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OXIDATION OF SULPHIDES.

(SECOND PAPER.)

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In a recent paper[1] the authors have shown that the rate of oxidation of certain natural sulphides is greatly increased by the presence of either marcasite or pyrite. Experiments were first undertaken upon the assumption that any such oxidation or solution was due (1) to the presence of oxygen carriers, in the form of iron salts; (2) to the free sulphuric acid formed by the oxidization of the iron sulphides; or (3) to autoxidation, or induced reaction. As the results obtained did not conform, in some respects, to the demands of theory, it became evident that the above assumptions were not adequate to explain the complete action although, in all probability, each process is a factor of greater or less importance.

Drs. E. T. Allen[2] and R. C. Wells[3] believe that the excess of sulphuric acid formed, by the oxidation of the iron sulphides, is sufficient to explain the increased solubility observed. However, as will be shown in the present paper, this assumption is hardly supported by experimental facts. Increased action is probably due chiefly to other factors—one of which is evidently electrolytic.

In this paper we shall endeavor to show: (1) that while there is, in mixtures of two sulphides, a large increase in the solution of one, there is also a protective action exerted on the other; (2) that there is a difference of potential between the different sulphides which can be arranged in a series similar to the electrochemical series shown by the metals; and (3) that this fact may be of the greatest importance in the process of oxidation.

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[1] Buehler and Gottschalk, ECONOMIC GEOLOGY, Vol. V., p. 28.

[2] Allen, ECONOMIC GEOLOGY, Vol. V., p. 387.

[3] Wells, ECONOMIC GEOLOGY, Vol. V., p. 480.

Theoretically, the oxidation of pyrite or marcasite, alone, may proceed in various ways—of which the following equations are examples:

$$FeS_2 + 7O + H_2O = FeSO_4 + H_2SO_4, \tag{1}$$

$$\begin{cases} 2FeS_2 + 3O = Fe_2O_3 + 4S, \\ FeS_2 + 4O = FeSO_4 + S, \end{cases} \tag{2}$$

$$FeS_2 + 3O + H_2O = FeSO_4 + H_2S, \tag{3}$$

$$FeS_2 + 6O = FeSO_4 + SO_2. \tag{4}$$

It is possible that the oxidation may also result, under certain conditions, in the formation of sulphites and thio-sulphates, in which case these compounds would be found in the resulting solution.

EXPERIMENTAL.

In general, the following experiments were carried out, under conditions similar to those cited in our previous paper. The finely powdered sulphides were placed upon filter paper, spread upon a Hirsch filter plate which was fitted in a 6 cm. funnel. In a number of the experiments the filter paper was replaced by asbestos which was packed between two filter plates. The sulphides were then washed twice daily with distilled water, the filtrate being caught in a 700 c.c. Jena flat-bottomed flask. The sulphides were treated alone and also when mixed with pyrite or marcasite or some other natural sulphide.

Experiment 1.—A series of the filtrates obtained from marcasite alone, and from marcasite mixed with galena, sphalerite, and copper sulphides, were tested for the presence of free SO_2, sulphites, and thio-sulphates. In no case were these compounds present. Under the conditions of the experiment the oxidation does not therefore appear to go according to equation No. 4. We find, however, that if finely powdered pyrite or marcasite is kept in ground stoppered bottles for any considerable length of time they evolve a strong odor of SO_2. Apparently, in this case, there has not been sufficient moisture and oxygen present for complete oxidation.

Experiment 2.—In order to test for the presence of free sulphur, in experiments with pyrite, the entire residue left on the funnel (5 to 20 grams) was treated with three portions of carbon disulphide. No sulphur was found in a series of eight experiments. The ten pound sample of marcasite, used in experiment 3, was also treated with carbon disulphide. This experiment shows the presence of free sulphur. The sample contains considerable organic matter and before use had only been washed to free it from soluble salts. The reaction may therefore form free sulphur although in thin layers and pure minerals the results were negative. The results have not been carried far enough to determine the influence of the presence of impurities or the conditions under which the experiment is carried out. According to H. N. Stokes, sulphur is formed during the oxidation of marcasite but not in the case of pyrite where these minerals are treated with a dilute solution of ferric sulphate.

