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[F O U R T H S E R I E S .]

ART. XXXII.—*The Stokes Method for the Determination of Pyrite and Marcasite*; by E. T. ALLEN and J. L. CRENSHAW.

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I. DEMAND FOR THE METHOD.

THE question whether a given specimen is pyrite or marcasite, in the case of well-crystallized natural material, will seldom arise; color and crystal form are generally sufficient criteria. For doubtful cases, which are more liable to be met with in synthetic products, few reliable tests exist, and for estimating either in mixtures with the other, the Stokes method is the only one known.

In a recent investigation by the authors, on the genetic conditions of certain allotropic forms, such a method became essential. We had already made some use of the Stokes method for identifying synthetic products, but had never carefully tested its accuracy. This has now been done; two serious sources of error have been detected and obviated, and some facts and relations of much more general interest have been discovered and worked out, in connection with it.

II. THE STOKES METHOD.*

The Stokes method depends on the difference in the behavior of the two minerals when boiled with a standard solution of ferric sulphate. The reaction takes place in two stages, thus:

Both minerals give the same products, viz., ferrous salt, sulphur and sulphuric acid; their difference is manifested in the relative *quantities* of the products, for experiment shows that about 52 per cent† of the sulphur in pyrite is oxidized to sulphuric acid, while only about 12 per cent of the sulphur in marcasite is oxidized. This behavior is not entirely unique. Penfield‡ found that concentrated nitric acid dissolved pyrite completely (i. e., all the sulphur is oxidized), while it leaves with marcasite a copious residue of sulphur. More recently, Arbeiter§ has made a long series of careful experiments with hydrogen peroxide and hydrochloric acid, in which he finds that marcasite always gives more free sulphur than pyrite under the same conditions. As the reagents are diluted the relation between the sulphur oxidized and the sulphur liberated approaches a simple constant ratio characteristic for each mineral. Arbeiter very plausibly infers that these phenomena are dependent on a difference in constitution between pyrite and marcasite.

To identify either pyrite or marcasite, Stokes determined the percentage of sulphur which was oxidized by a standard ferric sulphate solution. Before proceeding to show how the composition of a mixture of the two is determined, it will be best to explain the chemistry of the process in greater detail. The standard ferric alum solution, which contains close to 1 g.

* H. N. Stokes, Bull. U. S. Geol. Survey, 186.

† The numbers vary somewhat in different natural specimens. The numerical data here and in the sequel belong to a pyrite from Roxbury, Connecticut. Stokes' values were 60.5 and 16.5-18.0 for pyrite and marcasite respectively. These variations will be discussed farther on.

‡ Brush and Penfield, Determinative Mineralogy, 15th ed., p. 252.

§ Min. Chem. Untersuch. an Markasit, Pyrit und Magnetkies. Inaugural Dissertation, Breslau, 1913.

of iron and 5 g. free sulphuric acid per liter, is always used in the same quantity, 250^{cc} in each experiment. The sulphide, finely ground and purified, is used in large *excess* (about 1 g.). The water of the solution is kept constant by a reflux condenser, while the influence of atmospheric oxygen is prevented by a stream of moist carbon dioxide which traverses the apparatus during the process. At the end of the test the ferric iron of the solution should be entirely reduced, partly by iron and partly by sulphur. A quantity of iron in the ferrous state which is constant for each mineral has passed into solution and a constant percentage of the sulphur has been oxidized. From the iron dissolved in our own experiments, we calculate that about 155 milligrams of marcasite are required in the reduction of 250^{cc} of the standard solution, while only about 65 milligrams of pyrite are required for the same work. This of course is due to the fact that far less of the sulphur in marcasite is effective in reduction, nearly 90 per cent of it being precipitated in the free state. The complete data are given in the footnote.*

A. *Formula for the percentage of sulphur oxidized.*—Stokes determined directly the iron dissolved by the ferric salt, and calculated stoichiometrically the percentage of sulphur which was oxidized. Similarly, the percentage of sulphur oxidized in unknown *mixtures* of the two sulphides was estimated by him experimentally and a curve plotted which was used to determine their composition. The formula for the percentage of sulphur oxidized or the “oxidation coefficient” of either sulphide or of any mixture of the two was derived directly from equations *a* and *b*, viz. (1) $p = \frac{8.33b}{c-a} - 25$, where

