

DEPARTMENT OF THE INTERIOR
Hubert Work, Secretary

U. S. GEOLOGICAL SURVEY
George Otis Smith, Director

Bulletin 778

CHEMISTRY OF DEPOSITION OF NATIVE COPPER FROM ASCENDING SOLUTIONS

BY

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WASHINGTON
GOVERNMENT PRINTING OFFICE
1925

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CHEMISTRY OF DEPOSITION OF NATIVE COPPER FROM ASCENDING SOLUTIONS

INTRODUCTION

NATIVE COPPER DEPOSITS

Many theories have been proposed at one time or another to account for the deposition of native copper in ore deposits, but nearly every one of them is unsatisfactory for the reason that some factor has been neglected which would, if considered, greatly modify the theory if not entirely invalidate it.

As is well known, the Lake Superior district affords a conspicuous example of the occurrence of native copper. In studying this field a number of geologists of the Calumet & Hecla Consolidated Mining Co., including Mr. B. S. Butler, Dr. T. M. Broderick, and Prof. L. C. Graton, arrived at certain views as to the origin of copper.¹ These views were based more or less on geologic observations, but as they involved chemical changes about which little or no information was available, the problem was brought to the attention of the United States Geological Survey, with the hope that chemical experiments could be made which would decide some of the questions involved. The Survey undertook the investigation, which is really a continuation of the fundamental work of Stokes, and this paper presents some of the results so far obtained.

The writer visited the mines for a few days in June, 1922, and observed typical ores of the conglomerate, the amygdaloid rock, and the fissures, but he has necessarily relied chiefly on the work of others for the geologic features that bear on the origin of deposits of native copper. His endeavor has been principally to broaden the chemical knowledge relating to the problem. The subject is so large, however, that obviously, in spite of the large number of experiments made, much still remains to be learned concerning the chemistry of the ores and associated minerals.

It would be inappropriate to give an extensive description of the geology of Keweenaw Point, Mich., in this paper, as the literature

¹ Graton, L. C., explanatory statement read at the Ann Arbor meeting of the Society of Economic Geologists, Dec. 29, 1922.

on the subject is already very large.² Suffice it to say that the principal copper deposits are found in extensive lodes that parallel certain of the Keweenaw lava flows, now much tilted. The copper also occurs to some extent in faults and fissures.

SOURCE OF THE COPPER

From an extensive study of the minerals associated with the Lake Superior copper Pumpelly³ long ago concluded that the copper was reduced from oxidized compounds by ferrous compounds and that the copper compounds were already probably in part concentrated as sulphide, silicate, carbonate, and sulphate before their burial by later lava flows.

On the other hand Smyth⁴ advanced the view that the copper was brought to its present position from below by solutions that entered the formations after they were tilted.

These two ideas have both had their defenders up to the present time.

The work described in this paper was done primarily to throw light on chemical possibilities in ascending solutions, but much of the information obtained will doubtless be suggestive for other conditions as well. Little attention has been given to the well-known reactions that pertain to enrichment. The need suggested by the geologic evidence was rather for more knowledge of the chemical possibilities in deep or ascending solutions, especially those at high temperature and pressure or such as might have constituted magmatic emanations. Aqueous solutions have been studied up to 350° C. and a few melts up to about 450°. The results show that copper might be deposited by ascending solutions under certain conditions, and the work has gone far enough to refer the copper-bearing solutions to a source that was of a distinctly reducing character. Certain more or less oxidized products, however, such as sulphur, sulphuric acid, or cupric sulphate, have also been assumed in the discussion or used in many of the experiments.

The first part of this paper presents a discussion of the experimental evidence, old and new, that bears on the problem, and the second part gives a record of the experiments performed by the writer.

² Some of the more instructive treatises are: Irving, R. D., *The copper-bearing rocks of Lake Superior*: U. S. Geol. Survey Mon. 5, 1883; Van Hise, C. R., and Leith, C. K., *The geology of the Lake Superior region*: U. S. Geol. Survey Mon. 52, 1911; Lane, A. C., *The Keweenaw series of Michigan*: Michigan Geol. and Biol. Survey Pub. 6, 1911.

³ Pumpelly, Raphael, *The paragenesis and derivation of copper and its associates on Lake Superior*: Am. Jour. Sci., 3d ser., vol. 2, p. 352, 1871.