Experiment 3.—Tests for the presence of hydrogen sulphide were made as follows: The oxidation was carried out in an apparatus (Fig. 1) through which air could be drawn continuously. The air entering flask *A* passed slowly through alkaline lead

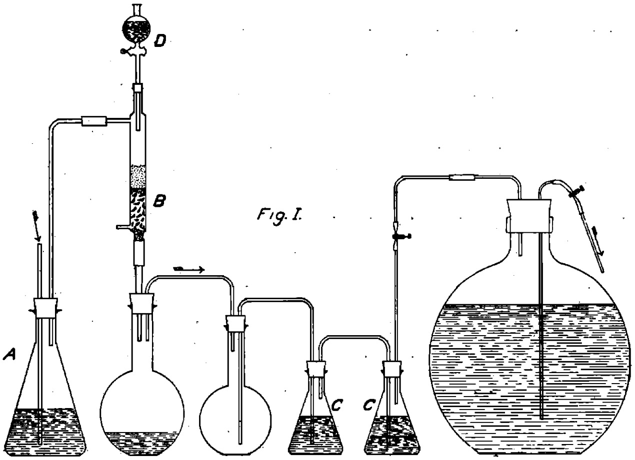

Fig. I.

nitrate solution to free it from H_2S; it then passed through tube *B*, in which the finely ground sulphide was placed upon a filter of asbestos wool; finally the air was again washed in lead solutions held in flasks *C*. The sulphides were washed twice daily by means of the separating funnel *D*. Marcasite, after four months' continuous treatment, shows no trace of blackening of the alkaline lead solution, indicating the absence of even traces of hydrogen sulphide. The marcasite oxidized normally, except that the asbestos filter apparently induced hydrolysis of the iron salts. This effect is shown by the deep stain of ferric hydroxide which colored the asbestos. The following analysis of the solution and precipitate in the flask also shows this hydrolysis:

Solution 1,068 c.c.

$FeSO_4$, 0.0602 grams; $Fe_2(SO_4)_3$, 0.1799 grams; SO_3 (excess), 0.2697 grams; Fe_2O_3 (in the precipitate), 0.0218 grams.

This analysis shows, in the solution, a ratio of the atoms of sulphur to the atoms of iron $S/Fe = 3.14/1$, instead of the theoretical ratio of 2.

A mixture of marcasite and galena treated in the same apparatus, under similar conditions, failed to give traces of H_2S, although the excess of sulphuric acid should dissolve the lead sulphide with the formation of H_2S, as follows:

$$PbS + H_2SO_4 = PbSO_4 + H_2S.$$

In order to make this test upon a larger scale, about ten pounds of marcasite were placed in a large covered funnel, upon the surface of which alkaline lead nitrate paper and small beakers of alkaline lead nitrate were placed. Although the mineral oxidized rapidly, there was no trace of H_2S shown. Later, 200 grams each of finely powdered galena and sphalerite were mixed with the marcasite. Continuous treatment for three months shows no trace of hydrogen sulphide.

The above experiments would indicate that H_2S is not formed even under the most favorable conditions; therefore equation No. 3 does not seem to hold.

As shown in experiment (3), ferrous sulphate and sulphuric acid are formed during the oxidation. Ferric sulphate is also formed by the further oxidation of the ferrous sulphate as follows:

$$2FeSO_4 + O + H_2SO_4 = Fe_2(SO_4)_3 + H_2O.$$

Through hydrolysis, a portion of the ferric sulphate so formed hydrolizes to

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4.$$

The Fe_2O_3 appears as a yellowish red precipitate in the flask and on the filter. No doubt this oxide is hydrated to some extent and may have the formula of limonite.

The occurrence of ferric and ferrous sulphates and free sulphuric acid indicates that the oxidation proceeds according to equation No. 1.

In the following experiments the iron is shown as Fe_2O_3, although it occurs chiefly as ferrous and ferric sulphates. The proportion of ferric and ferrous salts depends largely upon the method of treatment, the time the solution stands and the possible free access of air. The results, as quoted below, are figured to show (1) the total oxidation, (2) the ratio of the sulphur and the metallic molecules that have been transferred as compared to theoretical considerations, and (3) the percentage of the metal washed through or oxidized.

