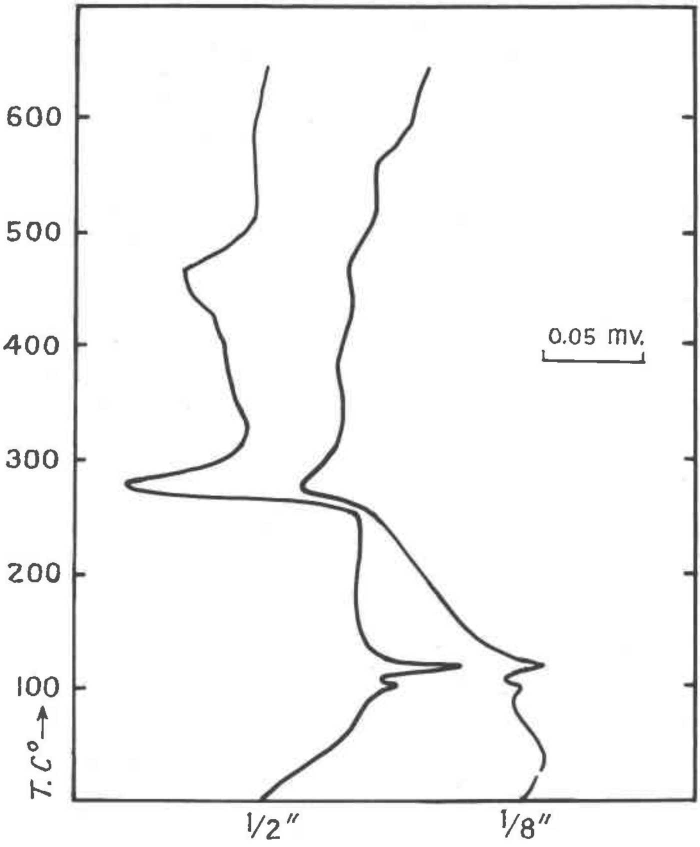

FIG. 10. Spacing of thermocouple from bottom of thermal well. Pyrosynthesis curves showing relative effect of differing path lengths from thermocouple junction to thermal head for the composition $FeS_{1.5}$.

outside diameter of the thermocouple insulator tube to make the radial path length from the wire to the head as great as possible in the low conductivity ceramic, or the use of a second ring of ceramic at the point of contact between the insulator and head, allowing the use of small insulator tubing; (3) reduction of the wire diameter to the lowest dimension compatible with optimum thermocouple life; (4) increase of the distance from the thermocouple junction to the metal head by a deeper thermal well; (5) increase in depth of the thermal well to obtain a minimum amount of metal to support the thermocouple insulator tubing; (6) the use of four hole insulator tubing to reduce the amount of ceramic in the tube.

The thermocouple insulator tubes may be prepared by casting a ring of ceramic* around the tube the same size as the diameter of the thermal well. The thermal well is then drilled completely through the head at a single diameter further increasing the low conductivity thermal path to the head. The casting of the tube and the ceramic ring is then cemented into the bottom of the thermal well.

Effect of Volume of Sample Vials

Many reactions observable in D.T.P. are dependent upon the vapor pressure of the anion. The volume of the sample, the volume of the sample vial, the composition of the reactants, and the temperature are effective in determining whether the internal pressure within the vials is equal to that over liquid sulfur, or equal to some lesser pressure, thereby causing differences in the observed reactions. If thermodynamic extrapolations are to be made of the data obtained by D.T.P. it is necessary to determine, within limits, the pressure effects upon the reactions.

The majority of the reactions in D.T.P., those below approximately 500° C., are little affected by the range of sample vial volume permissible in the present head design. Two factors are responsible for this. Sulfur has a relatively low vapor pressure at these temperatures, and the dissociation pressure of many sulfides is less than that of sulfur vapor in equilibrium with liquid sulfur at these temperatures. In this range of temperature, the low vapor pressure of sulfur readily allows the formation of a liquid phase which determines the pressure relations at any specific temperature, and the volume of the vial is not critical, within limits.

In compositions, where the ratio of sulfur to bulk composition is small so that negligible free sulfur is present, insufficient sulfur may be present to form a liquid phase. In these compositional ranges the effects of vapor pressure less than that over liquid sulfur are readily apparent, as in the lowered temperature of the dissociation of covellite in the Cu_2S end of the compositions in Figure 5.

