

case of CdS and CdSe but they do not specify which of their three methods were used with the other crystals.

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APPARATUS FOR CONTROLLED-ATMOSPHERE DIFFERENTIAL
THERMAL ANALYSIS OF CORROSIVE MATERIALS

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INTRODUCTION

While investigating the effects of regional metamorphism on sulfide minerals, the writer had occasion to design equipment with which to obtain differential thermal analyses of sulfide minerals in a controlled atmosphere. Although Stone (1952, 1954, 1960) has developed equipment for dynamic controlled-atmosphere differential thermal analysis, and Kopp and Kerr (1957) and Dunne and Kerr (1960) have devised equipment which enabled them to obtain differential thermal analyses of corrosive materials such as sulfides and arsenides in a non-dynamic system, there have been few differential thermal analyses of corrosive materials in continually-replenished atmospheres of controlled compositions. It is hoped that the following description of the equipment developed by the writer will be of some value to others engaged in differential thermal analysis work with corrosive compounds.

The writer's research was carried on at Stanford University under a National Science Foundation Postdoctoral Fellowship.

DESCRIPTION OF APPARATUS

Because of the corrosive effect of the sulfur gases on metals, both the sample block and the thermocouple beads were designed so no metal surfaces would be in contact with the internal atmosphere of the reaction chamber during a "run." The two cylindrical sample wells in the type 304 stainless steel sample block (Fig. 1) were lined with 97.6% alumina ceramic ("Wesgo AL-300") tubing which was internally tapered at both ends and cemented in place with alumina ("RA 1355 Alundum") cement. The thermocouple wells, which were cylindrical openings in the sides of

the sample block through which the two thermocouples were inserted into the sample wells, were likewise lined with 97.6% alumina ceramic tubing (see Fig. 1). The desired combination of gases for the reaction atmosphere entered the base of the sample wells through a pair of sillimanite ("Supertite") tubes (Fig. 2) which were attached to pyrex tubing outside the furnace with high-temperature epoxy resin. Gases produced by the studied reactions escaped through an identical tubing arrangement leading from the top of the sample wells. The ends of the sillimanite inlet and outlet tubes were externally tapered to fit the inside taper of the sample well liners. Resistance wire was wound around the inlet and outlet tubing and covered with an outer layer of asbestos tape to prevent vapor condensation in the tubing outside the furnace. Porous alumina ("RA 98 Alundum") filter discs were cemented into the ends of the sillimanite inlet and outlet tubes to confine the samples to the sample wells. The nearly gas-tight seals between the tapered sample well liners and the tapered inlet and outlet tubes were further improved by applying a paste made from finely-ground reagent-grade alumina and distilled water to the joints at the base and top of the sample block.

The four-wire chromel-alumel thermocouple beads (Stone, 1952, p. 78) were recessed in a short piece of four-hole ceramic tubing by cutting two central grooves in the tubing (Fig. 1), inserting the four 28-gauge thermocouple wires, forming a bead, and cementing the bead into the recess with alumina ("RA 1355 Alundum") cement. After the resulting thermocouple "heads" (see Fig. 2) were inserted through the thermocouple wells into the sample wells, the joint at the surface of each thermocouple well was sealed with the alumina-water paste described above. With proper application of the paste, a positive gas pressure could be maintained in the sample wells with no difficulty.

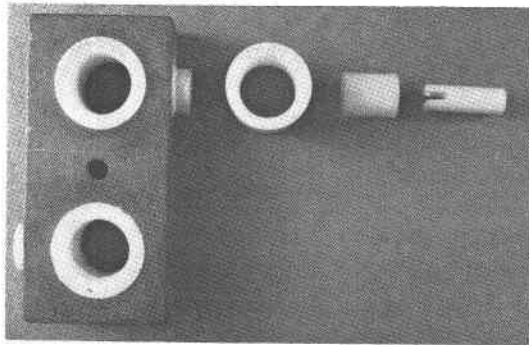


FIG. 1. Sample block showing alumina sample well liners, thermocouple well liners, and thermocouple "head" tubing.

