

Mechanism of Oxidation & Thermal Decomposition of Iron Sulphides

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Thermoanalytical techniques (DTA and DTG), chemical, and X-ray diffraction methods have been combined to study the courses of oxidation and thermal decomposition of synthetic iron pyrites and pyrrhotite. Pyrites is oxidized directly to ferrous sulphate, and no intermediate pyrrhotite is formed. Interaction of pyrites and ferrous sulphate, and decomposition of ferrous sulphate to normal and basic ferric sulphates are the other important reactions in the oxidation. Ferrous sulphate is the major oxidation product even in pure oxygen and abundant supply of air.

CONTRADICTION views regarding the mechanism of oxidation of iron pyrites (FeS_2) are expressed in the literature¹⁻⁴. Some workers^{1,2} suggest that the oxidation of pyrites proceeds primarily through the formation of sulphates [FeS_4O , $\text{Fe}_2(\text{SO}_4)_3$] which later decompose to ferric oxide (Fe_2O_3) and sulphur dioxide (SO_2). Others^{1,3,4} hold that the primary products of oxidation are the oxides (FeO , Fe_2O_3) which subsequently react with sulphur dioxide to produce sulphates. It is also believed that oxidation of pyrites is accompanied by thermal decomposition to pyrrhotite ($\text{Fe}_n\text{S}_{n+1}$, $n \geq 5$). Never, at least to the knowledge of the author, has there been any systematic approach to study the oxidation of synthetic iron sulphides.

The present investigation combines thermoanalytical techniques (DTA and DTG), chemical, and X-ray diffraction methods to follow the courses of oxidation and thermal decomposition of both synthetic and natural iron pyrites and pyrrhotite. Previous workers studied the oxidation and thermal characteristics only of natural samples of pyrite and pyrrhotite of various origins and hence containing different types of impurities. The present study is mainly confined to the synthetic sample to derive a generalized mechanism of oxidation which might also be applicable to natural samples of pyrites. The effect of a few solid additives on the oxidation of pyrites has also been studied.

The salient features of the present investigation have already been published by the author in a short communication⁵.

Materials and Methods

All the chemicals used in the preparation of sulphides and additives, and in the analysis were of reagent grade.

(1) *Preparation of synthetic iron pyrites* — Synthetic pyrite was prepared⁶ by heating an intimate mixture of ferric oxide, sulphur and ammonium chloride at 340° for 2 hr. The product was boiled with conc. HCl to remove ferric oxide, filtered and washed repeatedly with water till the filtrate was free from ferric and chloride ions. The solid mass was washed with acetone and dried rapidly. Free sulphur,

adhering to this product was removed by refluxing the sulphide with carbon disulphide in a Soxhlet apparatus for 12 hr. The black residue was dried in a vacuum desiccator. This sample on analysis gave: 18.48% $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ and 80.50% FeS_2 . The sulphate-free iron pyrites was prepared by washing this sample repeatedly with water and absolute ethyl alcohol and then drying in a vacuum drier. The purified and dried sample contained 99.32% FeS_2 (Found: Fe, 46.31; S, 53.01%; Fe/S, 0.874. Calculated Fe/S for FeS_2 , 0.873).

Pyrites ore was supplied by the Pyrites Development Corporation, Amjhore, India. On analysing a few representative samples, dried at 110° for 1 hr, the ore was found to contain 37.1% Fe and 41.7% S, silica (about 14%) being present as the chief impurity. There also contained appreciable amount of ferrous sulphate heptahydrate.

Preparation of synthetic pyrrhotite — The black precipitate of ferrous sulphide, obtained by adding ammonium sulphide to ferrous sulphate solution was filtered, washed with dil. aq. ammonium sulphide and then with cold water until sulphide ion was absent in the filtrate. The residue was kept under acetone for 1 hr (since simple washing with acetone made the sample pyrophoric) and then dried rapidly. Finally, the residual sulphur was removed by refluxing with carbon disulphide. The sample was stored under acetone, the required quantity being taken out and dried immediately before use.