⁴ Smyth, H. L., *On the origin of the copper deposits of Keweenaw Point*: Science, new ser., vol. 3, p. 251, 1896.

ACKNOWLEDGMENTS

The writer desires to express his appreciation to the geologists of the Calumet & Hecla Consolidated Mining Co., who very generously presented the available field and other information bearing on the subject and did everything possible to assist and expedite the investigation. He also wishes to thank the members of the United States Geological Survey who criticized his manuscript, Mr. A. C. Spencer especially having made many helpful suggestions.

CHEMICAL POSSIBILITIES RELATING TO THE
EXISTENCE OF COPPER AT DEPTH

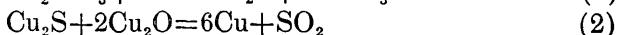
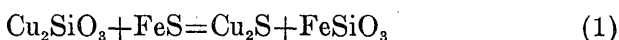
One of the first questions that arose in the investigation concerned the most probable form in which copper may exist at depth.

It has long been held that copper may exist in magmas in the form of a sulphide, as chalcopyrite and bornite are so generally found as primary minerals, but few investigators have considered the changes that might intervene between the magmas and the final ore deposits.

Perhaps the most significant point to decide first is whether water was present, or, if it is impossible to be sure on this point, it may be well to set forth the results to be expected in the absence and in the presence of water to see if there are significant differences in the two classes of reactions.

COPPER IN THE ABSENCE OF WATER

Some of the reactions that take place in the smelting of copper ores show what may be expected under dry conditions. For example,



The first reaction may explain the fact that copper silicate has not been found as a product of igneous origin. The next two reactions might explain the development of metallic copper in a dry magma if by chance sulphur was deficient, hydrogen was absent, and there was not enough oxygen present to oxidize both the copper and the sulphur.

The fact that cuprous sulphide and oxide melt at rather high temperatures, together with the oft-repeated statement that the mineralizers in magmas probably include chlorides and fluorides, turned the writer's attention to the relatively low melting point of cuprous chloride, 434° C., especially in view of a statement by Schnabel⁵ that

⁵ Schnabel, Carl, Handbook of metallurgy, translated by H. Louis, vol. 1, p. 11, Macmillan, 1898.

cupric chloride attacks copper sulphide, producing cuprous chloride with the separation of sulphur.

The reaction last mentioned has been verified (experiment 73, p. 53). It was also found, as expected, that the melting point of cuprous chloride is much lowered by the presence of other chlorides.

A mixture of anhydrous cuprous chloride with 23 per cent of calcium chloride appeared to melt at 384° . Menge,⁶ who studied this system much more carefully, found the eutectic to contain 12 per cent CaCl_2 and its melting point to be 393° .

Mixtures of cuprous chloride with 10, 20, 30, 40, and 60 per cent of sodium chloride all began to melt around 315° , indicating a eutectic at this temperature, but the exact composition of the eutectic mixture could not be determined by this method. It seems probable that other chlorides might lower this point still further.

Truthe⁷ has shown that Cu_2S and CuCl form a eutectic with 16.3 per cent Cu_2S , which melts at 392° . The writer hopes to study melts of this character further, as soon as opportunity can be found to do so, to see if such a study will lead a step nearer to the experimental realization of "magmatic solutions."

Small proportions of native copper in nickel-iron segregations in basalts have been described.⁸ It seems almost necessary to conclude that a very strong reducing agent, such as carbon or hydrogen, has acted in these places, providing the segregations are not ascribed to such a remote source as the interior metallic core of the earth or to meteorites.

The statement of certain investigators⁹ that dry hydrogen does not reduce cuprous sulphide to copper rapidly, if at all, below 600° seems to be supported by work of the writer. A preparation made by heating CuS in hydrogen at 600° gave 79.88 per cent copper and 19.86 per cent sulphur; the theoretical percentages for Cu_2S are 79.86 and 20.14, respectively. Microscopic specks of copper were visible in some preparations, however, the cause of which is not easily explained. The hydrogen sulphide produced when CuS is taken might prevent the formation of copper for a time, but the quantity of free copper did not seem to increase on continuing the heating for six hours.