* I. Pyrite. The increase of iron in solution after reduction with pyrite was equivalent to 4.46 g. KMnO ₄ solution per 100 ^{cc} , or for 250 ^{cc} .		
2.5 × 4.46 × .001544 (value of KMnO ₄ solution) = KMnO ₄	0.0172 g.	
Equivalent to Fe	.0304 g.	
Equivalent to FeS ₂	.0652 g.	
Total sulphur in .0652 g. FeS ₂	.0348 g.	
Fe reduced by Fe (see equation <i>a</i>)	.0608 g.	
Fe reduced by S, 0.2500 — .0608	.1892 g.	
S reducing Fe, or S oxidized (see equation <i>b</i>).....	.0181 g.	
Percentage of S oxidized $\frac{.0181}{.0348}$	52.2%	
II. Marcasite. The increase of iron in solution after reduction with marcasite was equivalent to 10.57 g. KMnO ₄ solution per 100 ^{cc} .		
Hence 2.5 × 10.57 × .001544 = KMnO ₄	0.0408 g.	
Equivalent to Fe	.0721 g.	
Equivalent to FeS ₂	.1546 g.	
Total sulphur in 0.1546 g. FeS ₂	.0825 g.	
Fe reduced by Fe (see equation <i>a</i>).....	.1441 g.	
Fe reduced by S, 0.2500 — .1441	.1059 g.	
S reducing Fe, or S oxidized (see equation <i>b</i>).....	.0101 g.	
Percentage of S oxidized $\frac{.0101}{.0825}$	12.3%	

p = the percentage of sulphur in the decomposed sulphide which is converted into sulphuric acid; b is the ferrous iron at the end of the experiment originating both from the reduction of the ferric salt and from the decomposition of the iron disulphide; c is the total iron, ferrous and ferric,* at the end of the experiment; while a is the iron originally present in the standard solution. Our experiments soon showed that the reaction normally proceeds to the complete reduction of the ferric salt; b and c are therefore identical. Hence $p = \frac{8.33b}{b-a} - 25$,

or better written, since b is variable, (2) $p = \frac{8.33x}{x-a} - 25$.

B. *Relation of the iron dissolved to the composition of the mixture.*—A simpler relation than this and one more satisfactory in estimating the quantities of pyrite and marcasite in a mixture of the two is obtained by comparing directly x , the total quantity of iron in solution at the end of the test, with y , the percentage of pyrite in the sulphide mixture. Some results obtained by us before any such relation was suspected, indicated, when plotted in this way, a rectilinear relation; only the mixtures lowest in pyrite deviated much from a straight line (see fig. 1). Stokes concerned himself only with the relation between the composition of the sulphide mixture and the percentage of sulphur oxidized, but when his results are put into the same form they confirm our own. Table 1 gives the values of x , the total iron in solution at the end of the test, calculated by means of equation (2) from Stokes' published values of p . Our own value for a was used. a is the concentration in iron of the standard ferric solution. Both x and a are given in terms of a standard permanganate solution, 1 g. of which contained .001544 g. KMnO_4 ; and 100° of the ferric solution, measured at 25°, required 36.71 g. of this solution to oxidize it after reduction by sulphur dioxide. In fig. 2, Stokes' values for $(x - a)$, the iron dissolved by 100° of the standard ferric solution from pyrite-marcasite mixtures, are plotted against y , the percentage of pyrite which they contained. Here also the points fall into a nearly straight line, excepting those which stand for mixtures low in pyrite.

1. *Cause of the deviation of the values of x from a straight line.*—It seems decidedly probable that the low values for x in mixtures which contained 75%–100% marcasite were due to some disturbance in the reaction. This hypothesis would simply mean that the chemical action of the ferric solution on each sulphide in the mixture was proportional to its surface; that each sulphide acted independently of the other; and that the

* Stokes did not get a complete reduction of the standard ferric solution.

deviation in the line indicated that, in those mixtures where it occurred, the surfaces of the two minerals were no longer proportional to their weights. There was in fact some positive ground for this view, since it had already been noted by Stokes that marcasite was inclined to *flocculate* during the oxidation

FIG. 1.

FIG. 1. Curve showing iron dissolved from pyrite-marcasite mixtures by a standard ferric solution. (Former results.)

tests. Flocculation would of course reduce the surface of the finely powdered marcasite, and if the pyrite were unaffected, the results would indicate too much pyrite, which as the reader may see, is exactly the direction of the errors in figs. 1 and 2. Many ways were tried to obviate the difficulty, but the only

TABLE I.

Stokes' values for α , the total iron in solution, and $(\alpha - a)$, the iron dissolved from pyrite-marcasite mixtures by ferric sulphate solution.

