

TABLE III
PRODUCTS FROM THE OXIDATION OF ZINC DIMETHYL IN THE
EXPLOSIVE REGION

Reactants		Change in pressure after explosion, mm.	Gaseous products				
Pressure zinc dimethyl, mm.	Pressure oxygen, mm.		% CO ₂	% CO	% O ₂	% H ₂	% CH ₄
30	170	-69	43	1	44	12	0
50	150	..	19	22	37	19	3
80	120	..	4	30	21	42	3
120	80	..	2	31	14	22	30

still in the neighborhood of 15 mm. as the last entry in Table I shows. Because of the violence of the explosion, it was necessary to limit the total pressure. A set of runs at 200 mm. total pressure, with a constant partial pressure of 25 mm. zinc dimethyl (well above the minimum required) and varying proportions of butane and oxygen, is given in Table IV. Gas analyses were carried out and the results converted to partial pressures after explosion. (These data do not include condensable products such as water.)

TABLE IV
OXIDATION OF *n*-BUTANE WITH ZINC DIMETHYL IGNITION
200 mm. total pressure, 20°

Initial pressure, mm.			Total pressure change, mm.	Composition after explosion, mm.					
(CH ₃) ₂ Zn	<i>n</i> - C ₄ H ₁₀	O ₂		O ₂	CO ₂	CO	H ₂	Olef.	Par- af.
25	0	175	- 82	90	27	1
25	10	165	- 79	22	64	6	29
25	20	155	- 63	10	8	74	44
25	35	140	+185	8	4	181	193
25	50	125	+172	15	0	156	182	15	4
25	95	80	+ 53	25	0	91	96	18	23

These data clearly indicate that the oxidation of butane may be induced by the ignition of the zinc dimethyl, though the precise mechanism is in doubt. No other induced combustions by metal alkyls have been reported. The studies of Taylor and co-workers⁵ and Frey⁶ have shown that methyl radicals from decomposing metal alkyls can set up a chain reaction to induce "cracking" reactions with hydrocarbons, such reactions occurring at significantly lower temperatures than in the absence of radicals from the metal alkyls.

One may speculate that when the rate of formation of the solid product of zinc dimethyl oxidation becomes sufficiently high, such free radicals as CH₃, CH₃O and CH₃OO are liberated. These radicals then set up a chain in the zinc dimethyl-butane-oxygen mixture, with self-heating and explosion as a result. Attempts at a material balance make it clear that condensable liquid products are also present. The nature of these will require further investigation.

Acknowledgment.—The authors wish to acknowledge the assistance of Stanley S. Weiss in preparative work.

Summary

1. The oxidation of zinc dimethyl with oxygen in clean Pyrex bulbs has been studied. The effect of nitrogen, helium and *n*-butane as inerts on the slow oxidation have been determined.

2. It has been shown that the ignition of a hydrocarbon, *n*-butane, may be initiated by the explosive zinc dimethyl oxidation at room temperature.

(5) See, e. g., H. S. Taylor and Jones, *THIS JOURNAL*, **52**, 1111 (1932); Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

(6) Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

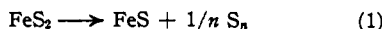
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Reactions of Iron Pyrite: Its Thermal Decomposition, Reduction by Hydrogen and Air Oxidation

BY GEORGE-MARIA SCHWAB AND JOHN PHILINIS

The thermal reduction of pyrite is said to begin at about 500°¹⁻⁵ and proceeds according to the equation



However, previous studies¹⁻⁹ have been rather

- (1) G. Marchall, *Bull. soc. chim.*, [4] **35**, 43 (1924).
- (2) L. d'Or, *Compt. rend.*, **190**, 1296 (1930).
- (3) L. d'Or, *J. chim. phys.*, **28**, 377 (1931).
- (4) I. N. Issakow, *J. Applied Chem.* (U. S. S. R.), **12**, 388 (1939); *Chem. Zentr.*, **111**, I, 2773 (1940).
- (5) W. S. Udinzewa and G. I. Tschufarow, *J. Applied Chem.* (U. S. S. R.), **14**, 3 (1941); *Chem. Zentr.*, **113**, II, 863 (1941).
- (6) A. F. Gill, *Can. J. Research*, **10**, 703 (1934).
- (7) G. Gallo, *Ann. chim. applicata*, **17**, 39 (1927).
- (8) R. Juza and W. Biltz, *Z. anorg. allgem. Chem.*, **205**, 273 (1932).
- (9) J. A. Hedvall and R. Hedin, *Die Chemie*, **56**, 45 (1943).

fragmentary and consequently little is known of the actual mechanism by which the decomposition occurs. To this end detailed investigations of the kinetics of the decomposition, which has been found to proceed with a conveniently measurable velocity in the range 600-650°, have been carried out.

The reduction with hydrogen takes place at a somewhat lower temperature, 500°, according to the equation



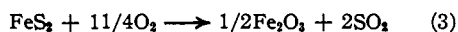
further reduction to metallic iron occurring only above 900°.^{7,10} Studies on the unknown kinetics

- (10) F. C. Thompson and N. Tilling, *J. Soc. Chem. Ind.*, **43**, T37 (1923).

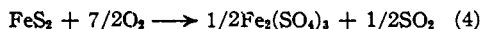
of this reaction were also conducted, with the particular purpose of ascertaining whether decomposition of the pyrite is a first step in the hydrogen reduction process.

In contrast to these reactions the roasting or air oxidation of pyrite is a highly complicated process, producing FeS , FeO , Fe_3O_4 , Fe_2O_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, S_2 , SO_2 , SO_3 , and possibly other products, for which Wendeborn¹¹ enumerates no less than sixteen concurrent reactions. Which of the products are formed in measurable quantities depends on the particular conditions under which the reaction is carried out. Because of this no clear-cut results for the kinetics of this important industrial process exist, although there are some data^{4,10,12-15} which will be discussed later.