⁶ Menge, O., Die binären Systeme von MgCl_2 und CaCl_2 mit den Chloriden der Metalle K, Na, Ag, Pb, Cu', Zn, Sn'' und Cd: Zeitschr. anorg. Chemie, Band 72, p. 162, 1911.

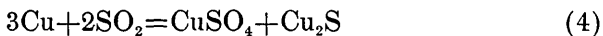
⁷ Truthe, W., Ueber das Verhalten der Sulfide von Pb, Cu', Ag und des Cu_2O in der Schmelzen der zuhörigen Chloride: Zeitschr. anorg. Chemie, Band 76, p. 167, 1912.

⁸ Beyschlag, F., Krusch, P., and Vogt, J. H. L., The deposits of useful minerals and rocks, translated by S. J. Truscott, p. 341, Macmillan, 1916.

⁹ Wegscheider, R., Bemerkungen zur quantitativen Bestimmung des Kupfers als Sulfur: Monatsh. Chemie, Band 14, p. 315, 1893.

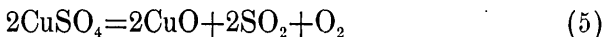
Posnjak, Allen, and Merwin find that chalcocite is stable in a vacuum even at its melting point ¹⁰—that is, 1,130° C.

According to Uhl,¹¹ dry sulphur dioxide reacts with copper at a red heat to form cupric sulphate and cuprous sulphide, thus:



This action does not seem to go on very fast at 500°, however, with dry sulphur dioxide (experiment 90), but the moist gas yields copper sulphide readily.

Prescott and Johnson¹² state that cupric sulphate is decomposed at a red heat, thus:



The point of decomposition is probably nearer a white heat, although there is no experimental evidence on this point.

The scanty evidence available therefore points to a few ways in which copper might be formed in a dry environment, mostly at high temperatures. They simplify to the oxidation of the sulphide or the reduction of oxidized compounds by hydrogen. But reduction by hydrogen yields water and illustrates how difficult it is to proceed without supposing water to be a possible component. In fact, the improbability that water is ever wholly absent justifies us in passing to other possibilities as more likely and common.

COPPER IN THE PRESENCE OF WATER

Morey¹³ has advanced the view that crystallization of a magma may cause increasing pressure to develop in the remaining fluids, provided these contain dissolved gases, especially such as water. Wherever vents exist the fluids will tend to escape. The fluids might be "melts," but as water and other mineralizers increase, the "melts" would have more and more the character of solutions. In what follows, water will be assumed to be one of the constituents.

In recent analyses of the Deccan and other traps by Washington¹⁴ the water content is uniformly high, and he considers this to represent water originally present in the basaltic lavas.

¹⁰ Posnjak, E., Allen, E. T., and Merwin, H. S., *The sulphides of copper*: Econ. Geology, vol. 10, p. 494, 1915.

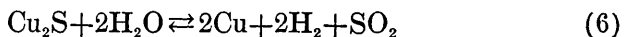
¹¹ Uhl, J., *Ueber Einwirkung von Schwefeldioxyd auf Metalle*: Deutsche chem. Gesell. Ber., Band 23, p. 2151, 1890.

¹² Prescott, A. B., and Johnson O. C., *Qualitative chemical analysis*, 5th ed., p. 325, 1901.

¹³ Morey, G. W., *The development of pressure in magmas as a result of crystallization*: Washington Acad. Sci. Jour., vol. 12, p. 219, 1922.

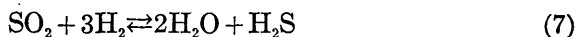
¹⁴ Washington, H. S., *Deccan traps and other plateau basalts*: Geol. Soc. America Bull., vol. 33, p. 765, 1922.

A few years ago the French chemist Gautier¹⁵ showed that steam acting on chalcocite at a bright-red heat produces metallic copper, thus



This reaction suggests that in hot magmas in which water is a prominent constituent the sulphide of copper might be changed to the free metal. But it must be noted that the reaction was obtained only when the resulting gases, sulphur dioxide and hydrogen, were swept away by fresh steam. With little opportunity for the escape of gas there would probably be an equilibrium instead of a one-way reaction. In fact, we must imagine that at depth there are many reversible reactions involving water, sulphur, hydrogen, hydrogen sulphide, the two oxides of sulphur, the two oxides of iron, various compounds of copper as well as the free metal and probably chlorides also, not to mention silica, carbon dioxide, and the different bases. The writer knows of few experiments at high temperatures with such systems as these, but certain reversible reactions have been studied which throw light on the relations that are to be expected.