Percent Pyrite	p = percentage of sulphur oxidized (experimentally determined)	α cal. from p by equation (2)	$(\alpha - a)$ (the iron dissolved) $a = 36.71$
100	60.5	40.68	3.97
95	52.9	41.11	4.40
90	48.9	41.38	4.67
80	40.3	42.08	5.37
60	29.0	43.41	6.70
40	22.3	44.58	7.87
20	17.1	45.78	9.07
10	15.2	46.33	9.62
5	16.0	49.09	9.38
0	18.0	45.54	8.83

one which proved of any value was to shake the ferric solution and sulphide together with coarsely powdered quartz* and beads by means of which the lumps of sulphides were thoroughly ground up. Some details may make the operation clearer to the reader. The 500^{cc} boiling flask used in the oxidation experiments was fitted to a rubber stopper through which passed the reflux condenser (the cooling jacket of which was 20^{cm} in length) and a glass tube reaching to the bottom of the flask through which the carbon dioxide entered. 250^{cc} standard ferric alum solution with 2 g. quartz and about fifty beads of Jena glass were then added. The solution was now freed from air by boiling for ten minutes in the stream of carbon dioxide, and then cooled for fifteen minutes while the gas was still passing. Stokes' device for introducing the sulphide was used, viz., a small glass bucket suspended above the liquid by a platinum wire which passed up through the condenser. After the sulphide had been purified and dried for an hour in a vacuum desiccator, as shown farther on, it was quickly removed and poured into the bucket, the bucket attached to the platinum wire, and the flask again closed. The solution was now brought to boiling, while the bucket remained suspended above the liquid. Finally the bucket was dropped by drawing out the wire and the flask vigorously rotated for five or ten minutes, or until the powder seemed to fill the liquid and so remained, neither floating on the surface nor sinking to the bottom. The boiling was continued for two hours, when the ferric iron should be entirely reduced.

* This quartz contained only 0.04 per cent of oxides other than silica.

In some instances, for some unknown reason, the solution would fail to wet the sulphide satisfactorily, and the results would then be unsatisfactory.

(a) *Explanation of the low results with pure marcasite.*—The abnormal results for the sulphide mixtures low in pyrite

FIG. 2.

FIG. 2. Stokes' results on iron dissolved ($x-a$) from pyrite-marcasite mixtures by a standard ferric sulphate solution. The values for x are calculated from Stokes' published values for p , the percentage of sulphur oxidized.

are very well accounted for, as we have seen, on the supposition that the reactive surface of the marcasite is reduced by flocculation. In mixtures which contain 25 per cent or more of pyrite, flocculation rarely if ever occurs. Marcasite alone, however, gives somewhat too low results for the iron dissolved

($x-a$) unless it is shaken with quartz. Here, to be sure, there is no pyrite to compete with the marcasite in the reduction of the ferric salt, but it is not improbable that the sulphur which is set free might act as a competitor to the marcasite, so that less iron would dissolve in case the marcasite surface were diminished by flocculation. Stokes found, it is true, that ordinary powdered sulphur had scarcely any effect on the ferric solution and we have confirmed his results. From this it appears that such oxidation of the sulphur as normally occurs in the Stokes reaction is probably contemporaneous with the solution of the iron (see equations a and b , p. 372). Still the particles of separated sulphur are doubtless at first very small, and if the surface of the marcasite should become much reduced by flocculation, the slow reducing action of the sulphur might cease to be negligible. At any rate, our value for ($x-a$), the quantity of iron dissolved, was only 10.30 without quartz, and this value rose to 10.57 and 10.58 when quartz was used.

(b) *The necessary excess of the sulphide.*—We have found one other important source of error in the application of the Stokes' reaction which must be discussed before our final results are presented, viz., the quantity of sulphide which must be used. It will be recalled that 250^{cc} standard ferric solution is taken in each test, and that the quantity of the sulphide must be such as to reduce completely all the iron (250 mg.) present. If reproducible results are to be obtained, the excess of sulphide must be considerable. 0.75 g. gives virtually the same results as 1.0 g. for all mixtures containing 25 per cent of pyrite or more, but for other mixtures and for pure marcasite as much as 1 g. should be used. It will be noted on p. 373 that it takes much more marcasite than pyrite to reduce a given quantity of ferric iron. The ratio as determined by us is 2.37:1,* while Stokes found 2.26:1. The discussion of the relation between weight per cent and surface per cent given on p. 381 shows why the use of weights of the sulphides which are but little in excess of the quantity actually decomposed by the solution, would result in error, for in that case the *surface percentage*, which is the all important matter, would vary decidedly during the reaction, while in the ideal case it should be constant. It may be seen from the table (Table II) that the same results were obtained whether 1.5 g. or 1.0 g. marcasite was taken, and the same is also nearly true for pyrite. Stokes states that the fineness of the sulphide makes no appreciable difference in the results. We have never found any systematic

* This is the ratio between the constants for marcasite from Joplin, Mo., and pyrite from Roxbury, Conn.; the ratio for the *purest* natural minerals is about 2.5:1.

difference due to the time of grinding, though marcasite was repeatedly tested after grinding from 2 to 5½ h., pyrite from 1 to 2 h., and synthetic products from 1 to 2 h. It seems, therefore, to be true that after a sufficient excess of the sulphide is reached the results are unchanged by increasing the surface further, though more work would have to be done before this statement could be made unqualifiedly.