The greenish-black sulphide of iron, thus prepared, was feebly magnetic which along with other physico-chemical evidences, (e.g. the dissolution of the sulphide in HCl with separation of sulphur) indicated that the sample was pyrrhotite.

Preparation of additives — Ferric oxide, γ -alumina, silica and cupric sulphide were prepared following the method adopted by Ganguly and coworkers^{7,8}. Vanadium pentoxide was obtained by the decomposition of vanadyl oxalate in a stream of air at 450° . Pyrolusite containing 85.0% manganese dioxide was used. Calcium oxide was supplied by the Hopkins and Williams Ltd, England.

Procedure — Thermal analyses (DTA and DTG) were carried out in conventional apparatus⁸; the

sample holder in DTA was made of stainless steel instead of nickel, and the Pt/Pt.Rh thermocouples were shielded at their tips by close-fit small platinum cups. This was necessary to avoid spurious thermal effects due to interaction between nickel and iron sulphides⁹. The thermal analyses were carried out in dynamic nitrogen or static air atmosphere at atmospheric pressure. The heating rate was maintained at 10°/min and $\alpha\text{-Al}_2\text{O}_3$ was used as the reference material. The particle size of iron sulphides was kept in the range -100+120 BS mesh. Preliminary studies showed that using a flow of air (20 litres/hr), either dried or undried, and change of particle size (-100+200 BS mesh), did not affect the oxidation of iron sulphides. The change in weight per 20° was noted in the TG analysis and this change was plotted against temperature to get DTG curves.

Synthetic pyrites was heated in air in a porcelain boat in a tubular furnace up to various temperatures in the range associated with important thermal changes. The samples were then cooled in a dry nitrogen atmosphere, and analysed by X-ray diffraction and chemical methods. X-ray diffraction analysis was carried out by the powder photograph technique using a Philips-make unit (Model No. PW 1008/30), cobalt radiation (1.79 Å), iron filter, and a camera of diameter 57.3 mm. The intensity of the lines was measured with a microphotometer. The d values were calculated by standard procedure by measuring the distance (in mm) between corresponding arcs of the same cone of diffracted rays.

Analysis — The quantitative chemical analysis^{10,11} of the oxidized samples was performed according to the following scheme. The sample was dissolved in water, warmed, filtered (filtrate-A) and washed with hot water till free from sulphates. All these procedures were carried out in CO_2 atmosphere in a specially designed apparatus to prevent oxidation. Ferrous and ferric iron contents in the filtrate-A were estimated by potassium dichromate and iodometric titrations respectively. The water-insoluble residue was treated with 1N hot acetic acid, filtered (filtrate-B) and washed with hot water. Basic ferric sulphate was estimated in the filtrate B by iodometric titration of iron. The residue from filtrate-B was dissolved in 5N HCl, boiled, washed and filtered (filtrate-C) in CO_2 atmosphere. The iron content in filtrate-C was estimated by the same procedure used for filtrate-A to assess the amounts of ferrous and ferric oxides. The residue from filtrate-C was dissolved in concentrated HNO_3 and evaporated to dryness. The solid mass was dissolved in water and the ferric iron content was estimated iodometrically to know the amount of iron pyrites.

The gaseous products (SO_2 and SO_3) were estimated by passing the gases through two absorbers containing respectively acidified barium chloride and standard iodine solutions. The total sulphur in the solid sample was estimated by the combustion method¹² and by absorbing the evolved sulphur dioxide in standard iodine solution.

Results and Discussion

The DTA and DTG curves of the iron sulphides in both nitrogen and air atmosphere are shown in

Figs. 1 and 2 respectively. The product distribution after oxidation of synthetic pyrites in air at different temperatures is given in Table 1. The solid phases at different temperatures identified by X-ray diffraction are recorded in Table 2. Fig. 3 gives the experimental relative intensities (I) and d values of the X-ray diffraction lines of the samples. The solid phases were identified by comparing the experimental d and intensity values with the standard data¹³.