Randall and Bichowsky¹⁶ have investigated the following reaction from 887° to 1,372° C.:



They find an equilibrium in which water is the predominant constituent; all the other gases are present, however. The concentration of any one constituent depends on that of all the others. As the temperature falls the concentration of H_2S increases, whereas that of the other gases decreases. Increasing pressure favors the reaction toward the right.

In view of this equilibrium it ought to be possible to reverse Gautier's reaction (6), starting with copper, hydrogen, and sulphur dioxide. The writer easily brought about this reversal, as shown in experiment 74, where copper sulphide and water are formed from copper, sulphur dioxide, and hydrogen. The results at 900°, then, indicate that the formation of either copper or chalcocite is possible according to the relative proportions of the gases present. The exact proportion of steam in the mixture that would be necessary to convert chalcocite into copper at any temperature remains to be determined, but it would probably be high. The equilibrium between ferrous oxide and water discussed later, equation (14a), would tend to increase the proportion of water to hydrogen as the

¹⁵ Gautier, A., Action de la vapeur d'eau sur les sulfures au rouge: *Compt. Rend.*, vol. 142, p. 1465, 1906.

¹⁶ Randall, Merle, and Bichowsky, F. R., Equilibrium in the reaction between water and sulphur at high temperatures: *Am. Chem. Soc. Jour.*, vol. 40, p. 368, 1918.

temperature rises. On the other hand, the relations demanded by the equilibrium corresponding to equation (7) are such that the concentrations of SO_2 and H_2 increase along with that of H_2O , which would be adverse to reaction (6). On this account as well as because of the probable significant proportions of sulphur and its compounds in magmatic gases it seems logical to conclude that copper would tend to crystallize from magmas as cuprous sulphide. At lower temperatures, however, by virtue of other equilibria that will be considered presently, equations (9), (10), and (11) and experimental work by the writer, the possibility is presented that copper might exist in solution as cuprous sulphate.

Hydrogen sulphide exists partly in a dissociated condition at elevated temperatures,¹⁷ but this is without effect on the stability of cuprous sulphide.

Hydrogen is well known to be an effective reducing agent at elevated temperatures. It will even reduce aqueous solutions of several oxidized salts of copper to metal at moderate temperatures under pressure, as shown by Ipatief and Verkhovsky.¹⁸ The acetate yielded the free metal after heating at 92° for four days with the hydrogen at a pressure of about 350 atmospheres. Copper was precipitated from the sulphate at a temperature above 90° and the hydrogen at a pressure above 120 atmospheres, but none was produced at 20° with the hydrogen under a pressure of 500 atmospheres.

Cupric chloride, 2 normal, was reduced to cuprous chloride at 155° by hydrogen at a pressure of 100 atmospheres; whereas at 180° a 0.2 normal solution was partly reduced to metallic copper, apparently yielding the following reversible equilibrium:



Thermodynamic calculations show that hydrogen, even at a pressure of 1 atmosphere, should precipitate copper from neutral cupric sulphate solutions of ordinary concentration, and higher pressures would be still more effective, but according to Ipatief the reaction is too sluggish to be within the range of experimental observation much below 90°C .

A current of pure hydrogen may be made to reduce sulphuric acid completely under certain conditions at 700° – 900° , yielding water and hydrogen sulphide,^{19a} but the reversibility of reaction (7) would

¹⁷ Preuner, G., and Shupp, W., Dissociation des Schwefelwasserstoffes: *Zeitschr. physikal. Chemie*, vol. 68, p. 157, 1909.

¹⁸ Ipatief, V. N., and Verkhovsky, V., Ueber das Verdrängen der Metalle aus wässrigen Lösungen ihrer Salze durch Wasserstoff bei hohen Temperaturen und Drucken: *Deutsche chem. Gesell. Ber.*, Band 42, p. 2078, 1909; Band 44, p. 1755, 1911. Also published in *Russian in Russ. phys.-chem. Soc. Jour.*, vol. 41, p. 779, 1909; vol. 43, p. 1746, 1911.