TABLE II.

Showing the relation between the composition of the sulphide mixture, the iron dissolved, and the sulphur oxidized.*

Per cent pyrite	(x - a) = iron dissolved			x	p = per cent of sulphur oxidized
	0.75 g. sulphide	1.0 g. sulphide	1.5 g. sulphide		
100	4.40	4.46	4.59	41.17	51.9
85	5.35	----	----	42.06	40.5
75	6.08	----	----	42.79	33.6
60	----	7.04	----	43.75	26.8
50	7.67	----	----	44.38	23.2
45	----	7.94	----	44.65	21.9
35	----	8.48	----	45.19	19.5
25	9.06	9.07	----	45.77	17.1
17	----	9.54	----	46.31	15.5
10	----	9.95	----	46.66	14.1
5	9.40	10.27	----	46.98	13.1
0	10.30	10.58	10.57	47.28	12.2

For all our work on either natural or synthetic products we have taken 1.05 to 1.1 g. and ground with water for 2 h. The sulphide is then removed from the mortar with a "policeman," filtered in a porcelain Gooch crucible on a hardened filter disc and kept in a vacuum desiccator till the next morning, when 1 g. of it is weighed out, boiled with dilute hydrochloric acid, poured on to a new hardened filter and finally washed, first with dilute hydrochloric acid and then with boiled water cooled in carbon dioxide. The washing is done in a special apparatus in which an atmosphere of carbon dioxide free from oxygen is maintained, for the details of which a former paper should be consulted.† *In these operations the total loss of material should be only a few centigrams.* If it is considerable

* The pyrite used was from Roxbury, Conn., and the marcasite was from Joplin, Mo.

† Allen, Crenshaw and Johnston, this Journal, (4), xxxiii, 169, 1912; Zs. anorg. Chem., lxi, 201, 1912.

from any cause, the results will be unsatisfactory for mixtures containing less than 25 per cent pyrite. Ignorance of this fact cost us much time in one stage of our work.

2. *Results on mixtures of the natural minerals.*—When the above precautions were carefully followed, we obtained the

FIG. 3.

FIG. 3. Iron dissolved ($x - \alpha$) from pyrite-marcasite mixtures by a standard ferric sulphate solution. Revised results. oo Results obtained by shaking with quartz. xx Results obtained without quartz. The pyrite was from Roxbury, Conn.; the marcasite from Joplin, Mo.

results given in Table II and graphically presented in fig. 3. It is evident that we have here a sensibly linear relation between the iron dissolved and the composition of the mixtures

reckoned in weight per cent, but before we consider in detail the meaning and accuracy of the results, it will be best to put the method on a safer footing by examining all other possible sources of error which we could discover.

3. *Other sources of error in the Stokes method.*

(a) *The ratio of the surfaces of the two minerals in weight percentage mixtures.*—In the first place if the active mass of each sulphide depends on its surface rather than its weight, as it should for solids, it will be obvious to the reader that the relation between $(x-a)$ the iron dissolved in the Stokes reaction, and y , the percentage of pyrite in the sulphide mixture, cannot be strictly linear in weight percentage mixtures, because the minerals naturally differ a little in density. They are of nearly the same hardness, and assuming that both are brought to the same degree of fineness when they are ground together, the percentage of surface of the marcasite, the lighter mineral, would be somewhat greater than its percentage by weight. Suppose that a mixture containing 50 per cent of each mineral by weight when ground in water,* consists of spherical particles of uniform size; then

$\frac{n_1}{n_2} = \frac{S_m}{S_p} = \frac{5.03}{4.89}$, where n_1 = the number of particles of marcasite, n_2 = the number of particles of pyrite, and S_m and S_p the total surface of the two minerals respectively. The ground mixture of the minerals in equal quantities would therefore contain only 49.3 per cent instead of 50 per cent pyrite surface. This error, however, is approximately compensated, under the conditions described, by the more rapid action of the ferric solution on the marcasite particles. If all the particles are of the same size, those of each mineral must be uniformly attacked, and assuming the action of each is independent of the other, the *final surface of the marcasite* would be $s_m = n_1 4 \pi R_1^2$, and the *final surface of the pyrite* would be $s_p = n_2 4 \pi R_2^2$, where R_1 and R_2 are the radii of the particles of the two minerals at the end of the oxidation. It follows from the above that the final weights of the two minerals in a 50 per cent mixture where 1 g. was taken would be:

$$0.500 - \frac{0.155}{2} = 0.423 \text{ for the marcasite, and}$$

$$0.500 - \frac{0.065}{2} = 0.468 \text{ for the pyrite. (See also p. 373.)}$$

* To insure a more uniform size of grain as well as a more uniform mixture, each mineral was screened within similar limits before mixing, after which the mixture was ground in water.