Thermal Decomposition of Iron Sulphides in Nitrogen

Pyrrhotite — Decomposition of pyrrhotite to ferrous sulphide and sulphur took place at 460-560° (Fig. 1, curve IA). The endotherm at 120° was due to the elimination of acetone (chemically identified)

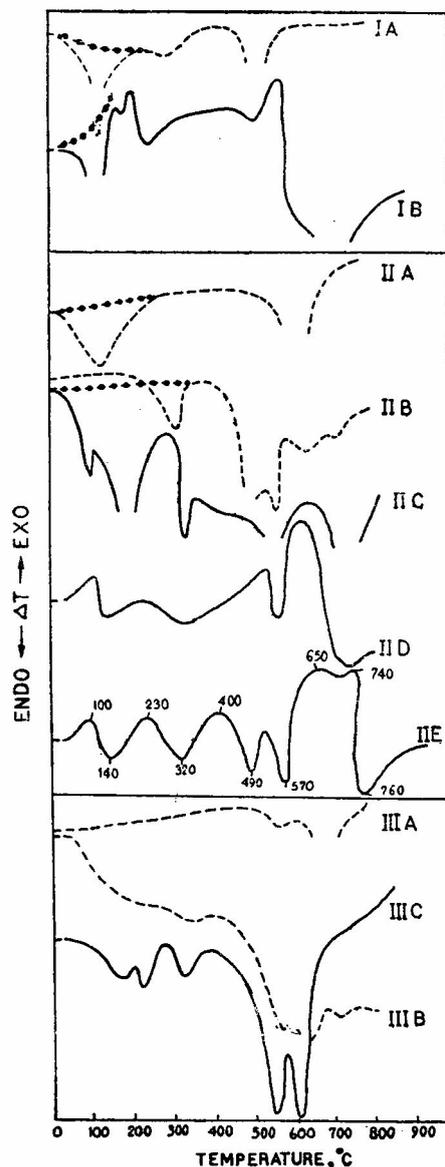


Fig. 1 — DTA curves of iron sulphides in air and nitrogen [(—) in air; (---) in nitrogen; IA, IB, synthetic pyrrhotite; IIA, IID, pure synthetic pyrites; IIB, IIE, synthetic pyrites (containing sulphate); IIC, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; IIIA, natural pyrites (sulphate free); IIIC, IIIB, natural pyrites (containing sulphate)]

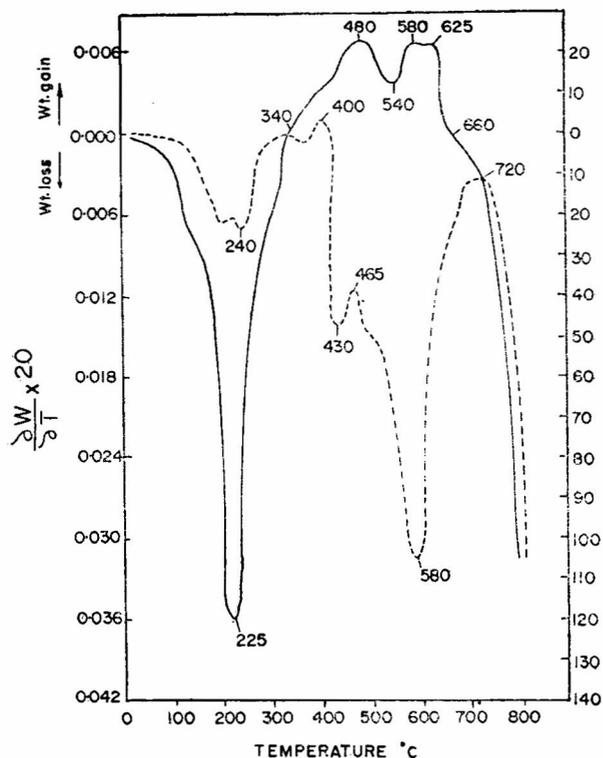


Fig. 2—DTG curves of iron pyrites in air [(—) synthetic pyrites (containing sulphate); (---) natural pyrites (containing sulphate)]. $\frac{\partial W}{\partial T} \times 20$ represents change in weight per 20°

adsorbed in the sample during its preparation. This endotherm was not obtained when the sample was preheated at 200° before starting the thermal analysis (shown by solid circles in the curve IA).