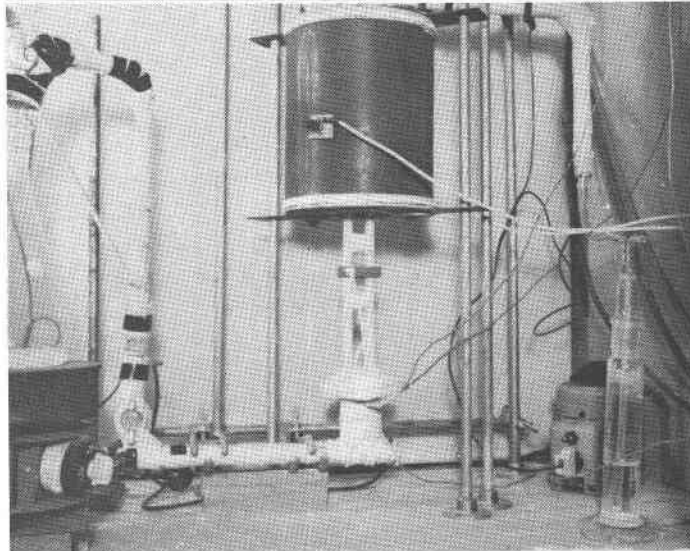
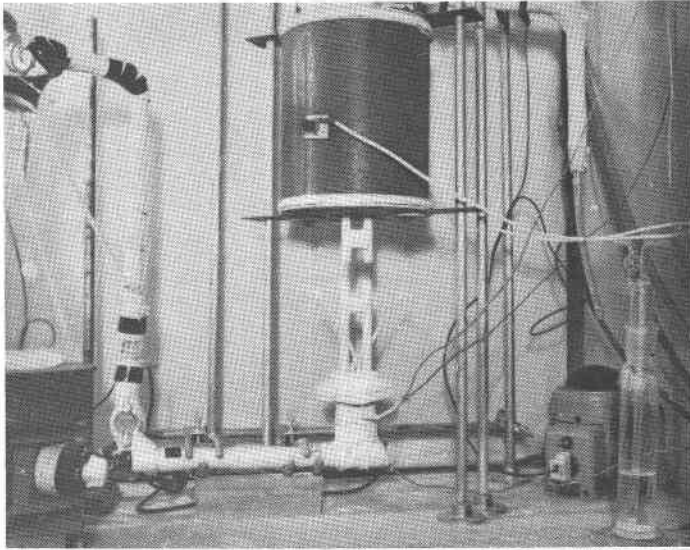


FIG. 2. (above) Apparatus before inserting sample block. Furnace and outlet tube assembly raised.

FIG. 3. (below) Apparatus with sample block and sample in place, thermocouple "heads" inserted, and outlet tube assembly lowered.

The heating unit of the furnace consisted of an externally-grooved ceramic furnace core wound with 18-gauge ("Nichrome") resistance wire. The shell of the furnace was made of stovepipe, and the ends of "Trans-

ite" and asbestos board. "Fiberfrax" was used for insulation. The furnace was suspended from above with a counterweight so it could be lowered over the sample block along two guide rods. Furnace end plugs were shaped from refractory brick.

Figure 2 shows the apparatus with the furnace and the moveable outlet tube assembly raised so the sample block can be inserted and charged. The sample block and sample, and the inlet and outlet tube assemblies, are in place in Fig. 3, and the thermocouple "heads" have been inserted into the sample block. Lowering the furnace and inserting the upper end plug is all that would be required to prepare the apparatus for a "run."