By carrying out the reaction isothermally between 400 and 500° with abundant air admission and a large specific pyrite surface it was possible to limit the reactions to



and



and to study the reaction kinetics under these conditions.

Experimental

Materials.—A well crystallized specimen of pyrite from the mine Cassandra (Chalcidice) was freed from surface carbonates with hydrochloric acid, then from residues of silicic acid with a brush and finally was powdered to 0.01–0.1 mm. grain size and dried. Analysis of this material, which was used for all experiments, showed: Fe, 45.3%; S, 51.9%; Fe/S = 0.873 (calcd. for FeS_2 : 0.872); therefore 97.2% FeS_2 . Impurities consisted almost entirely of calcium and magnesium carbonates and silicates, along with traces of lead and arsenic compounds.¹⁴

Hydrogen and carbon dioxide were prepared in air-free Kipp generators and purified by passage over hot copper. Each gas was passed through a drying tower, a manostat and a flowmeter before entering the apparatus.

Apparatus.—In order to measure continuously the progress of the pyrite reactions a small, all-glass, magnetically operated, beam balance, which was enclosed entirely within the reaction system, was constructed. Details are shown in Fig. 1. Into the 28-mm. glass tube, A, a glass rod, a, was cemented with kaolin-water-glass. To this was cemented the T-piece, b, blown from thin glass. The horizontal section of b, which was half ground away to form a semi-cylindrical furrow, acted as the bearing for the pivots, c, which were very fine glass tips fused into hemispherical shape. The all-glass beam, B, contained at one end an index, d, moving before a fixed scale and at the other end some notches, e, for rider weights. The stop, f, limited the movement of the balance in either direction.

The samples of pyrite were placed in the Jena-glass basket, g, which was suspended from the balance beam by means of hooked glass rods. From the other arm of the

balance a closed glass vessel, h, filled with iron powder, was suspended in exactly the same way.

Weighing with this balance involves the measurement of the current required in the magnetic coil, i, to bring the index, d, to the zero point. For an apparatus of the size described the current amounted to about 0.01 amp./mg. The weight could be determined with a sensitivity of about 0.3 mg. during a run, but the reproducibility of absolute values was only ± 5 mg. because of displacements of the non-ideal bearing. The current was accurately regulated by the adjustment of mercury levels along immersed constantan wires.

Below the ground joint, C, the apparatus was constructed entirely of Jena glass. A 12-cm. zone containing the basket was surrounded by the electric furnace, D, the temperature being measured by the thermocouple, K. The reaction gas, or carrier gas in which the reaction took place entered at l and left at m.

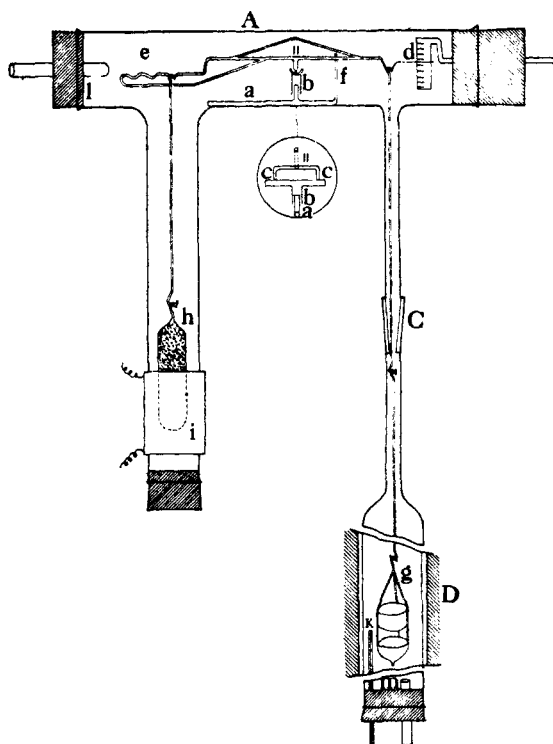


Fig. 1.

Experimental Determinations. (a) **Decomposition and Reduction.**—Determination of the weight loss of the pyrite during the course of a run was sufficient for following the progress of the decomposition and reduction reactions. For the decomposition experiments 745 mg. of pyrite was used in each case and carbon dioxide, which has been shown by Thompson and Tilling¹⁰ not to react with pyrite below 900°, was used as an inert carrier gas, its velocity being varied between 40 and 170 cc./min. The arrangement was exactly the same for the reduction experiments except that hydrogen gas instead of carbon dioxide was passed over the sample, its velocity ranging from 70–150 cc./min.

(b) **Air Oxidation.**—Preliminary experiments on the air oxidation of pyrite were carried out to determine whether the oxidation at 400–500° in

(11) H. Wendeborn, "Der Chemie-Ingenieur," Vol. III, 5, edited by A. Eucken and M. Jacob, p. 334.

(12) F. de Rudder, *Bull. soc. chim.*, [4] 47, 1225 (1930).

(13) O. Lunge, "Handbuch der Schwefelsaure-Fabrikation," 1st Ed., Vol. I, Braunschweig, 1916, p. 486.

(14) W. A. Rosenowitsch, *Betr. Lab.* (U. S. S. R.), 10, 484 (1941); *Chem. Zentr.*, 113, II, 2620 (1942).

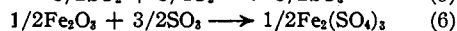
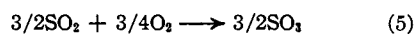
(15) K. M. Malin, *J. Chem. Ind.* (U. S. S. R.), 16, 4/5 (1939); *Chem. Zentr.*, 111, I, 612 (1940).

(16) We are indebted to the late Mr. Chalkiopoulos for the kind performance of these and numerous other analyses in the course of this work.

