DIFFERENTIAL THERMAL ANALYSIS OF GALENA AND CLAUSTHALITE

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ABSTRACT

Differential thermal analyses have been conducted on both natural and artificial lead-sulfur-selenium compounds. Thermal curves of twelve natural galenas exhibit a striking consistency regardless of the genetic associations of the minerals studied. In certain instances, limited (5–10° C.) variations from the overall average peak temperature of $783 \pm 2°$ C. appear, which seem to be related to lattice parameter differences.

A range of synthetic compounds at ten molecular per cent solid solution intervals from PbS to PbSe has been formed by pyrosynthesis. X-ray measurements of the series showing unidimensional lattice variation in relation to composition plot as a straight line. Thermal data, on the other hand, produce a more complex plot which may be interpreted in terms of both lattice energies and the nature of the observed reactions. DTA reaction temperatures are systematically related to cell dimensions in the range $PbSe - PbS_{0.7}Se_{0.3}$. DTA data taken from samples in the compositional range $PbS_{0.7}Se_{0.3} - PbS$ are believed to be affected by incongruent anion behavior and surface oxidation effects. Data on pyrosynthesis reaction (formation) temperatures exhibit a fundamental and systematic relation to molar composition throughout the entire compositional range.

INTRODUCTION

Differential thermal analysis has long been utilized in the study of minerals, beginning with the pioneer experiments of Le Chatelier (1887) and Roberts-Austin (1899). The method has found valuable application in the study of clay minerals, carbonates, sulfates and zeolites. Because of their destructive effects on thermocouples and metal heads, sulfides, arsenides and related minerals have until recently received little attention in DTA studies. The difficulties encountered in the study of these materials are discussed by McLaughlin (1957, p. 365), who presents several sulfide curves obtained with conventional DTA apparatus. Hiller and Probsthain (1955, 1956) subjected sulfide minerals to DTA in an inert atmosphere and also in air. The technique employed, however, failed to yield complete oxidation as shown by the resulting curves. At about the same time Kopp and Kerr (1957a) introduced a specially designed apparatus which, by means of alundum shielding for the thermocouples and head metal, allowed DTA of corrosive materials in air. The

thermal head used in the present work is a modification of this unit, and is described elsewhere (Dunne and Kerr, 1960). Sabatier (1956) and Levy (1958), using dilution techniques, have obtained DTA curves for sulfides with unshielded thermocouples. Their work is, however, not directly comparable to that of Kopp and Kerr because of the use of greatly different grain size and heating rates.

TECHNIQUE

The sample weight has been fixed at 50 mg., and grain size maintained in the range 100–120 mesh (149–125 microns), both being selected for convenience in handling and measurement. The weights and dimensions conform to those used by Kopp and Kerr (1957a). The sample is mixed with approximately 300 mg. of pure quartz sand which has been ground to a diameter which ranges from 50–100 mesh (149–297 microns). Quartz provides both an internal temperature standard and a loosely packed framework with interstices large enough to assure adequate sample combustion. Uniform mixing of the sample and the quartz is allowed by the flat alundum bottom of the modified sample well (Dunne and Kerr, 1960). Consistent packing is assured by tamping each charge with a specially constructed brass tamping tool. Reproducibility has been found to be a function of chart reading error. The 6″ chart of the Leeds and Northrup Speedomax H recorder can be read to an accuracy of $\pm 5°$ C. The 12″ chart of the Leeds and Northrup Speedomax G recorder can be read to an accuracy of $\pm 2°$ C. The latter instrument, part of the multiple point arrangement used by Kulp and Kerr (1948) and Kopp and Kerr (1957a), has been used in the galena study, while the Speedomax H, contained in a new, more rapid single point recording system, has been used in the study of the synthetic PbS-PbSe series. All samples were heated at a rate of $12\frac{1}{2}°$ C. per minute.

DIFFERENTIAL THERMAL ANALYSIS OF GALENA

Twelve galena samples from widely separated localities were analyzed, as tabulated in Table 1. Five representative DTA curves derived from these specimens have been selected as shown in Fig. 1. Sabatier (1956) and Levy (1958) present similar curves for galena with somewhat higher peak temperatures (850–860° C.). The temperature difference results from the use of different experimental procedures, particularly in the choice of grain size and heating rates. Temperatures are corrected by internal standard calibration to coincide with a quartz inversion temperature of 580° C., which corresponds to the value for this phenomenon given by the equipment used (Kopp and Kerr, 1957a). All samples exhibit a well defined exothermic deflection beginning around 740° C. and

reaching a peak value between 780 and 790° C. The reaction represented by this deflection is one of oxidation. X-ray diffraction diagrams of the reaction products exhibit a complex array of lines indicative of a mixture of sulfates, oxysulfates and oxides of lead.