Pyrites—The endotherm at 120° in thermogram IIA (Fig. 1) was due to loss of moisture and adsorbed ethyl alcohol, used during preparation of sulphate-free pyrites. This endotherm was not obtained with the sample preheated at 150° (shown by solid circles in IIA).

The endotherm at 320° in thermograms IIB and IIIB was characteristic of the loss of water of crystallization from $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. This endotherm was missing in the case of both sulphate-free and preheated samples of pyrites. That this peak was characteristic of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ is also evident from thermal changes of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (curve IIC). Natural and synthetic iron pyrites dissociated into

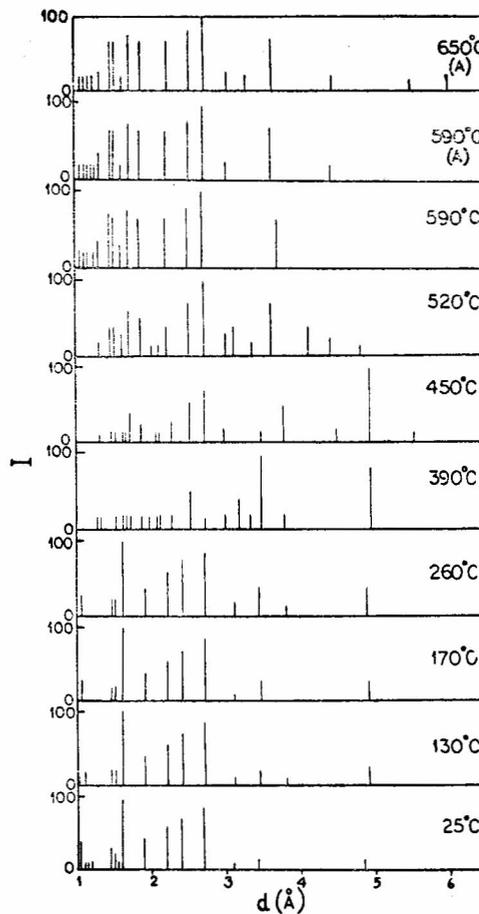


Fig. 3—X-ray diffraction lines of synthetic iron pyrites heated in a current of air at different temperatures. Patterns marked (A) were prepared in static air [I is the relative intensity based on the strongest line of intensity 100]

TABLE 2—SOLID PHASES AT DIFFERENT TEMPERATURES IDENTIFIED BY X-RAY DIFFRACTION

Temp. $^\circ\text{C}$	Phases identified
130°, 170°, 260°	FeSO_4 , FeS_2
390°	FeSO_4 , $\gamma\text{-Fe}_2\text{O}_3$, FeS_2
450°	FeSO_4 , $\gamma\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$
520°	FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, $\alpha\text{-Fe}_2\text{O}_3$
590°, 650°	$\text{Fe}_2(\text{SO}_4)_3$, $\alpha\text{-Fe}_2\text{O}_3$

TABLE 1—PRODUCT DISTRIBUTION IN THE OXIDATION OF SYNTHETIC IRON PYRITES AT DIFFERENT TEMPERATURES

Reaction temp. $^\circ\text{C}$	Wt % sulphate			Wt % oxide		Wt % pyrites
	Ferrous	Ferric	Basic(a)	Ferrous	Ferric	
130	27.10	0.00	0.00	1.98	0.00	69.50
260	55.01	0.00	0.00	5.25	0.00	39.50
450	68.36	4.35	0.00	5.22	20.71	1.50
560	0.50	35.10	4.03	0.00	59.87	0.00
650	0.00	38.18	4.29	0.00	56.52	0.00

(a) Basic sulphate was calculated on the basis of $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$.

pyrrhotite and sulphur in more or less the same temperature range 550-680° (curves IIA and IIIA). But, decomposition of iron pyrites containing ferrous sulphate (a product of spontaneous oxidation of pyrites in air) started much earlier at 350°. A comparison of the curves IIA with IIB and IIIA with IIIB would clarify this point.