In compositional ranges where sufficient sulfur is present to assure a liquid phase at 507° C., as shown by the constant temperature of the incongruent melting of covellite in the CuS end of the compositions of Fig. 5, it might be assumed that a liquid phase of sulfur is present at higher temperatures. However, the liquid-vapor curve as given by Kullerud and Yoder (1959, p. 541) shows an increasingly rapid rise in the pressure necessary to maintain a liquid phase above 600° C. Thus the pressure-volume relations become more critical as the temperature is increased.

The use of excess anion, such as sulfur to produce saturation vapor pressure within the system by the formation of a liquid phase, can be

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* Sur-Grade S-2, Castible Ceramic, Duramic Products Company, Palisades Park, New Jersey.

applied to end members of an anion substitution series of disulfides, or in the case where high sulfides do not exist, on monosulfides. Where anion substitution is a function of the composition, such a procedure is not possible, and the per cent equivalent of the partial pressures of the anions must be estimated.

The use of closely fitting glass rods to fill the space above the reactants is preferable to the alundum filling of the vials when pressure relations are studied.

A series of sample vials was prepared from one inch to two inches in length (Fig. 11) to determine the effect of vial volume on the dissociation, or incongruent melting, of FeS_2. A constant weight (0.2399 gms.) of elemental constituents of the composition FeS_2 occupied approximately one-half inch of each vial. The one inch vial (Fig. 11*a*) is too short to allow sealing without partial reaction by overheating of the constituents, and the two inch vial (Fig. 11*e*) extends beyond the top of the head. One of the normal length vials was filled with 120 mesh alundum to provide a minimum volume of the series (Fig. 11*d*).

The exothermic peaks of the above series below 600° C. show some variation which is primarily a result of non-equilibrium obtained at these heating rates as was indicated in Fig. 7. The large endothermic peak at 743° C. is the incongruent melting of pyrite to pyrrhotite+liquid+vapor (Kullerud and Yoder, 1959). No variation in peak temperature was observable. Thus it is assumed that liquid sulfur was present, determining the pressure relations at these temperatures.

An important feature is indicated by the data obtained from the above series. A gradual decrease in peak amplitude occurs with increasing vial volume, or, in other words, a decrease in the amount of alundum in the thermal well. If volume relations of the vial were responsible for this change, as would be the situation in the absence of liquid sulfur, the temperatures of dissociation would be affected as was the dissociation of covellite; within the limits imposed by the relative sensitivity of the dissociation pressures of CuS and FeS_2 to vapor pressure of sulfur. It is apparent that the heat flow from sample to the thermocouple junction is not restricted to the point of contact with the vial. The alundum envelope surrounding the vial and the thermocouple, as well as the walls of the vial, serve as heat transfer media. Thus the length of the sample vials should be closely controlled, thereby maintaining the same amount of alundum and silica in the thermal well, if peak areas or amplitudes are to be used for comparative data.

The decrease in the amplitude of the peaks in Figure 11 with increasing vial size may be caused by an increased heat capacity of the vial. As heat flow is in all directions from the reaction point, a certain amount of the