The uniformity which marks the five representative curves shown in Fig. 1 is found to characterize all of the specimens examined, regardless of their widely varied genetic associations. There are, however, certain constant variations from the overall average corrected peak temperature

TABLE 1. D.T.A. PEAK TEMPERATURES FOR GALENA

Sample No.	Locality	DTA peak temperature ($\pm 2°$ C.)	Lattice constant (Å)
P-1	Joplin, Missouri	783	5.935
P-2	Vinegar Hill—Barr mine, Tristate District	782	
P-3	Bonneterre, Missouri	782	
P-4	Potosi, Wisconsin	782	
P-5	Leadsville, Colorado	784	
P-6	Silver King mine, Park City, Utah	785	
P-8	Cornwall, England	783	5.935
P-9	Ana mine, Przibram, Bohemia	788	5.934
P-10	Freiberg, Saxony	783	
P-11	Los Lamentos, Chihuahua, Mexico	784	
P-12	Oruro, Bolivia	794	5.933
P-14	Sidney mine, Coeur A Alene District, Idaho	786	

of $783 \pm 2°$ C., notably in the case of the sample from Oruro, Bolivia ($794 \pm 2°$ C.) and the sample from Przibram, Bohemia ($788 \pm 2°$ C.). Lattice constant determinations were made on these and two average temperature samples, using standard x-ray diffractometer equipment with reference to tables prepared by Parrish, et al. (1953). The results of these four measurements are tabulated along with peak temperature values in Table 1. The small inverse relationship here indicated is considered a possibility, assuming cation substitution to be the controlling factor for both anomalies. Kopp and Kerr (1957a) showed a similar relationship between peak temperatures and lattice dimensions in ferrian sphalerites. As lattice constants increased in response to increasing iron substitution, peak temperatures decreased. It must be recognized, however, that DTA data are frequently not subject to interpretation in terms of lattice dimensions, as it may be shown that anion substitution in certain proportions can produce results that are entirely different from those indicated above.
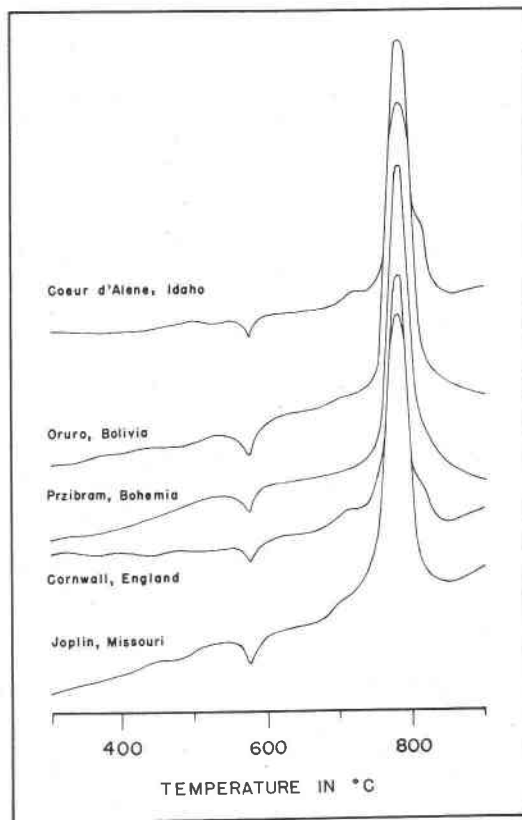
FIG. 1. Representative D.T.A. curves of galena. The endothermic peaks at 580° C represent the inversion of quartz, which is used as an internal temperature standard.

THE GALENA—CLAUSTHALITE SOLID SOLUTION SERIES

Earley (1950) in a comprehensive study of the selenide minerals, described a synthetic solid solution series between galena (PbS) and clausthalite (PbSe). More recently, Coleman (1959) demonstrated the existence of the series in nature associated with the vanadium-uranium mineralization of the Colorado Plateau. The samples discussed below have been formed by a dynamic method of pyrosynthesis, similar to the static pyrosynthesis described by Earley. The procedure followed is given below.