Then $n_1 4.89 \frac{4}{3} \pi R_1^3 = 0.423$ and $n_2 5.03 \frac{4}{3} \pi R_2^3 = 0.468$.

$$\frac{n_1 4.89 \frac{4}{3} \pi R_1^3}{n_2 5.03 \frac{4}{3} \pi R_2^3} = \frac{.423}{.468} \therefore \frac{n_1 4 \pi R_1^2}{n_2 4 \pi R_2^2} = \frac{2.832}{2.946} = \frac{49.0}{51.0}$$

So while the pyrite in a 50 per cent mixture by weight would possess only about 49 per cent of the surface; *after the oxidation* by ferric sulphate, it would possess about 51 per cent. The average variation of the surface percentage from the weight percentage in the course of the reaction is therefore slight. By the same mode of reasoning we find that in a mixture of the sulphides containing 90 per cent by weight of marcasite, the surface of the latter would be 90.2 per cent before, and 89.7 per cent after the oxidation. Here also the average variation of the surface per cent from the weight per cent would be small. In a mixture containing 90 per cent by weight of pyrite, the pyrite surface would vary from 89.8 per cent to 91 per cent. Here the average variation of the surface from the weight per cent is also comparatively small, viz. 0.4 per cent.

The assumptions regarding the size, shape and uniformity of the particles are of course only approximations; still no other error has been found which could compensate any considerable error here and the conclusions deduced from the assumptions are in accord with the experimental results.

The plan naturally suggests itself, of taking the density of the two minerals into account in making the mixtures, and then increasing the quantity of the sulphide to be oxidized, so that the ratio of the surfaces of the two at the beginning should remain sensibly constant throughout the process of oxidation. Small quantities, however, are far more readily purified and otherwise handled, and it should also be noted respecting the application of the method to synthetic products that the latter are troublesome to prepare in quantity.

Although a careful study of other sources of error was made before the disturbance caused by flocculation was entirely understood, none of them proved of any great importance. It may be wise, however, to discuss them as briefly as possible.

(b) *Loss of water during the oxidation process.*—Stokes asserts that if the reaction flask is provided with a reflux condenser, and if the carbon dioxide which passes through the liquid during the process is first bubbled through water, there is no appreciable change in the concentration when a blank test is made with the standard solution. We can confirm this assertion as far as the water is concerned, but find a slight pre-

cipitation of iron even when 5 g. sulphuric acid instead of 4 g.* per liter is contained in the standard solution. If correction is made for the precipitated iron, no change in concentration has taken place, i. e., there is no loss of water. It should be stated that in an actual oxidation experiment no iron is precipitated, since the ferric iron is pretty rapidly reduced to the ferrous state. The following results prove these statements:

C_1 is the original concentration of the iron solution in grams of KMnO_4 solution per 100^{cc} of the standard.

C_2 is the concentration after the blank test, to determine which 100^{cc} solution is then reduced with SO_2 and titrated.

	I	II	III
C_1	37.06	37.06	36.54
C_2	37.09	37.08	36.52
	37.03	37.04	36.44

(c) *Reduction of the ferric solution during the blank test.*—Stokes states that no reduction occurred during a blank determination. We found a small reduction due perhaps to some organic matter associated with the ammonium salt. It amounted to only 0.1 g. of the very dilute standard KMnO_4 solution per 100^{cc}. In actual oxidations it is probable that the error would be less on account of the presence of a competing reducing agent.

(d) *Errors in the determination of the iron.*—These are very slight as previous results would indicate. In standardizing the ferric solution, 100^{cc} are measured in a calibrated flask at 25°. The solution is washed into a 500^{cc} flask, reduced in a stream of washed sulphur dioxide, the excess of which is boiled out in a stream of carbon dioxide in which the solution is finally cooled. The titration is then made with a weight burette, using a permanganate solution containing 1.5 g. of the salt per liter. The following determinations† of the concentration of four different solutions show the accuracy of the method:

I	II	III	IV
36.60	36.51	36.50	36.69
36.62	36.60	36.51	36.69
36.63	36.59	36.46	
	36.58	36.46	

Sulphur dioxide seems to carry with it mechanically some non-volatile reducing agent. This occasions a relatively large blank, but a very constant one. Blank tests were made as fol-

* The quantity prescribed by Stokes.