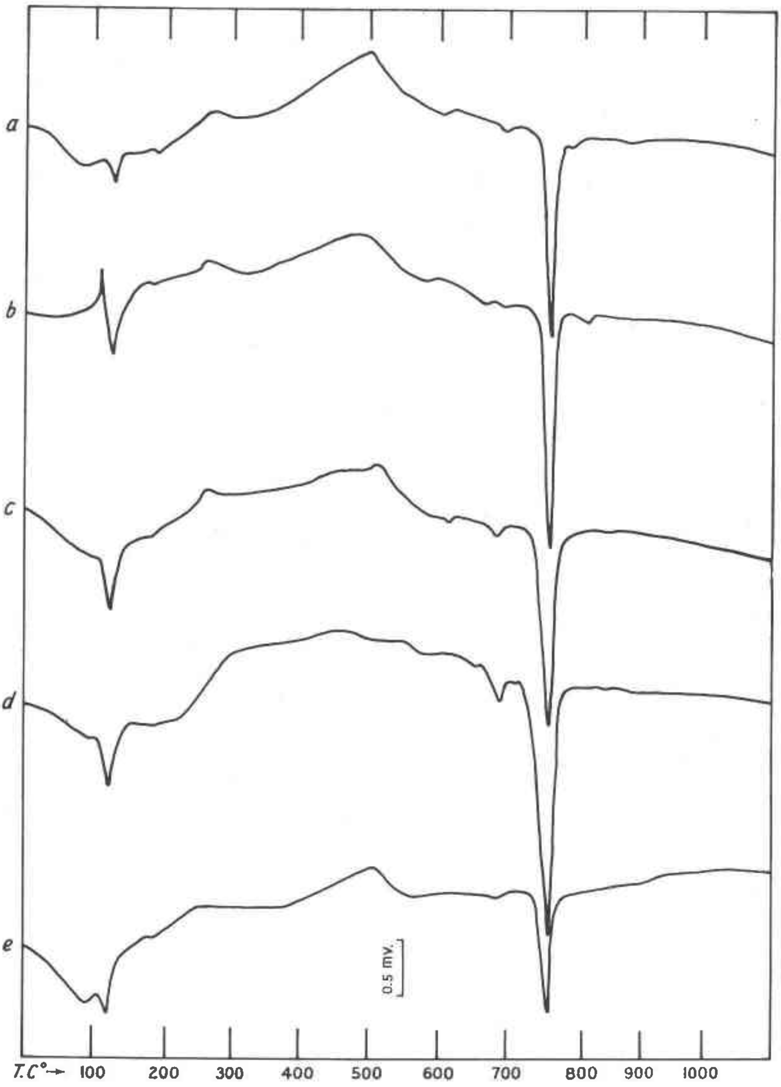

FIG. 11. Pyrosynthesis curves representing variation of sample vial length with constant weight of FeS_2. (a) 1 in. (b) 1¼ in. (c) 1½ in. (d) 1½ in. with Al_2O_3 filling empty portion of vial. (e) 2 in.

heat of reaction is carried to the upper part of the vial and is dissipated. The higher thermal conductivity of the vial, in comparison to the thermal conductivity of the granular aluminum oxide allows a greater part of the reaction to be carried away from the thermocouple with the larger vials.

The vial in Figure 11*d*, which is filled with alundum above the reactants, should transfer a greater portion of the reaction to the upper end of the vial and thus be dissipated. This is undoubtedly true; however, the short path length from the top of the reactants to the thermocouple allows more of the heat of reaction to be registered by the thermocouple than is dissipated at the top of the vial. In the absence of the alundum filler within the vial, the reaction of the top surface of the sample is not transferred effectively to the thermocouple or to the walls of the vial. The increase in the transfer of heat of reaction from the top of the sample, and the short path length to the thermocouple, more than compensate for the loss to the upper portion of the vial.

The relative heat flow distribution when silica rods are used to fill the vial has not been investigated; however it is believed that the rods would tend to transmit a greater portion of the reaction to the top of the vial because of the undisrupted flow along the rod. The disruption of the heat flow by the interface between the sides of the rod and the wall of the vial may also reduce the effectiveness of the short path length to the thermocouple. Thus the relative heat flow distribution would be greatly influenced by the closeness of fit between the rod and the vial. Loosely fitting rods should be avoided, and would be less preferable than an empty vial, as measurement of the heat of reaction is of more importance than pressure relations in a specific study.

The influence of volume-pressure relations in the higher temperature regions of Fig. 5 is complicated by multiple reactions and incomplete knowledge of the nature of the reactions. Early work on the Cu-S system (Allen and Lombard, 1917) assumed that covellite dissociated directly to chalcocite. Kullerud (1956) with the knowledge of the intermediate compound, digenite, from the work of Buerger (1942) recognized that the reaction was the dissociation of covellite to digenite and not chalcocite. Kullerud also stated, "Further experiments on the stability of this compound have shown that digenite, which decomposes to chalcocite and vapor, is stable up to about 925° C. in the presence of excess sulfur (liquid and vapor). . . , it is likely that the upper stability curve of digenite, similiar to the stability curves of covellite and pyrite, is very steep. Thus even under 30,000 psi of sulfur pressure, the breakdown temperature of digenite would probably not exceed 950° C. (1958, p. 217)." These statements refer to a digenite of a composition of $Cu_{1.8}S$ at these temperatures. The temperature at which digenite would dissociate to chalcocite under low vapor pressures of sulfur was not determined.