The weights of the constituent elements are calculated on the basis of their respective mole fractions in the desired mineral. After homogenization in a Wig-L-Bug mixer, a 0.5 gm. charge is extracted from the sample

mixture and introduced into a Pyrex tube which has been previously closed at one end. The tube is evacuated and sealed, then placed in a resistance furnace and heated at a uniform rate to approximately 450° C. After heating, the sample is removed from the furnace and allowed to cool to room temperature. A temperature record is furnished by a thermocouple inserted into a preformed recess in the bottom of the sample tube. This thermocouple and one similarly placed in a reference tube function as a differential pair, and a strip chart record of the reactions occurring during pyrosynthesis is obtained. This method for the differential thermal study of pyrosynthesis reactions is described elsewhere (Bollin, Dunne and Kerr, 1960).

LATTICE PARAMETER MEASUREMENTS

Lattice parameter measurements were made on all samples, using standard x-ray diffractometer equipment. As the measurements were made in an effort to secure data on the relative variation in lattice dimension with molar composition, they are not to be interpreted in terms of absolute lattice constants. Hence, the data are given as measured d-spacings, and have not been converted to a_0 values. The measurements were made at a goniometer speed of $\frac{1}{2}°$ 2θ per minute, and the standard chart speed of 30″ per hour. Thus, the charts can be read to an accuracy of $\pm 0.05°$ 2θ, which in the range of the d-values measured represents a maximum reading error of one part in twenty-five hundred. Since sets of determinations were taken consecutively over a small range in 2θ values (98.10–102.44° 2θ), relative errors arising from goniometer alignment may be considered negligible. Similarly, sample mount derivations were found to produce no measurable error. Hence, the maximum error inherent in the measurements is essentially the maximum chart reading error, *i.e.*, one part in twenty-five hundred, or approximately 0.004 Å in relative values.

Measured values for the (600) line of samples representing a ten molar per cent series between PbS and PbSe are shown plotted against molar composition in Fig. 2. The linear relationship between cell dimension and composition here indicated agrees with the conclusions of Earley (1950) and Coleman (1959). In terms of Zen's (1956) analytical treatment of Vegard's Law, these data indicate that the difference in the end member cell volumes in this series is so small that no measurable distortion results from the fact that cell edge data are plotted against composition, although it may be cell volume that varies linearly with molar composition.

On the basis of cell dimension measurements such as are shown in Fig. 2, it was discovered that a systematic compositional error exists in the
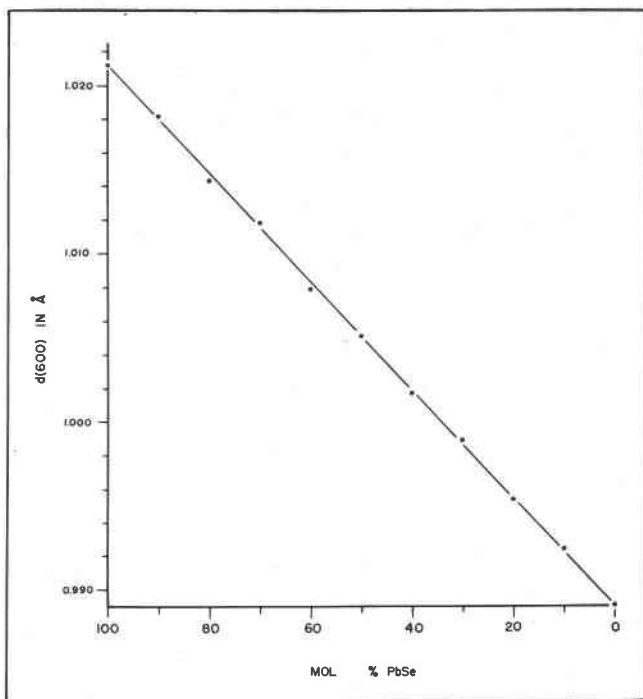
Fig. 2. Measured (600) *d* spacing vs. molar composition of samples comprising the synthetic PbS-PbSe series at intervals of ten mol per cent.

samples used in differential thermal analyses. This error is believed to have resulted from the use of oxidized Pb in the preparation of certain specimens, and appears in the unequal compositional intervals between samples described in the DTA discussion. The samples represented in Fig. 2 were prepared using unoxidized Pb.

REACTION TEMPERATURE DATA

Strip chart records of the reactions involved in the formation of certain of the synthetic samples were obtained, utilizing the method outlined in the discussion of synthesis. In order to obtain reproducible temperatures, it was considered desirable to control the volume of the sample mixture run. To this end, a scratch was made 16 mm. above the closed end of a 2 mm. (I.D.) glass capillary tube, and the volume thereby defined (0.05 cm.³) was used as the volume of all sample charges.