Complete oxidation of marcasite or pyrite (FeS_2) involves two atoms of sulphur and one atom of iron. In analyzing solutions derived from such oxidation the ratio of the iron to sulphur should stand as 1:2. In the following results there should be required, for every molecule of Fe_2O_3, four molecules of S, since it has required two molecules of FeS_2 to form one molecule of the ferric oxide, and, in the results quoted, the ratio for the theoretical oxidation of pyrite or marcasite compared to barium sulphate ($BaSO_4$), in which form the sulphur was weighed ($BaSO_4$ requires one sulphur), should therefore be $BaSO_4/Fe_2O_3 = 4/1$.

The columns headed "solution" and "precipitate" indicate the materials found both in the filtrate and in the small precipitate which usually coats the bottom of the flask. The column headed "residue" indicates materials derived from the treatment of the residue on the filter plates. The total amount of materials found in the flask is given in the last column.

PYRITE.

Experiment 4.—10 grams; through 60 mesh and on 100 mesh; 4 months; total solution 504 c.c. Considerable brown precipitate in flask.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
Fe_2O_3	0.1388	0.0291	0.1679
$BaSO_4$	0.8726	0.0109	0.8835

Ratio of number of molecules of $BaSO_4$ to number of molecules of Fe_2O_3 is $BaSO_4/Fe_2O_3 = 3.60$ (theory for FeS_2, 4.00).

Iron washed through, 2.5 per cent.

MARCASITE.

Experiment 5.—Same as for pyrite, total solution 513 c.c.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
Fe_2O_3	0.1149	0.0321	0.1470
$BaSO_4$	0.7177	0.0118	0.7295

Ratio of number of molecules of $BaSO_4$ to number of molecules of Fe_2O_3 is $BaSO_4/Fe_2O_3 = 3.40$ (theory for FeS_2, 4.00).

Iron washed through, 2.2 per cent.

SPHALERITE.

Experiment 6.—10 grams; through 60 mesh and on 100 mesh; 5 months; total solution 540 c.c.

$ZnO = 0.0273$ grams; $BaSO_4 = 0.0556$ grams.

Ratio of number of molecules of $BaSO_4$ to number of molecules of ZnO is $BaSO_4/ZnO = 0.71$ (theory for ZnS, 1.00).

Zinc washed through, 0.33 per cent.

GALENA.[1]

Experiment 7.—10 grams; through 80 mesh and on 100 mesh; 8½ months; total solution 750 c.c.

	Solution, Grams.	Precipitate, Grams.	Residue, Grams.	Total, Grams.
$PbSO_4$	0.0057	0.0044	0.1090	0.1191
$BaSO_4$	0.0368	0.0034	0.0839	0.1241

Ratio of number of molecules of $BaSO_4$ to molecules of $PbSO_4$ is 1.08 (theory for PbS, 1.00).

Lead oxidized, 0.94 per cent.

SPHALERITE WITH MARCASITE.

Two mixtures of 10 grams sphalerite with 5 and 20 grams, respectively, of marcasite, all through 60 mesh and on 100 mesh, were subjected to treatment, all for 5 months.

Experiment 8.—10 grams sphalerite with 5 grams marcasite; total solution 544 c.c.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
ZnO	0.2669	——	0.2669
Fe_2O_3	0.0109	0.0070	0.0179
$BaSO_4$	0.9167	0.0017	0.9184

Ratio of number of molecules of ZnO to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $ZnO : Fe_2O_3 : BaSO_4 = 1 : 0.034 : 1.20$ (theory $1 + (4 \times 0.034)$, or 1.14).[2]

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[1] The original galena contained some lead sulphate, for 10 grams of 200 mesh galena, before treatment, gave 0.49 per cent. extraction with ammonium acetate. This has not been subtracted in our data.

[2] This ratio indicates that virtually the total sulphur, combined with the zinc and iron as sulphides, has found its way into the solution; for one molecule of sphalerite gives one molecule of ZnO and one molecule of $BaSO_4$, while, as already explained (page —), each molecule of Fe_2O_3 was derived from that amount of FeS_2 which gives four molecules of $BaSO_4$. Therefore the sum of the molecules of $ZnO + 4$ times the molecules of Fe_2O_3 should be equal to the molecules of $BaSO_4$ found, if all the sulphur passes into the solution.