A tentative interpretation of the high temperature reactions shown in Fig. 5 may be attempted, although additional data would be necessary for complete evaluation. The unresolved double endothermic peak at approximately 815° C., at a composition of CuS may represent the incongruent melting of digenite and fusion of chalcocite. The upper peak of this pair rises to approximately 1105° C. and is explained by the data given by Kullerud and Yund (1960). At 815° C. a two liquid field appears in the system for compositions ranging from about 25.5 to more than 95.5 weight per cent sulfur. The maximum melting point of chalcocite at 1129° C., which occurs at a composition of $Cu_{1.989}S$ (Jensen, 1947, p. 9) is not shown in Fig. 5 as this composition is straddled by the sample compositions.

The lower peak of the above mentioned pair appears to split into two branches at a copper to sulfur ratio of 1.5:1. These are not well resolved because of a non-optimum heating rate. The lower part of these two branches may represent the dissociation of digenite as it appears to decrease in temperature toward the CuS end of the compositions. This would be the expected direction if the dissociation of digenite is affected by low vapor pressures of sulfur in a manner similar to the dissociation of covellite to digenite. The upper curve of these two branches may represent the change in the composition of the solid phase with incongruent melting to a digenite approaching the composition of chalcocite.

To investigate the effects of the vapor pressure of sulfur on the reactions a continuously evacuated vial was analyzed. In this procedure, previously synthesized covellite was placed in a vial six inches long which was not sealed. The thermal head was moved upward in the furnace allowing attachment of a vacuum line. The vacuum pump was operated continuously during the run. Sulfur vapor, evolved during dissociation, moved to the cooler portion of the vial extending out of the furnace and condensed. The melting point under vacuum had an initial deflection of 1130° C. This is in agreement with the melting point obtained by Posnjak, Allen and Merwin (1915) under similar conditions. Jensen (1947, p. 10) has indicated that their analyses of products with this melting point agrees with the maximum melting point composition, $Cu_{1.989}S$, and that the dissociation of digenite under vacuum conditions does not proceed beyond this composition. Similarly he indicates that the melting point of pure Cu_2S begins at 1107° C. and is not completed until 1127° C. which may be interpreted as the breakdown of Cu_2S on melting in a melt which is richer in copper and a solid which is richer in sulfur, or in other words, the final product approaches the maximum melting point composition, $Cu_{1.989}S$ from both sides of this composition.

In view of the complicated reactions in this portion of the temperature and composition range the recorded reactions in the upper part of Fig. 5 serve to indicate the complexity of the problem rather than to clarify the relations. Optimum heating rates, closely controlled volume relations, fixed temperature equilibirum studies, and high temperature *x*-ray diffraction studies are necessary to completely define the reactions in this portion of the figure. Further analysis was not attempted, as the purpose of the explanation of Fig. 5 is to attempt to show the use of the curves obtained by the instrumentation and not to define the system Cu-S.

The series CuS to CuSe and Ag_2S to Ag_2Se both show linear changes in fusion and upper dissociation temperatures from one end of each series to the other. This may be partially an effect of pressure and partially an effect of composition. The lower temperature dissociation, or incongruent melting, peaks of these two series also show a linear change from one end of each series to the other, in contrast to the nearly fixed temperature of incongruent melting of covellite to digenite in the range CuS to $Cu_{1.8}S$. By analogy with the composition range from $Cu_{1.6}S$ to $Cu_{1.9}S$ which shows a marked decrease in the temperature of this reaction with lowered pressure of sulfur vapor, the change in the temperatures of these incongruent melting points with the substitution of selenium for sulfur is mainly a function of the pressure change produced by the different proportions of the partial pressures of sulfur and selenium. Analyses of these three systems is not complete, and assumptions made are to be considered approximate until further data are collected.

Survey of Minerals

A number of sulfides, selenides, tellurides, arsenides, and antimonides have been produced to determine the range of the D.T.P. method in the synthesis of these minerals. A number of the curves resulting from these syntheses are reproduced in Fig. 12. Each curve is worthy of more detailed investigation than has been possible in the present study. Each synthesis properly requires such investigation to assure that parameters affecting peak configuration have been minimized and closely controlled. However, a general survey of the type attempted is a necessary prelude to the more detailed studies which should follow.

