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## Enthalpy of thermal decomposition of pyrite concentrate

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### Abstract

The enthalpy of thermal decomposition of pyrite concentrate (PC) in an inert atmosphere was measured by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The decomposition is a two-stage process and the enthalpy values of the overall process determined by the two methods are very close to each other: DTA,  $\Delta H = 72.2$  kJ per mol  $\text{FeS}_2$ ; DSC,  $\Delta H = 70.1$  kJ per mol  $\text{FeS}_2$ .

These values are quite different from the calculated standard enthalpy of  $\text{FeS}_2$  decomposition at 1000 K,  $\Delta H = 154.0$  kJ per mol  $\text{FeS}_2$ , and the enthalpy calculated from the Clausius–Clapeyron equation with dissociation pressure data for  $\text{FeS}_2$ ,  $\Delta H = 181.9$  kJ per mol  $\text{FeS}_2$ .

*Keywords:* Decomposition; DSC; DTA; Enthalpy; Pyrite; TG

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### 1. Introduction

Heating pyrite ( $\text{FeS}_2$ ) in an inert atmosphere yields sulphur vapour and non-stoichiometric iron sulphides, i.e. pyrrhotites ( $\text{Fe}_{1-x}\text{S}$ ) [1]. The gaseous product, sulphur vapour, contains a number of different types of molecules. Up to seven different species  $\text{S}_i$  ( $i = 2-8$ ) are present in measurable amounts at temperatures below 773 K [2,3]. At higher temperatures,  $\text{S}_2$  molecules are generally the predominant species, although sulphur atoms can also play an important role. As mentioned above, the composition of the solid products is not stoichiometric and varies with the decomposition temperature and the vapour pressure of sulphur.

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Mills [4] summarized the dissociation pressure data for  $\text{FeS}_2$  recorded by various investigators. The data recorded by Rosenqvist [5]  $\log(P/\text{atm}) = 19\,000 T^{-1} + 19.6$ ,  $T = 870\text{--}1030$  K, are recommended. The enthalpy of reaction can be calculated from the Clausius–Clapeyron equation.

The thermal behaviour of mono-mineral pyrite in an inert atmosphere has been the subject of numerous DTA studies [6–8]. It has been stated that three endothermic effects, increasing in height, are present on the thermoanalytical curves of pyrite: 723–753 K, 803–843 K and 903–963 K. Shkodin et al. [9] determined the specific thermal effects, defined as the ratio of the thermal effect values to the sample mass losses. Different interpretations of the thermal effects have been given.

The aim of this investigation is to study the enthalpy of thermal decomposition of pyrite concentrate by DTA and DSC. This is part of a more detailed study on the mechanism of the process and on the properties of the solid products.

## 2. Experimental

The specimen used in the present study was pyrite flotation concentrate from Chelopech Mine, Bulgaria. The size fraction 0.09–0.1 mm was dried to constant mass for 24 h at 373 K and was used in all experiments. The elemental composition of the working fraction is: 40.78% Fe, 49.41% S, 3.02% Si, 0.39% Zn, 0.29% Cu, 0.24% Pb, 0.29% As, 0.25% Ca, 0.079% Mn, 0.034% Co, 0.014% Ni.

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out using a MOM Q-1500 D derivatograph. Samples of 400 mg were heated at a rate of  $5\text{ K min}^{-1}$  in an argon stream flowing at  $5\text{ l h}^{-1}$ . Aluminium oxide was used as a reference. The values of the thermal effects were determined by the DTA peak areas, calibrated with standard  $\text{CaCO}_3$ .

A Setaram TG-DSC-111 differential scanning calorimeter was used for the enthalpy measurement using the following conditions: initial temperature, 298 K; heating rate,  $10\text{ K min}^{-1}$ ; final temperature, 1073 K; mass of the sample, 238.8 mg; argon flowing at  $5\text{ l h}^{-1}$ .