† The unit in these determinations is the gram of the above standard permanganate solution.

lows: A similar quantity of water to that used in the standardization tests was treated in the same way with sulphur dioxide and carbon dioxide successively. To the cooled solution was then added 0.86 g. ferric alum, thus giving practically the same conditions as those which obtain in the standardization itself. The quantity of the permanganate solution required in the blanks varied from 0.12 g. to 0.14 g. of permanganate solution, while 0.86 g. of ferric alum *alone*, with the usual amount of water, required always about 0.04 g. or one drop of permanganate solution. In the titration of an iron solution obtained in the Stokes process, the latter blank was subtracted, since here the ferric iron was reduced by the disulphide of iron and not by sulphur dioxide.

(b) *Oxidation of either ferrous solution or finely divided sulphide by atmospheric oxygen.*—The oxygen of the air, if not prevented, may affect the results in several particulars. First, when the finely ground sulphide is transferred from the desiccator to the reaction flask. This operation requires only about two minutes. The oxidation of 1–2 mg. of the sulphide would have an appreciable effect, but oxidation during this operation must be negligible, for a moist mixture of sulphides of similar weight to that used in the oxidation experiments exposed in a Gooch crucible to the air for 20 minutes gave an extract with distilled water which reduced only 0.1 g. permanganate solution.

The purification of the sulphide itself has been sufficiently insisted on by Stokes. He boiled it with hydrochloric acid, washed it successively with hydrochloric acid and boiled water cooled in carbon dioxide, in an atmosphere of carbon dioxide gas, and finally dried it in a vacuum desiccator. The apparatus which we employed in the washing has been described in a previous paper.* Whether necessary or not, we have dried the product more carefully than Stokes did. The washed sulphide in the Gooch crucible was removed from the above mentioned apparatus and put directly into a vacuum desiccator previously filled with carbon dioxide. The desiccator was then evacuated by a May-Nelson pump connected with driers which contained lime and phosphorus pentoxide. Thus any air in the desiccator was practically all removed in a couple of minutes. The sulphide was dried for about one hour, during which time the pump was kept running. It would seem impossible that any oxidation could have occurred during this process.

It may be said further that we assured ourselves by direct experiment with a titrated ferrous solution that no oxidation occurs when it is filtered in the described way. It has been

* Allen, Crenshaw and Johnston, loc. cit.

stated more than once by Baskerville and Stevenson* and others that an acid ferrous solution is not readily oxidized by the oxygen of the air, but we have here in addition the possibility of an oxidation of the finely ground sulphide. Since, however, moist sulphide oxidizes so very slowly even when exposed to the direct influence of the air, oxidation should be negligible when the filtration is done in our apparatus.

4. *Accuracy of the method.*—The systematic study of this problem has revealed only two considerable sources of error and means for obviating them have been explained. The results in fig. 3 involve errors of one per cent to two per cent. While this is a large error in ordinary analytical operations, it must be borne in mind that the two minerals are very similar and the method is very delicate. The total difference between the quantities of iron which the two minerals yield to the standard solution is, in terms of a dilute permanganate solution, only 6.1 to 6.4 g., according to the sample of pyrite taken, i. e., only 0.06 g. for every per cent. This amounts to about 1.5 drops of the permanganate solution, containing about 0.1 mg. of KMnO_4 and equivalent to only about 0.2 mg. of iron dissolved.

While the results are very constant for the same specimens of pyrite and marcasite, different natural specimens may show considerable differences.

Table III gives the results in tabular form. The only marcasites not of questionable purity which we have ever had in our hands, gave results which were almost identical. The results on the Joplin marcasite also served to show the constancy of the method; the first two results were obtained about a year later than the third with different standard solutions. The two determinations on Elba pyrite No. 1 were also made a year apart. The determinations for synthetic pyrite were made on two different preparations.

The variations on different occurrences of the same mineral species are due in part, if not entirely, to impurities. Thus the Leadville pyrite contains copper probably as chalcopyrite which Stokes found to give low results. Elba pyrite No. 1 is the purest we have ever found; the quantity at our disposal was unfortunately insufficient for this investigation. Elba pyrite No. 2 contained a little cobalt, but hardly sufficient to cause the irregularity noticed. It was selected from a large sample which contained considerable hematite, traces of which were probably retained by the sulphide even after purification. That the suspicion was well founded was proved by the fact that after the ground mineral had been treated for two days at 200° with two per cent sulphuric acid saturated with hydrogen

* J. Am. Chem. Soc., xxxiii, 1104, 1911.

TABLE III.

Showing the Stokes Constant for Different Pyrites and Marcasites.