X-ray diffraction of the final products has shown that nearly all syntheses were successful. Inversions below the formation temperatures of synthetic minerals are observable in cooling curves and in reheating curves of previously formed synthetics. The instrumentation is also readily adaptable to the study of naturally occurring minerals.

The cooling curves of recombination of dissociated phases were somewhat unexpected. The recombinations, in nearly every case, were as rapid and sharply defined as the dissociation peaks. These rapid recombinations occur in decomposed phases that have been fused and recrystallized. The anion vapor, trapped in the vial during dissociation diffuses through the solid regulus in a very rapid manner upon cooling.

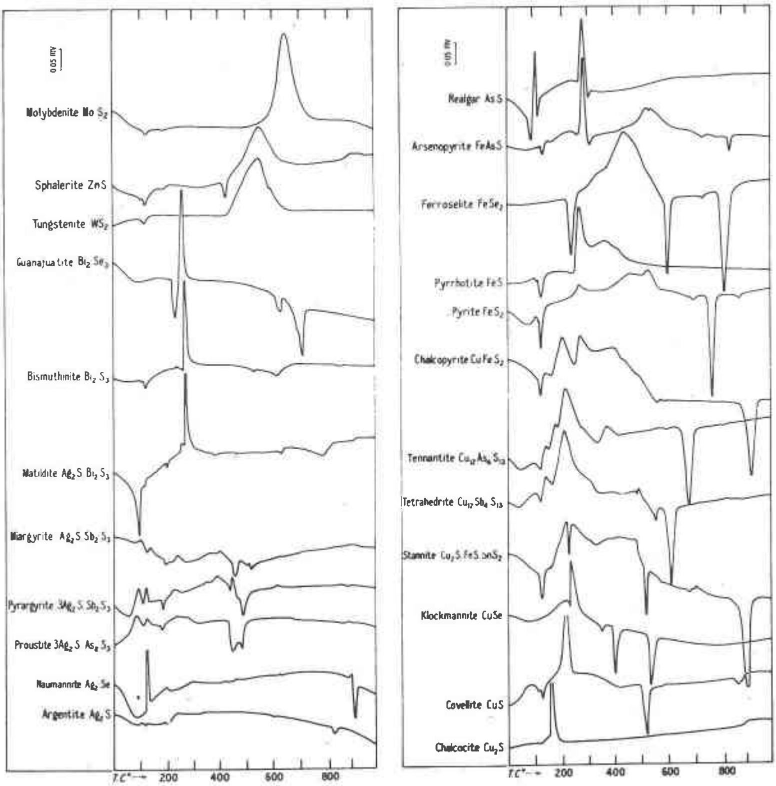

FIG. 12. Pyrosynthesis curves showing a survey of 23 minerals.

Cooling curves of powdered material that has been heated above the decomposition temperature, but not to the melting point, have not been studied yet. Comparison of the recombination of powdered material with fused material may give indications of the relative rate of diffusion of the liquid and vapor. However, the rapidity of the recombinations observed at 12.5° C. per minute indicates that the limiting factor is the slow rate of cooling and not the time required for diffusion through the crystal structure. It must be noted, however, that the diffusion under discussion has a considerable chemical gradient caused by the undersaturated, dissociated structures with a very high percentage of vacant lattice sites. The rate of recombination of some of the dissociated phases caused difficulty in quenching studies as many of the high temperature phases could not be quenched rapidly enough to prevent considerable recombination even when vials were dropped into water from temperatures far in excess of the dissociation temperature.

CONCLUSIONS

This study has shown that the instrumentation used for D.T.P. is able to furnish sensitive thermal data on processes which tend to give off or absorb heat during mineral synthesis and mineral stability studies. These processes include chemical combination, crystallization, dissociation, fusion, and inversion of one structure to another. The range of the method is large and it is readily adaptable to studies of differing types of reactions. The conflicting requirements of dissimilar reactions indicate that a rigid standardization of the technique is not justifiable; and that each system under study presents problems which somewhat alter the requirements of the instrumentation.

Data obtained from D.T.P. are in many cases directly applicable to a better understanding of processes which occur in the deposition of sulfide and mineralogically related ore bodies. It is believed that studies in the non-aqueous environment of D.T.P. and other "dry" studies can furnish much useful information in the study of mineral genesis and, when combined with hydrothermal methods, give a clearer understanding of the possible range of mineral deposit formation.

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