## Results and discussion

### 3.1. TG and DTA measurements

The TG and DTA curves for PC are shown in Fig. 1. The TG curve indicates vaporization of volatile inclusions from 363 to 623 K with a mass loss of 3.1%. The corresponding endothermic effect is very small, with a peak temperature at 398 K. Thermal decomposition of  $\text{FeS}_2$  starts at 623 K. Two stages are well defined on both the TG and DTA curves. The overall mass loss for  $\text{FeS}_2$  decomposition is 25.8% which is in fair agreement with the theoretical value of 26.7% for the reaction



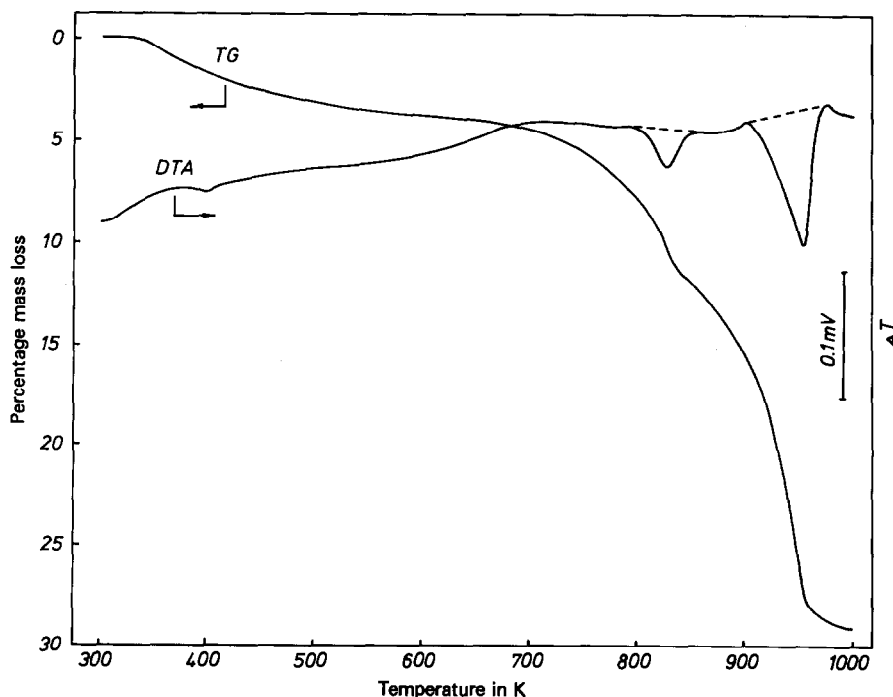


Fig. 1. TG and DTA curves of pyrite concentrate.

The first-stage enthalpy is 0.1 kJ per g PC or 13.7 kJ per mol  $\text{FeS}_2$  and for the second stage, 0.43 kJ per g PC or 58.5 kJ per mol  $\text{FeS}_2$ . The overall enthalpy of PC decomposition by DTA measurement is 0.53 kJ per g PC or 72.2 kJ per mol  $\text{FeS}_2$ .

### 3.2. DSC measurements

The DSC curve for PC is shown in Fig. 2. The shape of the DSC curve is similar to that of the DTA curve. The last two endothermic peaks on the DSC curve are closer to each other, but this is due to the higher heating rate. An exception is the small endothermic peak at 572 K. Enthalpy values of the thermal effects are given in Table 1.

The enthalpy of the overall process is 512.0 J per g PC or 70.1 kJ per mol  $\text{FeS}_2$ .

Accordinging to the Rosenqvist dissociation pressure data for  $\text{FeS}_2$ , it can be assumed that at 1000 K the reaction will go to completion. At this temperature the predominant species in the sulphur vapour is the  $\text{S}_2$  molecule. The enthalpy of reaction, calculated from the Clausius–Clapeyron equation with Rosenqvist data is  $\Delta H = 363.8$  kJ per mol  $\text{S}_2$  or  $\Delta H = 181.9$  kJ per mol  $\text{FeS}_2$ .