Oxidation of the Sulphides

Synthetic pyrrhotite — Thermogram (IB) showed three endothermic peaks at 140, 260 and 750° and two exothermic peaks at 210 and 570°. The products of oxidation at 210° contained γ -Fe₂O₃ and FeSO₄; ferric sulphate, basic ferric sulphate and α -Fe₂O₃ were the products at 600°. This shows that the oxidation of pyrrhotite to ferrous sulphate and γ -Fe₂O₃ was predominant in the range 140-210° and continued up to 500°. Beyond 500°, endothermic decomposition of ferrous sulphate to ferric sulphate and basic ferric sulphate and exothermic magnetic transformation of γ -Fe₂O₃ to α -Fe₂O₃ took place. The endotherm at 120° was due to loss of acetone. Somewhat different observation on the oxidation of pyrrhotite was made by Safiullin *et al.*².

Synthetic iron pyrites — Ferrous sulphate was the major product in the initial stage of oxidation of pyrites. An appreciable amount of ferrous sulphate was found even at 100°, the product up to 230° contained mainly ferrous sulphate and, up to 450°, this continued to be the major oxidation product (Table 1). The small weight loss at the initial stage in the TG was due to loss of moisture and ethyl alcohol, loss of water from hydrated ferrous sulphate (formed by aerial oxidation of pyrites during sample preparation), and oxidation of pyrites to ferrous oxide. These processes predominated over direct oxidation of pyrites to ferrous sulphate (which is a weight gain reaction) at the initial stage of oxidation, which is perhaps the reason for a resultant decrease in weight up to 320°.

Safiullin and Gitis² reported the formation of pyrrhotite at 175° during the oxidation of natural pyrites and suggested that the formation of pyrrhotite and its conversion to ferrous sulphate proceeded almost simultaneously. However, in the present investigation, ferrous sulphide or pyrrhotite (d : 2.09, 2.98, 2.67; I : 100, 90, 90) could not be detected, even in traces, either by X-ray or by chemical methods during any stage of the oxidation of either natural or synthetic pyrites, contrary to previous reports^{1,2}.

It appears that the oxidation does not proceed through the simultaneous formation of ferrous oxide and its conversion into ferrous sulphate, since by this mechanism a large gain in weight should have been obtained up to 320° instead of the observed weight loss. Also the formation of ferrous oxide and its partial conversion to sulphate are not considered to be predominant processes over direct sulphation. Had it been so, then we could have definitely detected ferrous oxide (d : 2.15, 2.49, 1.52; I : 100, 80, 60) in the X-ray diffraction patterns at 170°, 260° and 390° because the specimens at these temperatures were obtained in the dynamic

air atmosphere under which condition the formation of ferrous oxide would have been favoured and its conversion to sulphate hindered due to the expulsion of sulphur dioxide in the flow conditions.

Another important observation in support of the direct sulphation mechanism was that both synthetic and natural pyrites were oxidized to an efflorescence of hydrated ferrous sulphate (FeSO₄·H₂O) even at room temperature when kept open to the atmosphere for a few hours. This is contrary to the general belief that pyrites is stable in air⁶. The spontaneous oxidation product was FeSO₄·H₂O and not FeSO₄·7H₂O. This was verified by the DTA (curve IIB, Fig. 1) of iron pyrites containing ferrous sulphate (formed by aerial oxidation) in which the other characteristic peaks of FeSO₄·7H₂O were missing.

The maximum conversion of pyrites into ferrous sulphate was at 320-450°; this was supported by the strong exothermic trend and weight gain in the DTA and DTG curves, respectively. The X-ray lines (Fig. 3) also showed sharp change from 260 to 390°. At 260°, the lines characteristic of pyrites (d : 1.63, 2.71, 2.42; I : 100, 84, 66) were most intense, whereas at 390° those belonging to ferrous sulphate (d : 3.42, 4.85, 3.13; I : 100, 50, 38) became prominent and only a few weak lines of pyrites did appear.