Strip chart records of the pyrosynthesis reactions of samples comprising a twenty mol per cent series between PbS and PbSe are shown in Fig.
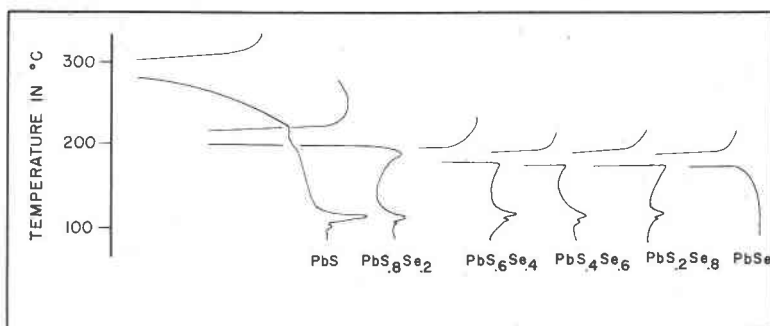
FIG. 3. Differential thermal pyrosynthesis (DTP) curves. The samples comprise
a twenty mol per cent synthetic PbS-PbSe series.

3. For the sake of brevity, such records will be referred to henceforth as
DTP curves. A small endothermic deflection at about 110° records the
melting of sulfur and characterizes all curves, except the one obtained
from PbSe. The large, well defined exothermic peaks are representative
of the formation of the compounds corresponding to the molar composi-
tion of the respective sample mixtures. Additional reactions were not
observed below 1000° C. The d (600) measurements of these samples
have been found to correspond closely to those of the samples whose
measurements are given in Fig. 2. In Fig. 4 initial temperatures of the
exothermic formation reactions on the DTP curves are plotted against
molar composition. Note that the peak areas (Fig. 3) exhibit a correspond-
ing increase with increasing mol per cent PbS. This relationship is to be
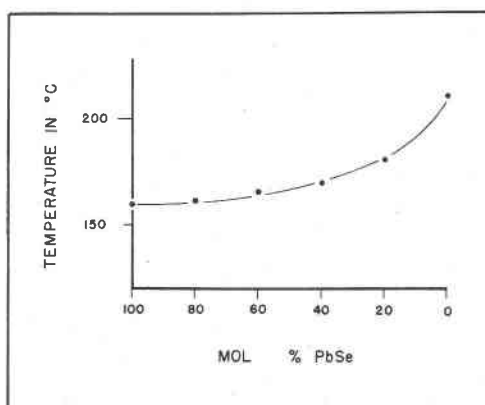

FIG. 4. Pyrosynthesis reaction (formation) temperature vs. molar composition.
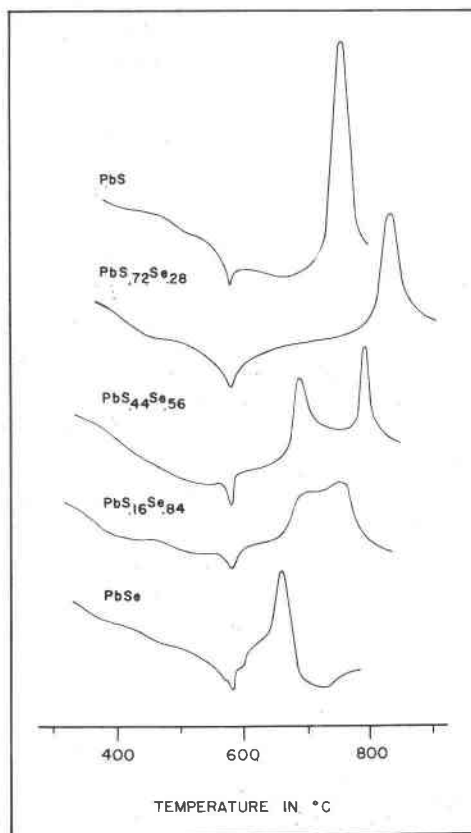The samples listed are those whose DTP curves are given in Fig. 3.

FIG. 5. D.T.A. curves of synthesized compounds. The samples comprise a twenty five mol per cent synthetic series. The uneven compositional spacing of the samples indicated here results from the use of oxidized lead in their preparation. This compositional error was found on the basis of x-ray measurements to characterize all of the synthetic specimens used for D.T.A. studies.

expected in light of the dynamic nature of the DTP technique. The observed initial temperatures do not represent equilibrium temperatures, being to a large extent a function of reaction kinetics and therefore closely related to ΔH, of which peak area is a direct function.