This enthalpy value for  $\text{FeS}_2$  (monomineral) decomposition is in good agreement with the thermodynamically calculated standard enthalpy of the reaction at 1000 K,

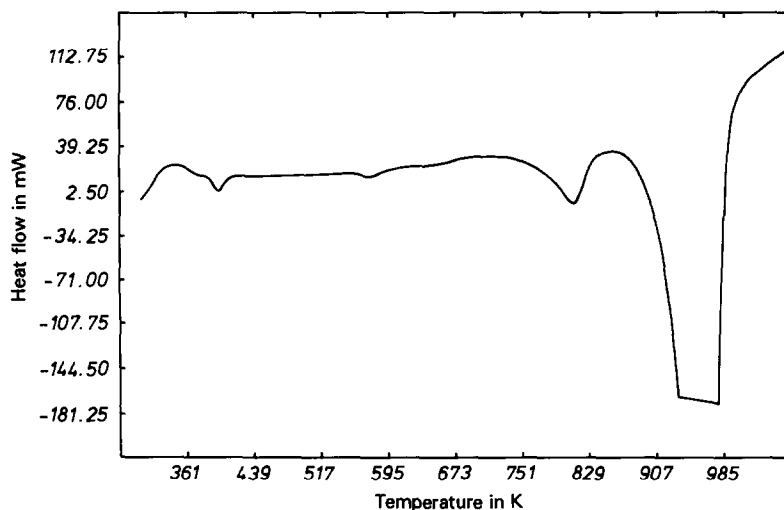


Fig. 2. DSC curve of pyrite concentrate.

Table 1

Enthalpies of the different stages of pyrite concentrate decomposition by DSC measurement

Peak start in K	380.8	544.4	728.4	853.9
Peak end in K	414.4	600.3	853.9	1014.2
Top of peak temperature in K	398.6	571.8	811.5	978.0
Enthalpy in J per g PC	3.9	2.5	49.6	456.0
Enthalpy in kJ per mol FeS <sub>2</sub>	0.53	0.34	6.8	62.4

$\Delta H = 154.0$  kJ per mol FeS<sub>2</sub>, but it is very different from the experimental values from DTA and DSC enthalpy measurements of PC decomposition. The standard enthalpy of the reaction is calculated with Barin and Knacke's thermochemical data [10].

#### 4. Conclusions

The thermal decomposition of pyrite concentrate in an inert atmosphere is a two-stage process, well defined on TG, DTA and DSC curves. The enthalpy values of the overall process, determined by DTA and DSC measurements are almost equal but they are approximately half the thermodynamically calculated standard enthalpy of the reaction and the enthalpy calculated from the Clausius–Clapeyron equation with Rosenqvist dissociation pressure data. The difference may be due to the influence of mineral and chemical inclusions in the pyrite concentrates on the thermal stability of FeS<sub>2</sub>. In such cases it is more correct to use thermal methods of analysis to obtain reliable information about enthalpy changes.

## References

- [1] R. Juza and W. Biltz, *Z. Anorg. Allg. Chem.*, 205 (1932) 273.
- [2] H. Rau, T.R.N. Kutty and J.R.F. Guedes de Carvalho, *J. Chem. Thermodyn.*, 5 (1973) 833.
- [3] B. Meyer, *Chem. Rev.*, 76 (1976) 367.
- [4] K.C. Mills, *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides*, Butterworths, London, 1974, p. 298.
- [5] T. Rosenqvist, *J. Iron Steel Inst.*, 176 (1954) 37.
- [6] R.A. Schoenlaub, *J. Am. Ceram. Soc.*, 52 (1969) 40.
- [7] F. Paulik, L. Erdey and S. Gal, *Bergakademie*, 14 (1962) 21.
- [8] L. G. Berg, E.N. Shlyapkina and B.V. Burov, *Fizika Mineralov*, Izd. KGU, Kazan, 1971, p. 91.
- [9] V.G. Shkodin, D.N. Abishev, A.K. Kobzhasov, V.P. Malyshev and R.F. Mangutova, *J. Therm. Anal.*, 13 (1978) 49.
- [10] I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances*, Springer-Verlag, Berlin, 1973.