The formation of γ -Fe₂O₃ (d : 2.52, 1.48, 2.95; I : 100, 53, 34) in the range 260-450° was due to the interaction of pyrites and ferrous sulphate. Safiullin⁴ reported that the interaction between natural pyrites and ferrous sulphate was appreciable at 600-800° to produce either ferrous ferric oxide or ferrous sulphide. However, in the present investigation, γ -Fe₂O₃ was obtained instead of ferrous ferric oxide (Fe₃O₄). Both the oxides are magnetic but only γ -Fe₂O₃ is soluble in dil. HCl. The solid oxidized samples at 390° and 450° were magnetic. The residue of these samples after boiling with dil. HCl was nonmagnetic and contained only iron pyrites. Moreover, the characteristic X-ray lines of Fe₃O₄ with proper relative intensities (d : 2.53, 1.48, 2.97; I : 100, 70, 60) were missing in the powder photographs. Hence, it is certain that the interaction of pyrites and ferrous sulphate produced γ -Fe₂O₃. This is an endothermic reaction accompanied by weight loss which might run parallel to direct sulphation of pyrites so that the resultant heat and weight changes in the temperature range 260-450° were not so pronounced. γ -Fe₂O₃ was converted to α -Fe₂O₃ by exothermic magnetic transition⁶.

The mechanism which explains the product distribution and thermal effects quite satisfactorily up to 450° may be explained in terms of the reactions (1-5). Sulphur dioxide was the only gaseous product up to 450° in the oxidation of synthetic pyrites. The formation of ferric sulphate (4.35%) up to this temperature was perhaps due to decomposition of ferrous sulphate by reaction (5). According to the stoichiometry of this reaction, 3.7% Fe₂O₃ would also be formed along with 4.35% ferric sulphate. Hence, the rest 16.36% Fe₂O₃ was definitely formed by reaction (3).

The values of free energy change (ΔG°) and heat of reaction (ΔH°) in kcal/mole refer to 25°. These values were calculated from the standard free energy and heat of formation of the substances¹⁵.

- (1) $\text{FeS}_2 + 3\text{O}_2 = \text{FeSO}_4 + \text{SO}_2$
 $\Delta G^\circ = -227.4, \Delta H^\circ = -250.0$
- (2) $\text{FeS}_2 + 5/2\text{O}_2 = \text{FeO} + 2\text{SO}_2$
 $\Delta G^\circ = -162.1, \Delta H^\circ = -163.1$
- (3) $\text{FeS}_2 + 5\text{FeSO}_4 + 3/2\text{O}_2 = 3\gamma\text{-Fe}_2\text{O}_3 + 7\text{SO}_2$
 $\Delta G^\circ = -16.5, \Delta H^\circ = +81.2$
- (4) $\gamma\text{-Fe}_2\text{O}_3 \rightarrow \alpha\text{-Fe}_2\text{O}_3$
- (5) $6\text{FeSO}_4 = \text{Fe}_2(\text{SO}_4)_3 + 2\text{Fe}_2\text{O}_3 + 3\text{SO}_2$
 $\Delta G^\circ = +25.5, \Delta H^\circ = +12.9$

The validity of the suggested mechanism is corroborated by the results in Table 3.

The solid phases at 520° contained α -ferric oxide (d : 2.69, 2.51, 1.69; I : 100, 80, 80) and ferric sulphate (d : 3.59, 6.08, 4.40; I : 100, 70, 70) together with small amount of ferrous sulphate. From the product distribution given in Table 1, it is clear that the total amount of ferrous sulphate and ferrous oxide were consumed within 560°. Sulphur trioxide was detected at 560° along with sulphur dioxide in the gas phase. These observations show that the decomposition of ferrous sulphate which started at 450° was complete at 560°; ferric sulphate [$\text{Fe}_2(\text{SO}_4)_3$], basic ferric sulphate ($\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$)^{1,14,16} and ferric oxide were identified as the products of decomposition. The exothermic peak at 650° and increase in weight up to 640° could be due to the reaction of ferric oxide, sulphur dioxide, and oxygen to form ferric sulphate³. This reaction also contributed for the formation of ferric sulphate up to

560°. The subsequent weight loss and endothermic peaks were due to the decomposition of both normal and basic sulphates.