TABLE I
 ANALYSIS OF PRODUCTS FROM AIR OXIDATION OF PYRITE

Time, min.	<i>v</i>	<i>w</i>	<i>x</i>	<i>y</i>	<i>u</i> , calcd.	<i>u</i> , obs.	<i>s</i> , calcd.	<i>s</i> , obs.	<i>n</i>
A. 400°									
10	0.0533	0.0425	0.240	0.0402	0.0543	0.043	0.480	0.435	0.479 (1.93)
35	.124	.040	.442	.035	.109	.115	.337	.328	.517 1.66
50	.161	.0475	.563	.040	.143	.145	.269	.267	.541 1.64
100	.239	.085	.846	.065	.238	.270	.070	.055	.590 1.54
150	.218	.1175	.838	.097	.238	.253	.057	.050	.579 1.55
B. 450°									
10	0.050	0.0113	0.1715	0.0107	0.038	...	0.466	0.443	... (1.10)
25	.095	.015	.312	.0136	.072405	.392	... 1.41
50	.160	.020	.514	.0168	.115306	.276	... 1.15
80	.210	.0425	.697	.0335	.185157	.176	... 1.46
120	.240	.0725	.830	.055	.233089	.054	... 1.37
									Mean 1.47

an abundant supply of air was adequately described by equations (3) and (4), the latter possibly being the sum of



Samples of pyrite (2.4–3 g.) in porcelain boats were heated for measured times in an electric oven with a dry air flow of 160 cc./min. and then were analyzed. Two sets of reactions, one at 400° and the other at 450°, were run. The relative weight loss of the sample, *v*, the relative sulfur trioxide content of the solid product, *w*, the oxygen content exclusive of that in sulfur trioxide, *u* (found by subtracting the total sulfur and the iron, *f*, from the weight of the product), and the content of unburned sulfur, *s*, were determined. If equations (3) and (4) represent the stoichiometry of the reaction under these conditions, then *s* and *u* should have the following relations to *v* and *w*

$$u = \frac{3vw + 3w^2 - 3vw^2}{5w - 5vw}$$

$$s = \frac{8 + 24vw - 24(v + w)}{15 + 20vw - 5(3v + 4w)}$$

Also, if *x* is the amount of reaction by equation (3) and *y* is that according to equation (4), the following expressions should be valid

$$x = 3v + 2w - 2vw$$

$$y = w(1 - v)$$

The results obtained from these experiments are shown in Table I. It is seen that the results agree satisfactorily with the proposed reactions, if the accumulation of analytical errors brought about by the form of the mathematical relationships is taken into account. Moreover, by subtracting the iron bound by sulfur from the total iron, *f*, the mean half valency of the iron atoms forming oxide and sulfate can be determined. This mean value, shown in the last column of Table I, corresponds closely to the theoretical value for trivalent iron. In addition both the aqueous and hydrochloric acid extracts of the solid product react strongly

with $\text{Fe}(\text{CN})_6^{4-}$ and hardly at all with $\text{Fe}(\text{CN})_6^{3-}$. Also, Debye-Scherrer photographs of a series roasted to correspond with percentages of reaction ranging from 20 to 100 showed no signs of Fe_3O_4 , but only of Fe_2O_3 , hematite. Therefore equations (3) and (4) describe quite completely the behavior of pyrite when roasted under these experimental conditions and may be used as a basis for the evaluation of the kinetic studies.

For the kinetic studies, in which the all-glass balance was used, it was convenient to use the sulfur dioxide content of the exit gases as a determination in addition to the weight loss, instead of the quantities determined in the preliminary experiments, which could be measured only after interruption of the run. For this determination the exit gases, generally corresponding to an air flow of 100 cc./min., were passed through 10 ml. of 0.1 *N* sodium hydroxide colored with methyl orange by means of an arrangement like that of Schwab and Drikos.¹⁷ The time required to cause the methyl orange to change color was measured and then the solution was replaced by a fresh portion. The values obtained were taken as corresponding to the middle of the time interval required for the collection of the sample.

Since sulfurous acid reacts as a monobasic acid with methyl orange,¹⁸ a measured time interval, *t*, meant a rate of sulfur dioxide-formation (expressed as sulfur trioxide)

$$dg/dt = 0.08/t$$

grams of sulfur trioxide/minute. The method was of no great accuracy, partly because of a small sulfur trioxide content in the sulfur dioxide, but sufficient for our purposes.

To know the composition of the solid at any time the integral

$$g = \int_0^t (dg/dt) dt$$

(17) G. M. Schwab and C. Drikos, *Z. physik. Chem.*, **A185**, 405 (1940).

(18) F. P. Treadwell, "Analytical Chemistry," 5th edition, Vol. II, 1911, p. 489.

where g was the unbound sulfur, expressed as sulfur trioxide, was required. Fortunately, as is shown in Fig. 2, dg/dt was a linear function of time in all the experiments and hence the integration was easy. Because of this relationship the values of g could be determined with considerable precision even though the initial values of dg/dt were not known very accurately.

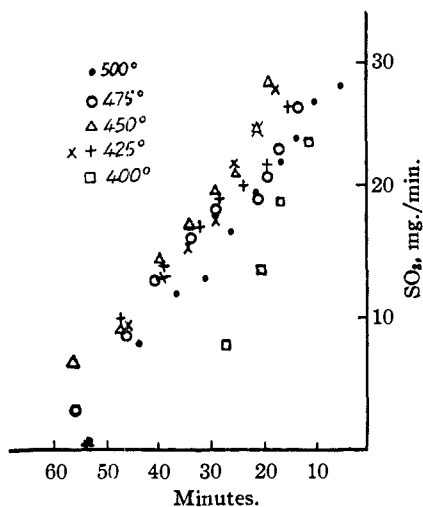


Fig. 2.