^{19a} Villa, A., Sur la réduction de l'acide sulfurique en hydrogène sulfuré: *Compt. Rend.*, vol. 179, pp. 1163–1165, 1924.

doubtless limit this action in nature, at least if the gases were confined.

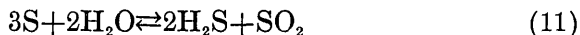
The following facts are noted with special reference to the presence of sulphur dioxide. It follows from reaction (7) that hydrogen converts sulphur dioxide partly into hydrogen sulphide. In the absence of hydrogen there is another equilibrium which was studied at 300° by Bichowsky.¹⁹



Bichowsky has found that an excess of water will displace this reaction almost wholly to the right, whereas an excess of sulphuric acid reverses it. Another equilibrium, which is closely associated with this one, is stated thus:



Lewis and Randall²⁰ also give the following equilibrium at 445°:



A consideration of these equilibria shows that the presence of sulphur or sulphur dioxide with water must necessarily yield some hydrogen sulphide over a considerable range of temperature. In fact, the writer has found that sulphur dioxide in the presence of water between 150° and 200° converts copper into cuprous sulphide without the necessity of having hydrogen present (experiment 48).

More recently it has been shown that the simultaneous presence of acid sulphides and sulphites—that is, the hydrosulphide radical, HS' , and the bisulphite radical, HSO_3' —in solution at ordinary temperature leads to the formation of thiosulphates, especially when the bisulphite is in excess and the acidity is no greater than that of the bisulphite itself.²¹ This observation suggests that thiosulphates should commonly occur in ore solutions. Of course, such solutions are not generally available for laboratory study, but thiosulphates have been reported in one or two so-called "mine waters." Tetrathionates might also be expected to occur in such waters.

A consideration of the equilibria referred to above shows that it makes little difference whether the substances used are hydrogen sulphide and hydrogen, sulphur dioxide and hydrogen at a high

¹⁹ Bichowsky, F. R., Equilibrium in the reaction between sulphur dioxide and water: *Am. Chem. Soc. Jour.*, vol. 44, p. 116, 1922.

²⁰ Lewis, G. N., and Randall, Merle, Equilibrium in the reaction between water and sulphur at the boiling point of sulphur: *Am. Chem. Soc. Jour.*, vol. 40, p. 362, 1918.

²¹ Foerster, F., and Mommsen, E. T., Beitrag zur Kenntniss der Thiosulfate: *Deutsche chem. Gesell. Ber.*, Band 57, p. 258, 1924.

temperature, sulphur dioxide and hydrogen sulphide, sulphur dioxide and water, or sulphur and water at 150° to 200°; the tendency over a wide range of temperature is to convert copper into chalcocite.

The results when iron compounds are also constituents of these systems would be of considerable interest from the viewpoint of a geologist. Lack of time has prevented a full investigation of these possibilities, but a number of the experiments described in this paper throw light on the problem under certain conditions.

That sulphur and sulphur dioxide should be considered possible components of magmatic gases perhaps needs explanation. They are well known as volcanic products, but their origin has generally been ascribed to reactions at or near the surface of the earth. Their existence in magmatic gases must obviously be governed to a considerable extent by the equilibria represented by such equations as (7) and (11), and accordingly it must largely depend on the proportion of hydrogen sulphide in such gases. If the partial pressure of hydrogen sulphide was reduced by any reaction to a small value that reduction would cause a shift in the equilibrium represented by equation (7), for example, and would practically remove SO_2 from consideration.

The experimental evidence on the possible concentration of hydrogen sulphide is very scanty, and much more work will be required to clarify our knowledge of the subject. We have, however, some data on the dissociation pressures of sulphides²² and may also feel certain that many sulphides are hydrolyzed by water at high temperatures. It is consequently logical to assume that appreciable concentrations of hydrogen sulphide may exist in magmatic gases, and if so the other components required by the equilibria that have been discussed would inevitably be present.

It has not seemed wise to limit the discussion in this paper to compounds which must necessarily have come directly from magmatic sources, for products may conceivably have been formed by partial oxidation at one period, buried beneath later formations, and at a subsequent period subjected to the influence of new accessions of steam. Likewise brines that may have been buried at one period could act as potent chemical agents under the influence of heat at a subsequent period. There is such a long range from oxidized compounds at the surface to deep magmas that the study of the possible intermediate conditions seems not only permissible but necessary.