DTA on the Galena—Clausthalite Series

DTA records were obtained from the synthetic samples comprising the PbS-PbSe series. The curves of a 25 mol per cent series are shown in Fig. 5. These curves are representative of over forty DTA curves covering the synthetic series. An exothermic peak representing sample

oxidation begins at the clausthalite end of the series as a multiple deflection which splits into two distinct peaks near the midpoint of the series. These, in turn, merge to form a single sharp deflection which then characterizes the remainder of the suite. The development of two peaks in the vicinity of the series midpoint and their subsequent merging may result from a combination of factors. A comparison of the end member curves shows the clausthalite oxidation peak to be distinctly broader than the galena deflection. This relationship is believed to be indicative of the lower partial pressures of Se reaction products, which result in a higher order of reaction retardation caused by surface oxidation effects. As the sulfur content of the samples rises, more thermal energy is required to cause sample oxidation, and the reaction temperatures rise accordingly. The energy required to effect complete sample destruction rises at a faster rate than does the specific heat of the oxidation reaction. This effect combines with surface coating and interstitial clogging by reaction products to produce two peaks. These merge when low Se content and high reaction temperatures reduce the retardation effect of the early reaction products to a vanishing point.

From the foregoing discussion, it appears that the most significant temperature on these DTA curves is that of the initial deflection accompanying sample oxidation, since other peak characteristics result in part from factors which have no relationship to the fundamental properties of the minerals under consideration. The effect of grain size, for example, is demonstrated by the fact that a finely ground sample of composition $PbS_{0.5}Se_{0.5}$ was found to be characterized by a single exothermic peak.

As is evident from an examination of Fig. 5, initial reaction temperature has been found to increase with mol per cent PbSe throughout most of the synthetic series. The reversal of this relationship, evident in the range $PbS_{.72}Se_{.28}$-PbS (Fig. 5) is believed to be caused by the decrease in the Se content of the samples, which in turn results in a decrease in the amount of surface coating by high stability Se rich reaction products. Oxidation products have been detected in Se-bearing samples which have been heated in air to temperatures as low as 200° C. Since surface area is held effectively constant by the control of both sample weight and grain size, it appears likely that all samples whose Se content exceeds a certain threshold value will suffer complete surface coating by reaction products rich in Se at temperatures below the DTA initiation temperature. Thus the effect of surface reaction on the initial deflection temperatures of these samples may be negligible in a relative sense. Within the experimental conditions under which the DTA data described herein were obtained, it appears that this threshold value lies near the composition

$PbS_{0.7}Se_{0.3}$. The conclusion that the reversal in the relationship between initiation temperatures and molar composition is not related to fundamental mineral properties is supported by the x-ray and DTP data given earlier.

The interpretation of the DTA data is based on the assumption that the recorded temperature of reaction is a function of the lattice energy of the material under analysis. That is to say, although reaction temperature is in no way an actual measure of lattice energy, it is fundamentally and linearly related to it. According to the Born-Lande expression for the lattice energy of binary ionic compounds, the relation between lattice energy and interionic distance is reciprocal in the first degree. Thus, if one assumes reaction temperature to be directly related to lattice energy, the reciprocal of this temperature should plot linearly with a measure of interionic distance. Figure 6 shows a plot of the reciprocal of DTA
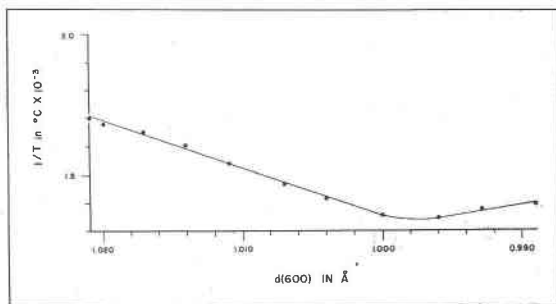

Fig. 6. Plot of the reciprocal of D.T.A. initial reaction temperature vs. measured d (600).

initiation temperatures against measured d (600) values for the series PbS-PbSe. The data apparently conform to the theoretical considerations just discussed through the compositional range $PbSe-PbS_{0.7}Se_{0.3}$. However, for those samples with compositions in the range $PbS_{0.7}Se_{0.3}$-PbS, this relationship does not obtain.

Conclusions

X-ray, DTA and DTP data show that a definite solid solution series exists between galena (PbS) and clausthalite (PbSe). A linear increase in cell dimensions corresponds to the increase in mol per cent PbSe. This relationship is also reflected through part of the series in the DTA data, but not through the entire series. However, measurements made on both natural galena and the synthetic specimens indicate that lattice parameter variations are systematically reflected in DTA reaction temperatures. Although data of this type must be interpreted with caution

in the case of systems characterized by anion substitution, the agreement between several lines of experimental evidence in the interval $PbSe\text{-}PbS_{0.7}Se_{0.3}$ is significant.

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