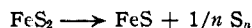
From the values of g obtained in this way the amounts of reaction according to equation (3), x , and according to equation (4), y , were evaluated by means of the relations

$$x = (5g + 20v)/12$$

$$y = (5g - 16v)/12$$

Results and Discussion

Thermal Decomposition.—The results obtained in the decomposition experiments for temperatures from 600 to 650° are shown in Fig. 3. The percentage decomposition was calculated from the observed weight losses on the basis of the equation



The first three curves, for which the individual observed points are shown, indicate the precision of the results. The other curves, all at 600°, have been separated by shifting the abscissa a hundred minutes for each successive curve. It is noted that the reaction proceeded quite rapidly even at 600° and at 650° it approached completion within an hour.

In agreement with Uchinzeva and Chufarow,⁵ no induction period was noted, indicating that—in contrast with many other reactions in the solid state¹⁹—a sufficient number of active spots, was present in the pyrite lattice from the start.

A striking phenomenon observed in all the reactions at 600° was the more or less distinct break in

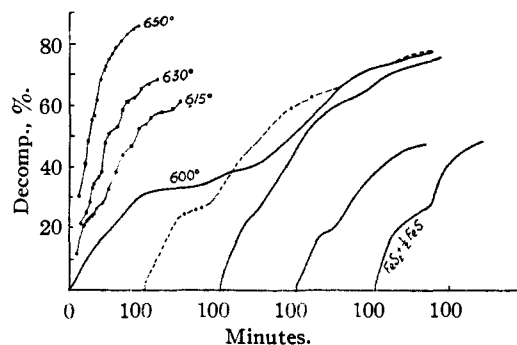


Fig. 3.

the rate between 20 and 30% decomposition. This phenomenon, which was also observed at 30% decomposition by Gill⁶ in similar experiments at 600°, was still noticeable at 615°, but only traces of it were visible at higher temperatures. The increase in the rate at this point cannot be attributed to a macroscopic interfacial catalysis caused by the ferrous sulfide formed, for a mixture of $\text{FeS}_2 + 1/2 \text{FeS}$ (the curve on the right in Fig. 3) showed the break at the point where 20–30% of the pyrite contained in it had been decomposed. Therefore the phenomenon must be localized within the secondary particles of the pyrite. In this connection Schwab and Karatzas²⁰ have shown that the phenomenon is accompanied by an increase in the catalytic activity of the solid residues on the decomposition of hydrogen peroxide.

Such a decomposition curve might be caused by the formation of intermediate sulfides like the Fe_3S_5 assumed by Gallo⁷ for the reduction by hydrogen, but X-ray studies on a series of partially decomposed specimens in the neighborhood of the point of acceleration showed no phases other than FeS_2 and FeS , in agreement with the findings of Juza and Biltz.⁸

According to Juza and Biltz the reaction is homogeneous up to 6% decomposition and then FeS separates to give a diphasic system. However, we found that in a sample which had undergone 18.5% decomposition at 580° no FeS phase could be detected even with the FeS_2 interferences much overexposed. Hence FeS must be much more soluble in the FeS_2 lattice at lower temperatures and it seems likely that the observed acceleration comes at the point at which the FeS , pyrrhotine, phase first appears. The velocity is presumed to increase at this point because of interface catalysis within the grains. Toward the end the velocity falls off again because the interfaces decrease.²¹

Equations for the quantitative kinetic evaluation of a reaction of this type have been devel-

(20) G.-M. Schwab and A. Karatzas, *Kolloid. Z.*, **106**, 128 (1944).

(21) Hedvall and Hedin⁹ observed that the decomposition rate of pyrite crystals was greater on cube planes than on octahedral planes and that this difference was most distinct at 600°. However, it would seem to require too detailed assumptions to account for a velocity change in a ground powder on the basis of this effect.

(19) "Handbuch der Katalyse" (Vol. IV and VI), edited by G.-M. Schwab, Julius Springer, Vienna, 1943.

oped,²² but the anomaly is not sufficiently distinct for reliable calculation of the constants required. However, for an estimation of the over-all activation energy the decomposition curves may be represented approximately by a first order curve. Except for the range of the anomaly the logarithm of the undecomposed fraction decreases linearly with the time until the reaction has proceeded to such an extent that the number of interfaces has decreased considerably. The logarithms of the first order constants determined in this way are shown in Fig. 4, plotted against the reciprocals of the absolute temperature. The values corresponding to 650° deviate from the Arrhenius relation, but if these be omitted, an activation energy of 29 kcal. is obtained for the initial period of the reaction and one of 33 kcal. for the final period of the reaction. These values can be attributed to the chemical process and not to a transport phenomenon, since alterations in the rate of flow of the carrier gas, carbon dioxide, between 40 and 170 cc./min. had no influence on the rate of decomposition. Therefore it is reasonable to assume roughly that the dissociation of a S_2^{--} ion together with the coordinated lattice destruction requires an activation energy of 30–40 kcal./mole.

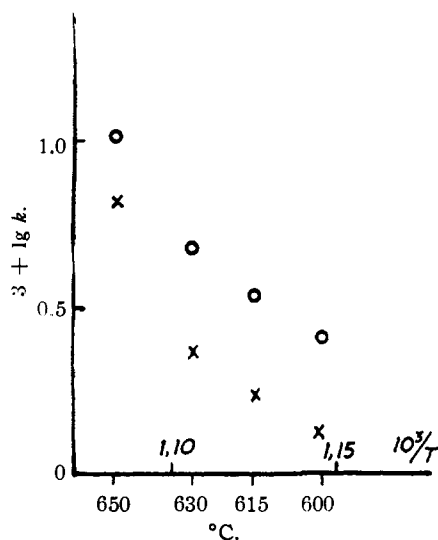


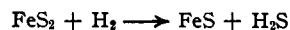
Fig. 4.—O, initial stage; X, final stage.

The only point difficult to understand is the statement of Uchinzewa and Chufarow⁵ that the decomposition is faster *in vacuo* than in the presence of nitrogen gas and that the rate decreases with increasing nitrogen pressure. This could only mean that, by analogy with non-ideal evaporation, in the presence of an inert gas only a fraction of the molecules escape from the surface. Marchall¹ does not mention such differences.