Zinc carried through, 3.20 per cent. Iron carried through, 0.54 per cent.

Experiment 9.—10 grams of sphalerite with 20 grams marcasite; total solution 530 c.c.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
ZnO	0.3864	——	0.3864
Fe_2O_3	0.0360	0.0101	0.0461
$BaSO_4$	1.3960	0.0005	1.3965

Ratio of number of molecules of ZnO to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $ZnO:Fe_2O_3:BaSO_4 = 1:0.061:1.26$ (theory $1 + (4 \times 0.061)$, or 1.24).

Zinc carried through, 4.63 per cent. Iron carried through, 0.35 per cent.

GALENA WITH MARCASITE.[1]

Three mixtures of galena (through 60 mesh and on 150 mesh) with 5, 10, and 20 grams respectively of marcasite (through 60 mesh and on 100 mesh) were treated as before described for 8½ months.

Experiment 10.—10 grams galena with 5 grams marcasite; total solution 530 c.c.

	Solution, Grams.	Precipitate, Grams.	Residue, Grams.	Total, Grams.
$PbSO_4$	0.0090	0.0005	0.6736	0.6831
Fe_2O_3	0.0037	0.0008	——	0.0045
$BaSO_4$	0.0562	0.0004	0.5186	0.5754

Ratio of number of molecules of $PbSO_4$ to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $PbSO_4:Fe_2O_3:BaSO_4 = 1:0.013:1.09$ (theory $1 + (4 \times 0.013)$, or 1.05).

Lead oxidized, 5.39 per cent. Iron carried through, 0.14 per cent.

Experiment 11.—10 grams galena with 10 grams marcasite; total solution 500 c.c.

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[1] See note under "Galena," Experiment No. 7.

	Solution, Grams.	Precipitate, Grams.	Residue, Grams.	Total, Grams.
$PbSO_4$	0.0095	0.0022	1.0753	1.0870
Fe_2O_3	0.0043	0.0018	——	0.0061
$BaSO_4$	0.0820	0.0045	0.9280	0.9145

Ratio of number of molecules of $PbSO_4$ to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $PbSO_4 : Fe_2O_3 : BaSO_4 = 1 : 0.0106 : 1.11$ (theory $1 + (4 \times 0.0106)$, or 1.044).

Lead oxidized, 8.58 per cent. Iron carried through, 0.09 per cent.

Experiment 12.—10 grams galena with 20 grams marcasite; total solution 500 c.c.

	Solution, Grams.	Precipitate, Grams.	Residue, Grams.	Total, Grams.
$PbSO_4$	0.0051	0.0005	1.6502	1.6558
Fe_2O_3	0.0030	0.0033	——	0.0066
$BaSO_4$	0.1130	0.0004	1.2706	1.3840

Ratio of number of molecules of $PbSO_4$ to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $PbSO_4 : Fe_2O_3 : BaSO_4 = 1 : 0.0076 : 1.08$ (theory $1 + (4 \times 0.0076)$, or 1.03).

Lead oxidixed, 13.06 per cent. Iron carried through, 0.05 per cent.

SPHALERITE WITH GALENA.

Experiment 13.—10 grams of each, 200 mesh; 10½ months; total solution 500 c.c.

	Solution, Grams
ZnO	0.0464
$PbSO_4$	0.0062
$BaSO_4$	0.1288

Zinc carried through, 0.56 per cent.

The lead sulphate remaining in the residue was not determined, so that the experiment is not completely comparable.

ENARGITE WITH PYRITE.

Experiment 14.—This is the same experiment quoted on page 31 of our previous paper. The enargite alone gave no copper, arsenic, nor iron, and only a trace of sulphur.

10 grams enargite and 10 grams pyrite; 4 months and 12 days; total solution 500 c.c.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
Cu_2S	0.2480	none	0.2480
Fe_2O_3	0.0165	0.0037	0.0202
$BaSO_4$	0.8310	none	0.8310
Arsenic	none	none	none

Ratio of number of molecules of Cu_2S to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $Cu_2S:Fe_2O_3:BaSO_4 = 1:0.081:2.29$ (theory, assuming that $Cu_2S \cdot \frac{1}{3}As_2S_5$ gives $Cu_2SO_4 + \frac{5}{3}H_2SO_4$, $2.66 + (4 \times 0.081)$, or 2.98).