The controlling and recording units used in the apparatus are sold by

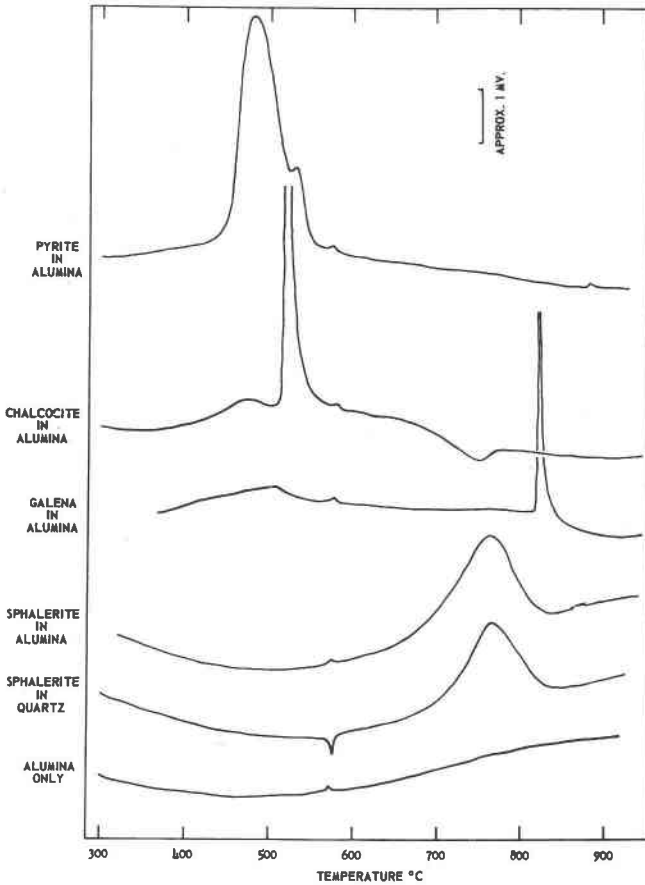


FIG. 4. Selected differential thermal analysis curves of sulfide minerals heated in flowing air.

TABLE 1. SOLID REACTION PRODUCTS OBTAINED BY DIFFERENTIAL THERMAL ANALYSIS OF SULFIDE MINERALS IN CONTROLLED ATMOSPHERES

Reaction Well Charge	Atmosphere	Solid Reaction Products	Identification Method
Pyrite in alumina ¹	Air	Black shiny flakes, some magnetic	Visual
Chalcocite in alumina	Air	CuO (tenorite)	X-ray diffraction
Galena in alumina	Air	Dull red compound	Visual
Sphalerite in alumina	Air	ZnO (zincite)	X-ray diffraction
Sphalerite in quartz	Air	ZnO (zincite)	X-ray diffraction
Sphalerite in alumina	Helium	None	Visual
Sphalerite in alumina	Steam	ZnO (zincite), ZnAl ₂ O ₄ (gahnite)	X-ray diffraction
Sphalerite in quartz	Steam	ZnO (zincite)	X-ray diffraction

¹ Alumina used was in the form of corundum (Al₂O₃).

Leeds and Northrup Company. The temperature in the inert well and the differential emf were recorded on L & N "Speedomax H" strip chart recorders. The furnace temperature was regulated through a magnetic amplifier by a current-adjusting-type controller which received its signal from a cam-type, motor-driven programmer.

PERFORMANCE OF APPARATUS

Differential thermal analyses of alumina-pyrite, alumina-chalcocite, alumina-galena, alumina-sphalerite, and quartz-sphalerite mixtures were obtained in atmospheres of air, oxygen-free helium, and steam. The charge in the reaction well consisted of 50 milligrams of sulfide mixed with 450 milligrams of alumina (corundum) or quartz, and the charge in the inert well consisted of 350 milligrams of alumina mixed with 250 milligrams of quartz which provided an internal temperature standard. The grain diameter of the sulfides and alumina used in the analyses was 120–150 microns, and that of the quartz was 150–300 microns. Inlet gas pressures were maintained at slightly greater than one atmosphere so gaseous reaction products forming in the reaction well were continuously swept out and replaced by the desired reaction atmosphere. Outlet gases were passed through a solution containing lead in order to detect the presence of emerging sulfur gas reaction products. The furnace temperature was increased at an average rate of 9½° C. per minute, but varied from 10° C. per minute at the beginning to 9° C. per minute at the end of each "run."

Differential thermal analysis curves of pyrite, chalcocite, galena, and sphalerite, obtained with the writer's apparatus, are shown in Fig. 4.

The curves compare well with those obtained by other investigators for the same minerals (Kopp and Kerr, 1957, 1958a, 1958b; Dunne and Kerr, 1960, 1961).

Differential thermal analyses of quartz-sphalerite and alumina-sphalerite mixtures in flowing steam gave no evidence of any reactions taking place. Thermograms of the analyses were identical with those obtained by heating alumina in flowing air (Fig. 4), and by heating sphalerite in oxygen-free helium.¹ In the case of the two "runs" in steam, however, a precipitate was formed when gases emerging from the outlet tube were passed through a solution containing lead. The contents of the reaction wells were therefore examined by x-ray diffraction methods, as were the solid reaction products of some of the analyses illustrated in Fig. 4. Solid reaction products detected in the examinations are listed in Table 1.

The identified solid reaction products were mainly those expected. Gahnite occurs in high-temperature mineral deposits (Palache *et al.*, 1952, p. 694-696) and has been found as a smelter product (Mellor, 1924, p. 297; Faber, 1936, p. 105). However, no peaks which could be identified with willemite were observed in the x-ray diffraction patterns of samples from a reaction well in which a quartz-sphalerite mixture had been heated in flowing steam.

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¹ The high thermal conductivity of helium should be borne in mind when using that gas in a dynamic process such as differential thermal analysis.