²² Allen, E. T., and Lombard, R. H., A method for the determination of dissociation pressures of sulphides and its application to covellite and pyrite: *Am. Jour. Sci.*, 4th ser., vol. 43, p. 175, 1917.

The relations involved in mixtures containing sulphur dioxide and oxygen will next be considered. Bodenstein and Pohl²³ have shown that the equilibrium



is displaced very largely toward the right at 900° but almost wholly to the left at 400° and lower. The dissociation of SO_2 need not be considered here,²⁴ as it barely begins at 1,000° C. We may therefore consider the action of sulphur trioxide and sulphuric acid on the substances under scrutiny.

It seems possible that concentrated sulphuric acid might be formed in nature under certain conditions—for example, by the escape of the more volatile gases or by the more rapid diffusion of lighter gases from mixtures like those considered above, just as hydrocarbons are believed to separate into various fractions in the earth through diffusion. The main question is whether the free acid, if formed, could long survive uncombined.

It is well known that concentrated sulphuric acid can be heated in glass tubes without attacking them very rapidly. Foerster²⁵ has shown that the attack by concentrated acids is less rapid than that by water, and that the attack increases with the dilution of the acid. The results found in experiment 115*b*, in which an acid solution was heated 4 days at 300° in a Jena glass tube, indicated that very little acid was neutralized by the glass. In experiment 120*a*, which lasted 20 days with half-normal acid at 200°, only 0.0293 gram of acid was neutralized, and in experiment 120*b*, which lasted 11 days at 300°, only 0.0100 gram was neutralized.²⁶

On the other hand, the attack of finely powdered minerals by acids has even been used in mineral analysis. Mitscherlich²⁷ found that the following minerals, when finely powdered, are decomposed at 200° by a mixture of 3 parts sulphuric acid to 1 part water: Some of the spinels, tantalite, ilmenite, pyroxenes, talc, asbestos, chlorite, beryl, garnet, feldspars, petalite, and cordierite. Even glass, in the form of a powder, seems to be decomposed and dissolved by water.²⁸ No investigators seem to have reached conditions of equilibrium in

²³ Bodenstein, M., and Pohl, W., Gleichgewichtsmessungen an der Kontaktschwefelsäure: Zeitschr. Elektrochemie, Band 11, p. 373, 1905.

²⁴ Ferguson, J. B., The thermal dissociation of sulphur dioxide: Am. Chem. Soc. Jour., vol. 41, p. 69, 1919.

²⁵ Foerster, F., Ueber die Einwirkung von Säuren auf Glas: Zeitschr. anal. Chemie, Band 33, p. 305, 1894.

²⁶ Compare Allen, E. T., Crenshaw, J. L., and Merwin, H. H., Effect of temperature and acidity in the formation of marcasite and wurzite: Am. Jour. Sci., 4th ser., vol. 38, p. 397, 1914.

²⁷ Mitscherlich, Alexander, Jour. prakt. Chemie, Band 81, p. 116, 1860.

²⁸ Mylius, F., and Foerster, F., Ueber die Beurtheilung von Glasgefäßen zu chemischen Gebrauche: Zeitschr. anal. Chemie, vol. 31, p. 264, 1892.

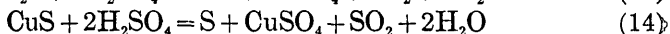
the attack of glass by any solution. The suggestion that possibly alunite was formed in experiment 120a seems to be a step in that direction.

In experiments 129 and 130 the quantity of sulphuric acid neutralized by finely powdered leucite rock and Jena glass tubing during 2 days heating at 250° was quantitatively determined. The leucite rock was found to be attacked over 10 times as fast as the glass tubing under similar conditions. The detailed figures are given with the description of the experiments elsewhere in this paper (p. 59).

That sulphuric acid, if formed in nature, is probably as a rule soon converted into sulphates is undeniable; on the other hand, acid waters from volcanic sources have been reported from certain localities, so that it is no great stretch of imagination to assume that they may have assisted in chemical reactions, even granting that the acidity in some of them is due to oxidation of sulphides.²⁹

In this connection it should be noted that cuprous sulphide and silver sulphide may be dissolved by concentrated sulphuric acid (experiments 35, 58, and 70). The writer believes that such solutions would under certain conditions deposit the free metals, as well as the sulphides, on dilution and cooling. As few solvents for copper sulphide are known this one has chemical if not geologic interest.