PYRITE OR MARCASITE ABOVE SPHALERITE.

In the following experiments, a funnel containing pyrite or marcasite, prepared as previously described, was placed over a funnel containing sphalerite so that the washings from the pyrite or marcasite dripped upon and washed the sphalerite. The same minerals were used as in the above experiments.

Experiment 15.—10 grams pyrite and 10 grams sphalerite; total solution 375 c.c. Time 4 mo.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
ZnO	0.0094	———	0.0094
Fe_2O_3	0.0759	0.0023	0.0782
$BaSO_4$	0.2992	trace	0.2992

Ratio of number of molecules of ZnO to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $ZnO:Fe_2O_3:BaSO_4 = 0.235:1:2.62$ (theory, 4.235).

Zinc carried through, 0.11 per cent. Iron carried through 1.18 per cent.

Experiment 16.—Same as experiment 15; total solution 410 c.c.; no precipitate.

ZnO = 0.0946 grams,
Fe_2O_3 = 0.1228 grams,
$BaSO_4$ = 0.6630 grams.

Ratio of number of molecules of ZnO to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $ZnO : Fe_2O_3 : BaSO_4 = 1.51 : 1 : 3.69$ (theory, 5.51).

Zinc carried through, 1.13 per cent. Iron carried through, 1.85 per cent.

Experiment 17.—10 grams marcasite above 10 grams sphalerite; total solution 549 c.c.

ZnO = 0.0888 grams,
Fe_2O_3 = 0.2339 grams,
$BaSO_4$ = 1.2270 grams.

Ratio of number of molecules of ZnO to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $ZnO : Fe_2O_3 : BaSO_4 = 0.927 : 1 : 3.59$ (theory, 4.93).

Zinc carried through, 1.08 per cent. Iron carried through, 3.52 per cent.

Experiment 18.—In this experiment, another pyrite was used, for which the following figures are given when treated alone.

10 grams, through 100 mesh; 2 months and 18 days; total solution 1,033 c.c.

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
Fe_2O_3	0.0594	0.0494	0.1088
$BaSO_4$	0.5247	0.0254	0.5501

Ratio of number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $Fe_2O_3 : BaSO_4 = 1 : 3.46$ (theory, 1 : 4) = $Fe_2O_3/BaSO_4$.

Iron carried through, 1.64 per cent.

10 grams of this pyrite placed so that the washings from it dripped over 10 grams of sphalerite (also 100 mesh), for 2½ months, yielded 885 c.c. of a solution, which gave the following analysis:

	Solution, Grams.	Precipitate, Grams.	Total, Grams.
Fe_2O_3	0.0717	0.0195	0.0912
$ZnNH_4PO_4$	0.0779		

Ratio of number of molecules of $ZnNH_4PO_4$ to number of molecules of Fe_2O_3 to number of molecules of $BaSO_4$ is $ZnNH_4PO_4 : Fe_2O_3 : BaSO_4 = 0.76 : 1 : 1.95$ (theory, 4.76).

Zinc carried through, 0.43 per cent. Iron carried through, 1.37 per cent.

PYRITE WITH SILICA.

Experiment 19.—10 grams pyrite and 10 grams silica, finely divided and mixed, subjected to oxidation and moisture for 5 months and 11 days, gave 405 c.c. solution, containing the following:

	Grams.
Silica	0.0047
Ferrous sulphate	0.1734
Ferric sulphate	0.0109
Excess sulphur trioxide	0.0125

Ratio of number of molecules of Fe_2O_3 to number of molecules of SO_3 is $Fe_2O_3 : SO_3 = 1 : 5.59$ (theory, 1 : 4).

FeS_2 oxidized, 1.44 per cent.

DISCUSSION OF EXPERIMENTAL RESULTS.

The foregoing experiments confirm the results shown in our previous paper; namely, that there is a decided increase in the percentage of lead, zinc, and copper sulphides oxidized when these are mixed with the sulphides of iron. They also show that, in the case of such mixtures, the amount of iron transferred is but a small fraction of the amount transferred where the sulphides of iron are treated alone. Such mixtures evidently materially hinder the transfer of iron.