Mineral.	Locality.	$x - a$	Impurities.
Pyrite	Leadville, Col.	3·95	0·1 per cent of copper.
"	Elba, No. 1	4·17 4·20	none found except ·04 per cent quartz.
"	Elba, No. 2	4·35	0·04 nickel and cobalt—mostly the latter, ferric oxide suspected.
"	" " after heating with sulphuric acid at 200°	4·18	
"	Roxbury, Conn.	4·46	1·4 per cent arsenic.
"	Synthetic, prepared by heating synthetic marcasite	4·14 4·11	
Marcasite	Joplin, Mo.	10·57 10·58 10·52	only quartz found
"	Galena, Ill.	10·57	
"	* Synthetic at 25°	10·20 10·34	may contain pyrite
	" " 200°	10·27 10·42	" " "
	" " 300°	10·20 10·34	" " "

* See this Journal, The effect of temperature and acidity in the formation of marcasite and wurtzite, (4), xxviii, 411, 1914.

sulphide, the value of the Stokes constant agreed with the purest pyrite. The hematite had evidently been removed by the treatment. The Roxbury pyrite which was used for the most part in the present work was selected on its macroscopic appearance, the higher results being at first regarded as more accurate. Later, when the lower results with synthetic pyrite had thrown them under suspicion, an analysis showed the presence of arsenic. Stokes found that arsenopyrite gave high results; 1 per cent arsenic in that form having the same effect in the Stokes test as 2 per cent marcasite, while it may be seen from the table that 1·4 per cent arsenic in the Roxbury pyrite has the same influence as 4 per cent marcasite.

5. *Linear relation between any pyrite and any marcasite.*—It is important to note in this connection that the constants of any pyrite and marcasite are additive in their mixtures. Thus a number of tests showed this to be true of the Elba pyrite No. 2 and the Joplin marcasite, while more numerous experiments (see fig 4) show the same thing for the Joplin marcasite and Elba pyrite No. 1. This is a fact of importance in the appli-

cation of the method to synthetic mixtures, which has been the object of the present investigation.

(a) *Independence of the chemical action of the two sulphides.*—Since the quantity of iron which dissolves in the Stokes reaction is approximately a linear function of the composition of the sulphide mixtures, each sulphide in the mixture behaves

FIG. 4.

FIG. 4. Iron dissolved from pyrite-marcasite mixtures by a standard ferric solution. Pyrite from Elba; marcasite from Joplin, Mo.

with the solution practically as it does when alone. The iron which dissolves comes only from decomposed sulphide, consequently in a sulphide mixture the quantity of each decomposed is directly proportional to its percentage in the mixture. Thus in a 50 per cent mixture, one half as much of each mineral is decomposed as when each reacts alone with the solution.

Further, each sulphide in the mixture must reduce only its proportional fraction of the solution; in a 50 per cent mixture the pyrite must reduce one half of the ferric solution and the two sulphides must reduce the two portions at the same rate,—otherwise the one which worked faster would encroach on the province of the other and the results would not be linearly related. In other words, the results are the same as if one should first separate the two minerals, divide the solution between them in proportion to their percentages, and allow each constituent to reduce its own portion separately.

The rate at which the solution is reduced by the two sulphides must then be the same for each mineral, but the rate at which each mineral is decomposed is quite different; *that* is proportional to the quantity of iron ($x-a$) which each yields to the solution. This quantity, in terms of the standard permanganate solution, is 4.20 for pyrite (Elba No. 1) and 10.57 for marcasite. *Marcasite is therefore decomposed 2.5 times as rapidly as pyrite, while the solution is reduced at the same rate by each.*

(b) *Electrolytic effect in the Stokes reaction.*—From the findings of Gottschalk and Buehler,* and of R. C. Wells,† one would expect an electrolytic effect here. If there is one, it must be very small. The results in fig. 3 do indeed appear to form a slightly convex curve which means of course that the marcasite seems to have a little more than its proportionate effect. Possibly this may be attributed to electrolytic influence.

(c) *Stokes' curve.*—If the relation between x and y is linear, $x = by + c$. By substituting in this equation the values x_0 and x_{100} for x , when $y = 0$ and $y = 100$ respectively, i. e., when we have pure marcasite and pure pyrite, we obtain

$$(3) \quad x = \frac{x_{100} - x_0}{100} y + x_0.$$

Now substituting this value for x in equation (2) (page 374) the latter becomes

$$(4) \quad y = \frac{(p + 25)a - (p + 16.66)x_0}{(p + 16.66) \left(\frac{x_{100} - x_0}{100} \right)}$$

or if we replace x_0 , x_{100} and a by their experimental values, viz., 47.28, 41.17 and 36.71, we have $y = \frac{10.57 p - 129.8}{.0611 p + 1.018}$. This curve, which is evidently a hyperbola, is plotted in fig. 5. The *plotted curve* is a true hyperbola *calculated* from the values which fall on the line drawn between the values of $(x-a)$ for pyrite and marcasite respectively; the *points plotted* are the values of p calculated directly from experimental values of x .