Reduction with Hydrogen.—The theoretical weight loss of our samples of FeS_2 , taking account

(22) See, for example, G.-M. Schwab, H. S. Taylor and R. Spence, "Catalysis," New York, 1937, p. 326 f.

of the non-reducible impurities, corresponding to the reaction



was 25.95%. A constant experimental end value of 24% was obtained at temperatures up to 550°, thus substantiating the statement of Thompson and Tilling¹⁰ that no further reduction to Fe occurs under these conditions.

The detailed results of the reduction experiments are shown in Fig. 5, in which $a - x$, the final weight loss minus that at time t , has been plotted logarithmically against the time. Not all of the experimental points have been included.

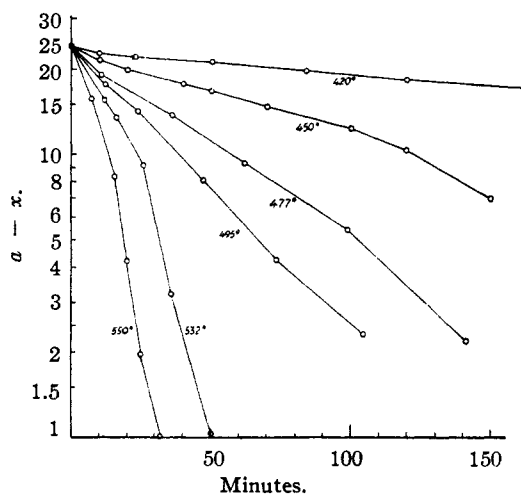


Fig. 5.

For all of the experiments the flow rate of the hydrogen, 70–150 cc./min. was more than ten times as great as the rate of reaction; hence no effects due to variation in flow rate were observed. Although the curves, except for the ones at 420 and 495°, show deviations from the straight lines characteristic of a first order reaction in the neighborhood of 60% decomposition, their approximate linearity allows interpretation of the reaction mechanism on a first order basis. In Fig. 6 the constants obtained from the mean slopes of these curves have been plotted logarithmically against the reciprocals of the absolute temperature and are seen to lie on a straight line, its slope yielding an activation energy for the reaction of 30 kcal./mole, constant over a 130° range.

Despite the closeness of this value to that previously found for the decomposition reaction, the rate-determining step in the reduction process cannot be the same as that for the decomposition, since the reduction proceeds at temperatures at least 100° lower. Consequently, the number of reaction occasions, given by the temperature independent factor of the Arrhenius equation, must be much greater for the reduction.

The experimental value of the temperature independent factor for the reduction by hydrogen, determined by extrapolation of the line in Fig. 6,

is $k_0 = 3 \times 10^6 \text{ min}^{-1}$. On the other hand, since under the experimental conditions of 500° and 760 mm. pressure a surface anion was hit by hydrogen molecules about 2×10^9 times per second, a theoretical collision factor of $k_0 = 5 \times 10^{10} \text{ min}^{-1}$ is obtained assuming that every surface anion was available for reaction. A difference is to be expected, for the experimental k_0 refers to the total mass of the reactant rather than to the surface anions. The two figures are in agreement if the fraction of surface anions is equal to the ratio of these quantities, 6×10^{-5} .

The figure may be tested by calculating the grain size necessary to produce such a ratio. A pyrite sphere of radius, R , containing z times the identity period of the lattice, $5.4 \times 10^{-8} \text{ cm.}$, has a fraction of surface ions

$$4\pi z^2 / (4/3)\pi z^3 = 3/z = 6 \times 10^{-5}$$

This gives $z = 5 \times 10^4$ and $R = 2.7 \times 10^{-3} \text{ cm.}$, equivalent to a grain diameter of 0.05 mm. Microscopic determination of the grain size gave 0.01 – 0.1 mm. It appears that hydrogen reacts indiscriminantly with all surface anions which have a minimum energy of 30 kcal. per mole in the moment of collision. This partly explains why the phase boundaries appearing above 20% reaction do not exert a catalytic effect on the reduction reaction as they do on the decomposition reaction.²³

In contrast the thermal decomposition does not by any means use all of the reaction opportunities. If all the vibrations of the critical bond, 10^{13} per second, contributed to the decomposition, k_0 would be of the order of $6 \times 10^{14} \text{ min}^{-1}$; even if only vibrations of surface ions resulted in dissociation, a value of $k_0 = 4 \times 10^{10}$ would be expected. Actually, extrapolation of the low temperature values in Fig. 4 gives $k_0 = 2 \times 10^5 \text{ min}^{-1}$. Thus, only a small fraction of the surface ions with the requisite activation energy is able to react. They are presumably those situated at active points or on phase boundaries, in agreement with the observed catalysis in the thermal decomposition when the new phase is formed.

Air Oxidation.—The preliminary tests described in the experimental part showed that in the range 400 – 500° with an abundant supply of air, oxidation of pyrite proceeds chiefly by reaction (3). Sulfate formation according to equation (4) amounted only to 12% of the oxide formation at the lower temperature and decreased with increasing temperature. Rates of oxide formation and of total reaction were found to be nearly independent of temperature.

(23) Properly speaking such calculations are only valid in the first stage of the reaction, because they presuppose free diffusion of FeS and FeS within the grain. However, the FeS shell formed, because of a 61% decrease in volume, is sufficiently porous to allow free access of hydrogen to the pyrite nucleus. The later decrease of the reaction rate is thus caused by a surface diminution of the nucleus rather than by a concentration decrease. The results show that this mechanism may be interpreted sufficiently well by the same first-order constant as that used for the monophasic initial stage. The calculations refer to the initial rate, but the information so obtained about the mechanism undoubtedly applies to the reaction in general.