If solution of the various sulphides is due, as suggested by Allen and Wells, to the presence of the free sulphuric acid, there is no reason why the transfer of the iron should not proceed normally, and an equal amount be found in the solution derived from such mixtures.

Assuming that the iron sulphides oxidize according to equation No. 1, there is liberated one molecule of H_2SO_4 for each molecule of FeS_2 oxidized. The solution of a sulphide by this free sulphuric acid should take place according to the following equation: *e. g.*, sphalerite:

$$ZnS + H_2SO_4 = ZnSO_4 + H_2S.$$

There would be dissolved, in this case, approximately one molecule of ZnS to each molecule of FeS_2 oxidized, or about 0.8 as much by weight. If any free acid passes into the filtrate, the amount of zinc transferred would be correspondingly less. On the other hand, such solution should in no way effect the transfer of the iron other than abstracting the free H_2SO_4, thereby inhibiting, to some extent, the oxidation of ferrous sulphate to ferric sulphate. Such action would assist the transfer of iron by lessening the possibility of hydrolysis. As a matter of fact, the amount of zinc and lead oxidized is much greater than the amount specified above, and the amount of iron transferred is only a small part of that required by this theory. The absence of H_2S (as shown by experiment No. 3) indicates that if this gas is formed it must be wholly oxidized to sulphuric acid at once. This would hardly seem true in the case where ten pounds of marcasite were used and no air was forced through the mass.

One might assume, however, that as the FeS_2 is oxidized, virtually the entire amount of ferrous sulphate formed is oxidized at once to ferric sulphate, which hydrolizes instantly to ferric hydroxide and sulphuric acid and that the sulphuric acid dissolves the metallic sulphides before being washed into the flask below. This, however, requires a completed series of reactions that are hardly possible under the conditions. In experiment No. tion and hold the iron in the ferrous form, in which case it should

14, the cuprous copper of the enargite would prohibit such oxidabe washed through into the flask. This experiment, however, indicates that there was only a slight transfer of the iron, comparable in all respects with the transfer in the other experiments. Neither the copper nor the iron show any definite relation in the amounts transferred.

In the case of experiments 15, 16, 17, and 18, in which the marcasite and sphalerite were not in contact, the results indicate that in every case the iron carried through is greater than the zinc and that the zinc is much less than in the case of the two minerals being mixed. The oxidation of the zinc in these experiments was doubtless caused by the presence of iron salts, or the ZnS has been dissolved by H_2SO_4. They indicate, however, that the action of the iron sulphides is much more vigorous in the case of mixtures.

To retain the theory that the increased solubility of sphalerite or galena, when mixed with iron sulphides, is due to the free sulphuric acid, we must assume an almost complete hydrolysis of the ferrous sulphate solution after the free sulphuric acid is neutralized by the admixed sulphides. Such an assumption would be possible if the iron were present as ferric sulphate. This, however, is not the case, since in every instance the iron in solution is both ferric and ferrous, the latter usually in as large a proportion as the former. By comparing the experiments on galena and sphalerite, it is apparent that the hydrolysis would be greater in the presence of lead sulphide than in the presence of zinc sulphide, while actually a larger number of equivalents of the latter are carried through than of the former.

POSSIBLE ELECTROLYTIC ACTION.

It was these apparent inconsistencies with the demands of the solution theory that led to a consideration of the possible influence of electrolytic action, due to contact.

If there is a difference of potential between the sulphides in contact, and these sulphides are conductors, there should be created, by such contact, small batteries that would induce oxidation and solution of the more negative mineral and protect or inhibit similar action on the positive mineral. .This action would be analogous, in every respect, to the action of metals. It is well known that when two metals are placed in contact and moistened, one is oxidized in the air much more rapidly than it would be if alone, and that the other metal is almost completely shielded from oxidation, a fact used largely in a commercial way. It is found that the metal, forming the positive pole,[1] in a combination similar to an ordinary battery, is protected from change while the metal forming the negative pole is attacked more readily. This fact is most conveniently expressed by the electro-chemical series, in which the metals are arranged in such order that they progress from the more electro-negative to the more electro-positive. According to this order, any of the metals will cause those higher in the series to oxidize more rapidly when placed in contact and moistened and will itself be protected.