The probable reactions in the temperature range 450-800° are:

- (6) $6\text{FeSO}_4 + 3/2\text{O}_2 = 2\text{Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{O}_3$
 $\Delta G^\circ = -8.0, \Delta H^\circ = -25.6$
- (7) $2\text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$
 $\Delta G^\circ = +26.8, \Delta H^\circ = +39.5$
- (8) $2\text{FeSO}_4 + 1/2\text{O}_2 = \text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$
- (9) $\text{FeO} + \text{FeSO}_4 = \text{Fe}_2\text{O}_3 + \text{SO}_2$
 $\Delta G^\circ = +5.2, \Delta H^\circ = +16.8$
- (10) $\text{Fe}_2\text{O}_3 + 3\text{SO}_2 + 3/2\text{O}_2 \rightleftharpoons \text{Fe}_2(\text{SO}_4)_3$
 $\Delta G^\circ = -130.1, \Delta H^\circ = -230.6$
- (11) $\text{Fe}_2(\text{SO}_4)_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 3\text{SO}_3$
 $\Delta G^\circ = +79.3, \Delta H^\circ = +160.1$
- (12) $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \rightleftharpoons \text{Fe}_2\text{O}_3 + 2\text{SO}_3$

The nature of decomposition of ferrous sulphate was further established from the DTA of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (curve IIC, Fig. 1) and from the products formed at different temperatures. The decomposition of ferrous sulphate to normal and basic ferric sulphates occurred at 450-560° followed by the decomposition of the normal and basic ferric sulphates at 650-800°.

Basic ferric sulphate (4%) was found in the temperature range 460-740°. The major portion of basic sulphate was formed by the decomposition of ferrous sulphate. The presence of basic sulphate even at 700° was detected by the following experiments: (i) synthetic pyrites was heated in air at 700° for 1 hr and the oxidized mass thoroughly washed with water to remove ferrous and ferric sulphates. The dried residue was burnt in nitrogen atmosphere at 1000° when sulphur trioxide was evolved. This is only possible by reaction (12). (ii) Sulphur trioxide was passed over ferric oxide at 700° for 30 min. when both ferric and basic ferric sulphates were formed.

Effect of partial pressure of oxygen — To study the effect of partial pressure of oxygen on the oxidation of pyrites, synthetic pyrites was heated in dry oxygen atmosphere up to 230° at the heating rate of 10°/min. Ferrous sulphate was the major oxidation product (64.1%). The oxidation in air under similar conditions yielded 55.0% FeSO_4 (Table 1). Thus, sulphation of pyrites is facilitated by an increase in the partial pressure of oxygen.

Effect of flow rate of air — The product distribution up to 450° was independent of the flow rate of air. This means that the sulphation of pyrites was independent of the flow rate. However, the decomposition of ferric sulphate was essentially over within 590° in a flow of air (6 litres/hr). This is evident from the absence of characteristic X-ray lines of ferric sulphate in the X-ray pattern of the sample at 590° prepared in dynamic air atmosphere. However, in static air the decomposition of ferric sulphate was complete at 760°. This was verified from the X-ray patterns of the sample at 590° and 650° prepared in static air atmosphere, in which the characteristic lines of ferric sulphate were

TABLE 3 — VALIDITY OF THE SUGGESTED MECHANISM (REACTIONS 1-5) UP TO 450°

Temp.	FeS ₂ converted ^(a) (% by wt)		Sulphur eliminated ^(b) (% by wt)		Reaction number
	Theor. ^(c)	Obs. ^(d)	Theor. ^(e)	Obs. ^(f)	
130°	15.1	14.0	8.3	9.0 (9.4)	1, 2
230°	49.1	50.9	28.4	27.5 (27.9)	1, 2
450°	95.0	98.2	66.1	67.2 (68.2)	1, 2, 3, 5

(a) Amount of FeS₂ (g) converted per 100 g of original FeS₂.

(b) Amount of sulphur (g) eliminated per 100 g of original sulphur.

(c) Theoretical amount (g) of FeS₂ converted per 100 g of original FeS₂ corresponding to the amounts of different products formed from FeS₂ by the stoichiometry of the reactions suggested. Calculated by finding out the theoretical amount (g) of FeS₂ which should react according to the suggested reactions for forming different products and expressing the conversion of FeS₂ as in (a) (see Appendix).