The early experiments of Pickering³⁰ on the action of concentrated sulphuric acid on copper sulphide are of historic interest. In his experiments any gas that formed was allowed to escape at atmospheric pressure. He gives the following equations for the reactions:



The time allowed for these experiments was only 30 minutes or less, and the temperature ranged from 19° to 220°.

One of the most noteworthy equilibria that may relate to the alteration of rocks and the genesis of ores is that between water and the two oxides of iron:



This equilibrium has recently been investigated very carefully from 675° to 1,000° C. by Eastman and Evans,³¹ who find that the hydrogen in the gaseous mixture ranges from 46 to 9.9 per cent by

²⁹ For acid waters see Clarke, F. W., *The data of geochemistry*, 5th ed.: U. S. Geol. Survey Bull. 770, p. 199, 1925.

³⁰ Pickering, S., *The action of sulphuric acid on copper*: Chem. Soc. Jour., vol. 33, p. 118, 1878.

³¹ Eastman, E. D., and Evans, R. M., *Equilibria involving the oxides of iron*: Am. Chem. Soc. Jour., vol. 46, p. 888, 1924. References to the earlier literature are given.

volume between these two temperatures respectively. The presence of such percentages of hydrogen would in consequence of the equilibria that have already been discussed tend strongly to keep copper reduced to sulphide, possibly even to metal at the highest temperatures.

In the paper last mentioned Eastman and Evans also refer to the equilibrium



At temperatures between 500° and 900° both carbon dioxide and carbon monoxide are present in considerable proportions at equilibrium. It is believed that carbon monoxide, like hydrogen, would reduce most of the oxidized compounds of copper to free metal, but according to Schnabel it is without action on cuprous sulphide below a red heat.

OXIDATION-REDUCTION REACTIONS

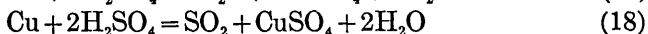
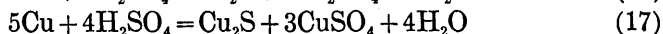
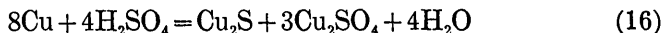
In what has been said and in what follows the frequent occurrence of the terms oxidation and reduction will be noted. These terms mean more than simply the addition or removal of oxygen, for, in the most general sense, any reaction that increases the positive charges on an atom, or its positive valence, may be considered an oxidation. For example, the changes of Cu^+ to Cu^{++} or of S^- to S are oxidations, and the reverse changes are reductions. To refer to a reaction as an oxidation is generally ambiguous, as it is clear that the oxidation of one substance is invariably linked with the reduction of another substance; this includes the reaction in which oxygen passes from free oxygen to oxide. Copper may exist in at least three valences—zero valence, or the free metal, and cuprous and cupric. Sulphur is even richer in forms—sulphide, S^{--} ; the free element, S ; the dioxide, SO_2 , corresponding to S^{+++} ; and the trioxide, SO_3 , corresponding to S^{++++} . In many oxidation-reduction reactions sulphur passes only from S^- to S ; in others, as will be shown, it passes from S^- to S^{++++} , thus exhibiting its maximum shift of eight positive charges.

Let us next consider briefly the solubility of copper and certain of its compounds in different reagents, returning later to reactions involving the precipitation of copper.

SOLUBILITY OF COPPER AND SOME COPPER COMPOUNDS

Dilute sulphuric acid, in the absence of air or other oxidizing agents, has very little action on copper at ordinary temperature.

Even at 200° C. experiment 49 showed solution to the extent of only 8 milligrams per liter. Above this temperature the attack goes somewhat further and yields a number of products, including cuprous sulphide. At least three reactions take place simultaneously, in order of prominence, as follows:



In experiment 137 a tube containing copper and sulphuric acid was heated and observed while hot. Some Cu_2S was seen after heating two days at 200°. The solution was not noticeably blue, which may have been because the copper was largely in the cuprous state. At 250° the solution first turned a very pale yellow and later a pale blue.