* Gottschalk and Buehler, Econ. Geol., vii, 28, 1912.

† R. C. Wells, *ibid.*, vii, 571, 1913.

These are the figures for Roxbury pyrite and Joplin marcasite. We have seen above that these results are affected by the presence of arsenic in the Roxbury pyrite. In fig. 6 are graphically shown the Stokes constants ($x-a$), for the purest natural pyrite and marcasite (Curve 1, 1) and also for the synthetic minerals (Curve 2, 2). It must be admitted that the

FIG. 5.

FIG. 5. Curve showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. Roxbury pyrite. Joplin marcasite.

value 10.3 for synthetic marcasite is open to the suspicion that the products may have contained a little pyrite.* Fig. 7 shows the hyperbolas calculated from these results, the assumption being made that the constants are exactly additive in their mixtures, while the points plotted are, as in fig. 5, calculated from the experimental values as given in fig. 4.

Fig. 8 shows Stokes' published values for p plotted against y . The plotted curve is again a true hyperbola calculated from the values of x which fall on the line in fig. 1. The minimum in his curve which Stokes obtained at 10 per cent pyrite seems therefore to have no real existence.

Summary.

1. The Stokes method for determining pyrite and marcasite, alone or in mixtures, depends on the estimation of the

* This Journal (4), xxxviii, 411, 1914.

iron dissolved when the finely ground and purified sulphide is treated with a boiling standard solution of ferric alum. The *same* pyrite or marcasite gives very constant values and the influence of each in mixtures is additive, i. e., there exists a linear relation between the iron dissolved and the composition of the mixture. The sum of the errors usually amounts to

FIG. 6.

FIG. 6. 1, 1. Values of the Stokes' constant ($x-a$) for the purest natural pyrite and marcasite, and their mixtures.

2, 2. Values of the Stokes' constant for synthetic pyrite, synthetic marcasite and their mixtures.

about 1 per cent, reaching a maximum of 2 per cent. There are two important sources of error. First there must be a sufficient excess of the sulphide, which is many times greater

FIG. 7.

FIG. 7. Curves showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. 1, 1. Curve for purest natural pyrite and marcasite. 2, 2. Curve for the synthetic minerals.

FIG. 8.

FIG. 8. Curve showing sulphur oxidized in pyrite-marcasite mixtures by a standard ferric solution. Stokes' results. The curve is a true hyperbola.

(7-15) than the amount required by theory. With such an excess the percentage of the surfaces remains on the average nearly the same as the percentage by weight, the basis on which the mixtures are made up. About 1 g. is sufficient for 250^{cc} of the standard solution. Secondly, the marcasite has a characteristic tendency to flocculate and thus reduce its reacting surface. This difficulty may be avoided by shaking the reaction mixture with pure quartz and beads until the lumps of the powder are thoroughly disintegrated. *Different specimens* of pyrite and marcasite give with the Stokes reaction values which differ somewhat. The differences are due in some cases, if not in all, to the presence of impurities. It is unfortunate that small quantities of impurities which will reduce ferric iron or give up iron to the solution exercise a serious influence. It is therefore not always possible to decide between a natural pyrite and a pyrite containing several per cent of marcasite by the Stokes reaction alone, nor to determine accurately the percentage of each in a natural mixture. In an investigation on the conditions of formation of pyrite and marcasite, this method has been very useful.

2. The results with the Stokes method plainly indicate that each mineral behaves in a mixture of the two just as it does alone; each appears to reduce a quantity of solution which is proportional to its surface; and each appears to reduce the solution at practically the same rate. The rates at which the sulphides are decomposed is quite different for the two minerals, because more of marcasite than of pyrite is required to reduce a given quantity of ferric iron. The ratio of these rates is not far from 1 : 2.5.

3. That ferric sulphate dissolves from pyrite a smaller quantity of iron than it does from marcasite means simply that more reduction is effected by sulphur in the case of pyrite, in other words that more of the sulphur in pyrite is oxidized. Stokes considered only the relation of p , the percentage of sulphur oxidized, to y , the percentage of pyrite in the sulphide mixture. We have shown that this curve is a hyperbola. This characteristic behavior of pyrite and marcasite towards oxidizing agents is probably general. It has been found by other observers that nitric acid and hydrogen peroxide both oxidize more of the sulphur in pyrite under the same conditions.

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