(d) Obtained by subtracting the amount of unconverted FeS₂ from the original amount of FeS₂.

(e) Sulphur which should be eliminated (as SO₂) corresponding to the amounts of different products formed following the stoichiometric equations (see Appendix).

(f) Sulphur equivalent to the amount of SO₂ actually evolved. Values in parentheses were obtained by subtracting the amount of sulphur present at any temperature from the total amount of sulphur present in FeS₂ originally.

present (Fig. 3). Some workers^{3,4} reported ferric oxide as the major oxidation product up to 500° under abundant air supply which is contrary to the present observation.

Effect of ferrous sulphate — The presence of the initial amount of ferrous sulphate (16.5%) in pyrites did not affect the nature of thermal curves and oxidation products. The remarkable influence of ferrous sulphate on the oxidation of pyrites was the lowering down of the temperature range for both the processes of sulphation and decomposition of sulphates. A comparison of the DTA curves IID and IIE in Fig. 1 would clarify this point.

Oxidation of natural pyrites — The thermal effects¹⁷ (Fig. 1, IIIC and Fig. 2) and nature of oxidation products of natural pyrites were similar to those of the synthetic sample. The oxidation proceeded mainly through the formation and decomposition of sulphates. Basic sulphate was present even at 850°.

The difficulty in the complete removal of sulphur from pyrites is generally attributed to the formation of solid solution of sulphur in iron. However, the present author feels that it is the presence of basic sulphate which decomposes only at high temperatures and that too at a slow rate, which makes the complete removal of sulphur from pyrites or pyrrhotite so difficult. The total removal of sulphur will render the calcine useful for iron metallurgy.

Effect of additives — It was, therefore, with the idea to see whether the presence of any foreign substance could in any way facilitate the total desulphurization of iron sulphides either by lowering the temperature range or by increasing the rate of the two fundamental processes, namely sulphation and desulphation. The effects of additives, V₂O₅, MnO₂, SiO₂, γ-Al₂O₃, Fe₂O₃, CaO and CuS, were studied by comparing the DTA curves of natural and synthetic pyrites with those of pyrites admixed with 10% additives. These results are not reproduced due to lack of space. It was found that vanadium pentoxide and pyrolusite facilitated the oxidation of both natural and synthetic pyrites. However, the influence of these additives were more prominent on the oxidation of synthetic pyrites. These additives could not help in the complete removal of sulphur from iron pyrites.

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APPENDIX

Sample calculation to show the theoretical amount of FeS₂ transformed at 230° as given in Table 3

Original amount of pyrites (FeS ₂)	= 0.970 g
Wt of FeSO ₄	= 0.495 g
Wt of FeO	= 0.0472 g

Amount of FeS₂ converted to FeSO₄ according to

$$\text{reaction (1)} = \frac{120}{152} \times 0.495 = 0.3968 \text{ g}$$

Amount of FeS₂ converted to FeO according to

$$\text{reaction (2)} = \frac{120}{72} \times 0.0472 = 0.0787 \text{ g}$$

Hence total amount of FeS₂ converted as per reactions (1) and (2) is:

$$= 0.3968 + 0.0787 = 0.4755 \text{ g}$$

$$\% \text{ FeS}_2 \text{ convert (by wt)} = \frac{0.4755}{0.970} \times 100 = 49.1$$

$$\% \text{ S in pyrites} = 53.01$$

Wt of sulphur originally present in pyrites

$$= 0.514 \text{ g}$$

Sulphur eliminated as per reaction (1)

$$= \frac{32}{152} \times 0.495 = 0.1042 \text{ g}$$

Sulphur eliminated as per reaction (2)

$$= \frac{64}{72} \times 0.0472 = 0.0419 \text{ g}$$

Total amount of sulphur eliminated

$$= 0.1042 + 0.0419 = 0.1461 \text{ g}$$

Theoretical (%) sulphur eliminated (by wt)

$$= \frac{0.1461}{0.514} \times 100 = 28.42$$

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