Thus zinc, iron, and tin occur in the electro-chemical series in the order named, starting with the most electro-negative. Iron, coated with zinc (galvanized iron) is protected not only because the zinc forms a thin film of insoluble oxide, but because the zinc protects the iron electrolytically as long as the film of moisture touches both metals. Iron, coated with tin (tin plate), is protected from rusting only so long as the tin coating is perfect, as even the minutest hole in the tin will, through electrolytic action, induce rusting of the iron beneath. In this case the iron will oxidize more rapidly than if alone.

These well-known facts of electro-chemistry are stated here in order to show the analogy in the case of two minerals in contact provided such minerals show a difference of potential and are conductors.

That many of the sulphides and oxides are comparatively good conductors is shown by the following table taken from Landolt-Boernstein-Meyerhoffer (values shown in reciprocal ohms) :

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[1] We regard an electrode as positive when it assumes a positive charge or gives a negative charge to the solution. See Whitney and Brown's edition of LeBlanc.

TABLE I.

Copper	600,000
Zinc	165,000
Nickel	105,000
Platinum	92,400
Mercury	10,444
Bismuth	9,190
Galena	8,470
Siberian graphite	820
Nickel ore	313
Electric light carbon	300
Pyrrhotite	119
Chalcocite	91.0
Ferrous sulphide	8.98
Hematite	2.41
Magnetite	1.68
Chalcopyrite	0.983
Pyrite	0.661
Stannous sulphide	0.000935
Siderite	0.000140
Distilled water	0.00001
Glass	0.0000000000000202
Hard rubber	0.000000000000000486
Mica	0.000000000000000114

Many of the sulphides, as shown, are similar to the metals in conductivity and will readily act as efficient electrodes.

The authors were unable to find figures showing the difference of potential shown by the various natural sulphides and oxides. Measurements made with an Ostwald potentiometer and a Lippman capillary electrometer, indicate that there is a decided difference in potential between the minerals when placed in contact and moistened, and the minerals can be arranged in a series similar to the electro-chemical series.

The following table is a selection of measurements made with distilled water. For convenience, the various minerals were measured against copper wire; the "+" or "—" sign indicates the charge assumed by the minerals. The figures are given in volts.

TABLE II.

Marcasite$^+$	0.37
Argentite$^+$	0.27
Cassiterite$^+$	0.27
Chalcopyrite$^+$	0.18 to 0.30
Enargite$^+$	0.18 to 0.23
Molybdenite$^+$	0.20
Covellite$^+$	0.20
Pyrite$^+$	0.18
Bornite$^+$	0.17
Mixed copper ore$^+$	0.15
Galena$^+$	0.15
Chalcocite$^+$	0.14
Hematite$^+$	0.08 to 0.26
Cuprite$^+$	0.05
Niccolite$^+$	0.02
Domeykite$^+$	0.01
Metallic copper	0.00
Stibnite$^-$	0.17 to 0.6
Sphalerite$^-$	0.2 to 0.4
Corundum$^-$	0.25 to 0.6
Metallic zinc$^-$	0.83

According to this table, marcasite shows the highest E.M.F., while corundum shows the lowest for the minerals, the difference being more than 0.6 of a volt. Metallic zinc shows a negative voltage to copper of 0.83 of a volt, there being a difference between the highest and lowest member of the series of 1.2 volts.

Since, as already shown in Table I., many of the natural minerals are good conductors, this difference in voltage should, where two minerals are in contact and moistened, form a small battery in which the current will flow out of the solution from the mineral having the highest potential. By such action the mineral lowest in the series would dissolve more rapidly, while the one higher in the series would be protected from oxidation.

In order to test the truth of the above assumption, a number of experiments have been carried out, as follows:

Experiment 20.—Pieces of pyrite and galena, two inches in length and approximately one inch square, having copper wire attached near one end, were placed in a small dish containing ordinary distilled water; the wire did not touch the water, nor were the minerals in contact. Upon short-circuiting, through a galvanometer, the same electro-motive force was obtained as shown in the above table, and a current of about 5 microamperes was recorded. In the course of a few days the galena became coated with lead sulphate, while a similar piece of galena, placed in the same solution, but not short-circuited, remains perfectly bright. There is no action on the pyrite.