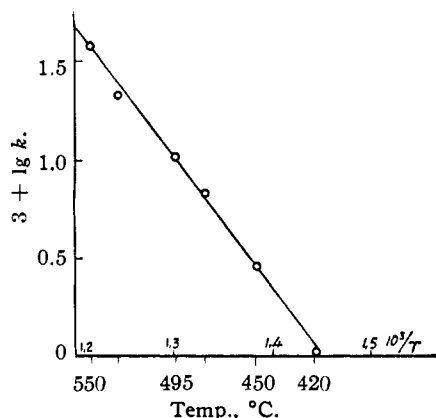


Fig. 6.

The experiments carried out on the special balance confirmed these results in greater detail. At all temperatures weight was lost at approximately the same rate, but reached a final value of 26% weight loss at 500° and only 7% weight loss at 400° . At temperatures below 475° a small maximum in weight loss, about 1% greater than the final value, was passed through before the final value was attained. If pure Fe_2O_3 were formed ($x = 1$) the weight loss should have been 33.3% ; formation of $\text{Fe}_2(\text{SO}_4)_3$ ($y = 1$) should have given a final weight increase of 66.7% . Weight losses corresponding to the former possibility were never attained, because of the large counterbalancing effect of even a small proportion of sulfate. However, the greater weight losses at the higher temperatures show clearly that sulfate formation was less significant under those conditions.

Values for the total amount of reaction and the amount of reaction according to equation (3), calculated from the observed data, are shown, plotted against the time of reaction, in Fig. 7. The horizontal lines drawn at the ends of the curves in these graphs represent values of x and of $x + y$ calculated from analyses of the final solid products for water-soluble sulfur and for HCl -insoluble sulfur. The analyses for soluble sulfate at 400 and 425° may be low because of the formation of water insoluble basic sulfates.²⁴

Calculations based upon the initial slopes of the curves in Fig. 7 at various temperatures show that an activation energy of only a few kilogram calories at most is involved. This indicates that the reaction rate is determined not by a chemical process, but by the rate of diffusion of the gas phase. Apparently the oxidation of pyrite proceeds very rapidly at the air interface, but oxygen diffuses slowly through the nitrogen-sulfur dioxide mixture contained in the pores of the oxide-sulfate layer formed on the surface.

The only previous kinetic evaluation of this re-

(24) Gmelin, "Handbuch der anorganischen Chemie," System No. 59 (Iron) Part B, p. 444.

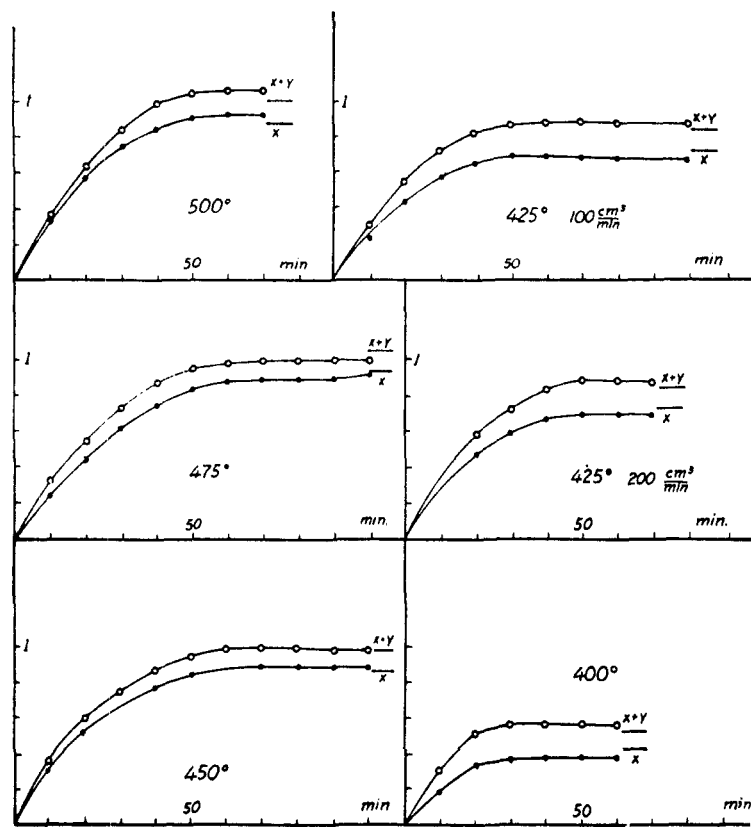


Fig. 7.

action was carried out by Malin,¹⁵ who gave the integrated equation

$$t = \frac{(R-r)^2}{PR_0e^{-A/RT}}$$

where R is the initial grain radius, r the radius at time t , P the oxygen pressure and k_0 and A are constants. This corresponds to the differential equation

$$-\frac{dr}{dt} = \frac{k_0PR_0e^{-A/RT}}{2(R-r)}$$

A theoretical kinetic equation can be developed as follows. Spherical pyrite particles of outer initial diameter $2R$ are assumed, the volume remaining unchanged during the oxidation except for the formation of a pore system. At time t , the unchanged pyrite core has been reduced to radius, r , and the oxide layer has a thickness, $R-r$. The density of oxygen in the gaseous phase is represented by s and its amount by m . Then the spherical analog of the second Fick equation gives

$$\left(\frac{ds}{dt}\right)_s = D \left(\frac{d^2s}{dx^2} + \frac{2}{x} \frac{ds}{dx}\right)$$

where D is the effective diffusion coefficient in the pore system and x is the coordinate in the r direction. For the stationary state $ds/dt = 0$. Solution of the equation for stationary diffusion at a fixed depth, $R-r$, using the marginal conditions $x=r, s=0$ and $x=R, s=S$, gives

$$\left(\frac{ds}{dx}\right)_{x=r} = \frac{SR}{r(R-r)}$$

This, substituted in the first Fick equation, the diffusion cross-section being $4\pi r^2 = Q$ at $x=r$, yields

$$-\frac{dm}{dt} = \frac{4\pi DSRr}{R-r}$$

for the reaction velocity as a function of r . The measured relative amount of reaction x may be substituted for m and r by means of the equations

$$x = 1 - r^3/R^3 = 1 - \frac{m}{(4/3)\pi R^3\sigma}$$

σ being the amount of oxygen in 1 cc. of reaction product. These substitutions give

$$\frac{dx}{dt} = \frac{3DS}{\sigma R^3} \frac{1}{(1-x)^{1/3} - 1}$$

an equation identical with one derived by Fischbeck²⁵ by using a "diffusion resistance," $1/D \int_R^r dr/Q$ and a "driving force," S , the chemical reaction velocity being assumed infinite. The integrated form of this equation is

$$1 - (1-x)^{1/3} - (2/3)x = \frac{2DS}{\sigma R^3} t \quad (I)$$

By substitution of dm/dt for dr/dt the equation of Malin¹⁵ previously discussed takes the form

$$\frac{dm}{dt} = 4\pi DSR \frac{r^2}{R-r}$$

which differs from the theoretical equation by a factor, r . In terms of x this equation becomes

$$\frac{dx}{dt} = \frac{3DS}{\sigma R} \frac{(1-x)^{2/3}}{1 - (1-x)^{1/3}}$$

which integrates to

$$1 + (1-x)^{1/3} - (1-x)^{2/3} = \frac{2DS}{\sigma R} t \quad (III)$$

The present experimental results can be formulated empirically on the basis of the equation

$$dx/dt = a - bt$$

since sulfur dioxide formation, dg/dt , was proportional to $d(x+y)/dt$ or dx/dt (which are approximately proportional to one another) and was linear with time. Integration and transformation of this yield

$$\frac{dx}{dt} = k(1-x)^{1/3}$$

which, on further integration leads to

$$1 - (1-x)^{1/3} = \frac{kt}{2} \quad (II)$$

(25) K. Fischbeck in "Der Chemie-Ingenieur," Vol. III, 1, edited by A. Bucken and M. Jacob, Leipzig, 1937, p. 308.

In Fig. 8 equations I, II and III have been compared with the experimental data at 475 and 500° by plotting the function, $f(x) = kt$ against t for each of the equations and temperatures. Values from equation I have been multiplied by three so that in all three cases the final theoretical value for $x = 1$ is $f(x) = 1$. Neither equation I nor Malin's equation, III, conforms with the data, since they give S-shaped curves rather than straight lines. In the integrated form only the empirical equation, II, corresponds with the results, giving an approximate straight line which bends rather sharply to the final value. (Equations I and III show an even poorer correspondence in the differential form, yielding curves strongly convex to the time axis, instead of straight lines.)

It is not surprising that the theoretical equation, I, should not hold, for simplifying assumptions were made in its derivation. Such factors as dispersity of grain size, deviations from sphericity, swelling or contraction of the grains, changes in gas composition in the pores, and changes in the size of the pores as the reaction proceeds would all limit greatly the validity of the equation. Although it is difficult to establish the exact cause of the deviations observed, it is of interest to attribute the deviations entirely to changes in pore size, which is equivalent to an alteration in the diffusion cross-section, Q , and to consider the implications of this.

If, following Fischbeck,²⁵ the empirical equation

$$\frac{dm}{dt} = \frac{S}{1/D \int_R dr/Q}$$

be accepted, then equation II predicts $Q \sim r^2 \sqrt{r}$ and Malin's equation, III, gives $Q \sim r^2 [r/(2R - r)]$. Both expressions indicate a more rapid diminution in the mean cross-section than would be the case with spherical particles of uniform size ($Q \sim r^2$).

Such a pore closing does in fact occur, for the reaction never attains 100% completion, stopping at $x = 0.9$ at 500° and as low as 0.4 at 400° (Fig. 8). Apparently sulfate formation, favored at lower temperatures, closes the pores. Actually, by conversion to $1/2\text{Fe}_2\text{O}_3$ the molecular volume of pyrite decreases by about 37%, whereas by conversion to $1/2\text{Fe}_2(\text{SO}_4)_3$ the volume increases by about 161%. Hence the former process would result in the formation of pores and the latter in closing them. If just 18.5% of the reaction were sulfation, no pores should be formed, a condition which may very well obtain in the outer layers toward the end of the reaction.

An absolute value for the reaction velocity can be obtained only from the theoretical equation, I, in spite of its failure to fit the experiments exactly. An approximate application of this equation to the curves of Fig. 8 gives

$$k = 2DS/\sigma R^2 = 0.003 \text{ min.}^{-1}$$

By definition S/σ is the ratio of the spatial density

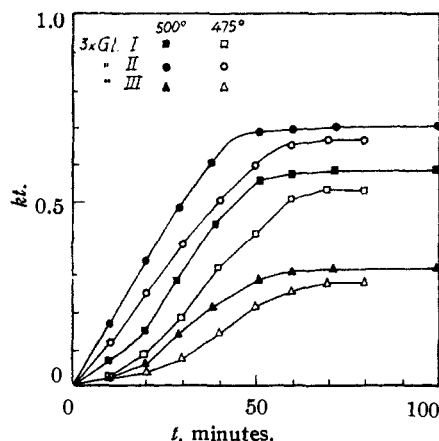


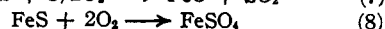
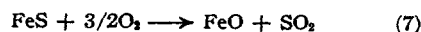
Fig. 8.

of oxygen in the gas phase to that in a porous iron oxide structure isosteric to pyrite. It is found to be 10^{-4} from the gas laws and the density of pyrite. Since R^2 has been shown to be 5×10^{-5} sq. cm., the effective diffusion coefficient calculated from the previous equation is 7.5×10^{-4} sq. cm. $\text{min.}^{-1} \approx 10^{-5}$ sq. cm. sec.^{-1} .