Replacing the galena with sphalerite, the electro-motive force is much greater, as shown by the table, while the current, on short circuiting, is at least ten times as great but drops to nearly zero in a few seconds. If the sphalerite electrode is removed, the surface cleansed with a dry cloth, and replaced in the circuit, it gives the original value with the same rapid drop of the electro-motive force.

According to this action, pyrite and marcasite, when in contact with galena and sphalerite, are prevented from oxidation, while the latter minerals are dissolved with greater rapidity. This has been shown to be the case all through our experimental work.

If the conception that such contact action protects the sulphides higher in the series, certain of them, occurring near the middle of the series, should exert an accelerating action on those minerals above it in the series, and a protective action on those below, while metallic copper and metallic zinc should retard the oxidation of most of the minerals of the series.

In order to test this fact, the following series of experiments was carried out.

Experiment 21.—Five funnels and flasks were prepared in the usual way. The following metals and mixtures were placed upon these filters, and washed twice daily with distilled water for one and one half months:

Exp. 1. Marcasite, 20 grams, through 80 mesh and on 120 mesh,
Exp. 2. Metallic zinc, C. P., 40 grams of 30 mesh,
Exp. 3. Metallic copper (finely precipitated from solution by zinc), 25 grams,
Exp. 4. Mixture of { Marcasite, 20 grams, Metallic copper, 25 grams.
Exp. 5. Mixture of { Marcasite, 20 grams, Metallic zinc, 40 grams,

During the washing, the metallic copper, both alone and in admixture, became dark in color, indicating that it had changed in part to the oxide. The metallic zinc, in both cases, shows oxidation to the oxide of zinc, which is perceptible, due to its very white color. The marcasite alone oxidized in the normal way, showing hydrolysis in the flask and iron salts along the rim of the funnel.

Table No. 3 shows the results of these experiments; amounts given in grams; solutions approximately 500 c.c. in each case.

TABLE III.

No.	Substances.	Fe_2O_3.	Cu.	Zn.	S.
1	Marcasite	0.1495	—	—	0.158
2	Zinc, metallic	—	—	none	—
3	Copper, metallic	—	none	—	—
4	Marcasite, zinc, metallic	none	—	none	none
5	Marcasite, copper, metallic	none	none	—	none

Only in the case of marcasite, alone, has there been any transfer of iron or sulphur. The presence of the copper and zinc has completely prevented even the slightest oxidation of the marcasite. Had there been any oxidation of the marcasite, the sulphuric acid formed would have readily dissolved the copper or zinc, which would have been washed through, into the flask, as zinc or copper sulphates.

In a series of incomplete experiments, ullmannite ($NiS_2 \cdot NiSb_2$) is being treated alone, and in mixtures with other minerals, including hematite, molybdenite, sphalerite, franklinite, stibnite, and crystallized stannous sulphide, respectively. Time of treatment two months.

From the depth of the nickel-green color of the solutions, and from the amount of greenish salt on the sides of the funnels, it is apparent that the greatest amount of oxidation is being obtained with the hematite-ullmannite mixture. The mixtures with molybdenite and with stannous sulphide show marked action, and the mixtures with franklinite and with sphalerite have slightly greenish filtrates. Alone, or with stibnite, the amount of nickel in solution is too small to be detected by the eye. Hematite apparently has a decided accelerating effect in this case, while franklinite, which is also an oxide, apparently has the same effect to a lesser degree. This series of experiments indicates that contact action with oxides may produce the same results as in the case of the sulphides.

A number of experiments are now being carried on to determine still further the protective or accelerating action of minerals other than the di-sulphides. The number of possibilities which can be predicted from the table of electro-motive force measurements will give us crucial experiments upon which to test the limits of such action.

SUMMARY.

In this paper we have (1) confirmed our observations on the increased solubility of sulphides, in the presence of marcasite or pyrite; (2) shown that there is a complementary protection from oxidation of the pyrite or marcasite; (3) shown that there exists a difference of electro-motive force between the various natural minerals and arranged a number of these in a series analogous to the electro-chemical series of the metals; (4) shown that the minerals, when in contact and moistened, act as batteries; (5) indicated that such contact may be an important factor in the general process of oxidation of the natural minerals.

A majority of the above analyses were made by Mr. A. X. Illinski, chemist to the Bureau of Geology and Mines.