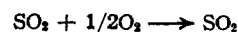
The diffusion coefficient of oxygen in nitrogen-sulfur dioxide mixtures is of the order of 10^{-1} sq. cm. sec.^{-1} . Hence it was depressed under the experimental conditions about 10^4 times, indicating that the porosity of the reaction product was very low.²⁶ This may be attributed either to small pore diameter or to a small number of pores, but in either case it helps to explain the phenomenon of pore-closing.

Oxidation of Ferrous Sulfide.—In order to determine whether the oxidation of ferrous sulfide comprises one step in the roasting of pyrite, a few oxidation experiments with ferrous sulfide were carried out in the same way as the pyrite combustion experiments. Because the results were very similar to those obtained with the pyrite, only a summary is presented.

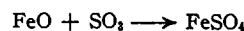
The maximum weight loss corresponding to the formation of pure ferrous oxide amounts to 18.2%. At 500° the weight loss observed was 17.2%, at 425° was 2% and at 400° was negative, -1.1%. These changes correspond to increasing amounts of sulfate at the lower temperatures. Analysis of the final product showed that the iron to sulfate ratio in the iron sulfate formed corresponded to FeSO_4 . The main reactions may thus be represented by the equations



the latter possibly being the sum of



and



(26) K. Zimens, "Handbuch der Katalyse," Vol. IV, edited by G.-M. Schwab, Vienna, 1943, p. 151.

As in the combustion of pyrite the rate of sulfur dioxide production varied linearly with the time. Maxima in the weight loss curves were again observed. Also as with pyrite the rate of oxide formation did not change with the temperature between 425 and 500°. Pore closing was again observed, for the reaction stopped at $x = 0.7$ at 500° and at $x = 0.45$ at 400°. Sulfate formation amounting to 15.5% should just prevent pore formation in this case.

Application of equations I, II and III to this reaction gave results similar to those obtained with pyrite. Evaluation of the absolute reaction velocity by means of equation I gave $k = 0.0017 \text{ min.}^{-1}$ and S/σ were found to be 1.2×10^{-4} . Hence D is of the same order of magnitude as in the oxidation of pyrite and the analogy between the two reactions is complete. The question as to whether ferrous sulfide is an intermediate in the oxidation of pyrite cannot be determined from these experiments, for both phenomena are diffusion processes controlled as to rate by geometry, their chemical mechanisms being inaccessible because of their great rapidity.

Summary

The thermal decomposition, reduction by hydrogen and air oxidation of iron pyrite and the air oxidation of ferrous sulfide have been investigated kinetically by measuring continuously the weight losses of the solids during the course of the reaction with an all-glass balance enclosed within the apparatus. The course of the air-oxidation

reactions was further followed by measurements of the sulfur dioxide produced and by analyses of the final solid products.

The thermal decomposition of pyrite begins at the homogeneous surface, proceeding at active spots until at about 20% reaction ferrous sulfide separates as a new phase. The phase boundaries thus formed cause an autocatalytic acceleration of the reaction at temperatures below 615°. An activation energy of 30 kcal. per mole or more is required.

The rate of reduction of pyrite by hydrogen is proportional to the fraction of pyrite remaining to be reduced and has an activation energy of 30 kcal. per mole. All surface anions hit by hydrogen molecules and possessing the requisite activation energy react.

The air oxidation of pyrite yields largely ferric oxide along with small quantities of ferric sulfate which amount to about 10% of the reaction product at 400° and decrease with increasing temperature. The rate of the reaction is almost independent of temperature between 400 and 500° and apparently is controlled by the rate of diffusion of oxygen through pores in the ferric oxide layers produced. Formation of sulfate tends to close the pores and stop the reaction short of completion.

The air oxidation of ferrous sulfide proceeds kinetically in exactly the same way as the air oxidation of pyrite. The principal product is ferrous oxide, along with some ferrous sulfate.

ATHENS, GREECE

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The Nature of Precipitated Sodium Fluoaluminates

BY J. M. COWLEY AND T. R. SCOTT

Introduction

In a study of the complex fluorides of aluminum, Brosset¹ has described, *inter alia*, the preparation and crystal structure of the alkali fluoaluminates precipitated from aqueous solutions. Although both penta- and hexa-fluoaluminates of potassium were characterized, he found no evidence for the existence of corresponding sodium salts other than cryolite (Na_3AlF_6). In both instances the hexa-fluoaluminates were deficient in alkali fluoride, which was replaced by water. Nikolaev,² however, has described the preparation of a compound, approximating in composition to chiolite ($5\text{NaF}, 3\text{AlF}_3$); by the addition of stipulated quantities of sodium sulfate and hydrofluoric acid to aluminium fluosulfate solutions, while Yatlov³

has cited analyses for compounds having the formulas $\text{NaAlF}_4 \cdot \text{H}_2\text{O}$ and Na_2AlF_6 , produced by the partial neutralization of solutions of "fluoaluminic acid" (H_3AlF_6) with sodium carbonate. Reference to "pseudo-cryolite" ($\text{NaAlF}_4 \cdot n\text{H}_2\text{O}$) has been made by Caglioti,⁴ who claims that "the structure . . . is identical with that of cryolite save for a slight widening perpendicular to the c axis."

In an attempt to clarify the position, the work described in the present paper has been undertaken. Compounds obtained by methods similar to those of Nikolaev and Yatlov have been analyzed and the crystal structure determined by X-ray diffraction methods.

Experimental

All materials used in the preparation of the sodium fluoaluminates were of A. R. grade, with the exception of Laboratory Reagent aluminum metal used for the prepara-

(1) Brosset, "Electro-chemical and X-Ray Crystallographic Investigation of Complex Aluminium Fluorides," Stockholm, 1942.

(2) Nikolaev, *J. Chem. Ind. U. S. S. R.*, **14**, 1087 (1937).

(3) Yatlov, *J. Gen. Chem. U. S. S. R.*, **7**, 2439 (1937).

(4) Caglioti, *Chim. industria Italy*, **20**, 274 (1938).