That both cuprous and cupric sulphates are formed when copper dissolves in sulphuric acid is probably connected with the fact that an equilibrium tends to be reached between these two salts in the presence of metallic copper, thus



It seems probable that a rapid shift of this equilibrium with changes of temperature explains a feature noted in many experiments—the separation of copper on cooling, as observed in experiments 104, 128, 132*a*, and 132*b*. In experiment 133 all the copper was recrystallized. Although a shift of equations (17) and (18) with changes of temperature should eventually be considered, the shift of reaction (19) appears to be more rapid. The copper appears in the form of beautiful crystals, generally separate or easily separable from the copper originally taken. In several experiments it was determined separately.

If the recrystallized copper was formed by the shift of an equilibrium according to equation (19) on cooling, its amount should measure the copper that existed as cuprous sulphate when hot, except for the small amount which does not precipitate on cooling. As the cuprous salt and total dissolved copper left after cooling are known, the copper in each state when hot was calculated by the following equations:

$$\text{Cu}'' \text{ (hot)} = \text{total dissolved Cu (cold)} - (\text{Cu (cold)} + \text{Cu recrystallized}) \quad (20)$$

$$\text{Cu}' \text{ (hot)} = (\text{recrystallized Cu} \times 2) + \text{Cu}' \text{ (cold)} \quad (21)$$

The results obtained in this way are shown in Table 1, and, derived from them, the mass-law "constant" for reaction (19),

$$K_{19} = \frac{[\text{CuSO}_4]}{[\text{Cu}_2\text{SO}_4]} \quad (22)$$

as well as the constant used by Abel,³²

$$K_A = \frac{\sqrt{[\text{CuSO}_4]}}{[\text{Cu}_2\text{SO}_4]} \quad (23)$$

the theoretical basis for which may be found in his paper. The bracketed quantities in these expressions represent concentrations of the molecular species written in the bracket, and the "constants" are supposed to be constants at any given temperature.

TABLE 1.—*Mass-law constant for reaction (19)*

[Concentrations in gram-molecules per 1,000 grams of water]

Experiment	Temperature (°C.)	[CuSO ₄]	[Cu ₂ SO ₄]	K ₁₉	K _A
Abel.....	0	0.0154	0.00045	34.2	275
Abel.....	25	.0151	.00077	19.5	159
Abel.....	40	.0149	.00095	15.7	128
Abel.....	100	.0145	.00143	10.1	84
132a.....	250	.0041	.025	.16	2.5
138.....	300	.0264	.258	.10	.63
139.....	350	.0729	.324	.22	.84

It appears from Table 1 that both "constants" are in general smaller at high temperature than at ordinary temperature, although the figures do not fall on perfectly smooth curves. It is evident that equilibrium (19), at least over a wide range, is displaced strongly to the left with rising temperature and in the opposite direction as the temperature falls.

It is known from Abel's work that K₁₉ is not strictly constant at constant temperature. Doubtless the reason for this failure in constancy is that the measured concentrations do not represent the concentrations of the molecular species written in reaction (19). Part of each salt is ionized but in different degrees. The reaction may be expressed in ionic form, thus



giving the mass-law constant

$$K_{24} = \frac{[\text{Cu}^{++}]}{[\text{Cu}^+]^2} \quad (25)$$

³²Abel, E., Ueber das Gleichgewicht zwischen den verschiedenen Oxydationstufen desselben Metalles: Zeitschr. anorg. Chemie, Band 26, p. 396, 1901.

but here again the difficulty is immediately encountered of evaluating the ionic concentrations. Abel has pointed out the necessity of considering that the cuprous copper enters very largely into a complex ion, and more recently it has been found that cupric sulphate is also unusually abnormal in its ionization.³³ The correct evaluation of K_{24} and its variation with temperature is an interesting problem for the physical chemist, but to make any considerable progress on it would require more space than should be given to it in this paper.

From Table 1 it is possible to arrive at the total dissolved copper calculated to exist at each temperature for the strength of acid then present, according to the preceding assumptions. This amount may be considered to represent the solubility of copper in sulphuric acid and is shown in Table 2 in grams per 1,000 grams of water.

TABLE 2.—*Solubility of copper in sulphuric acid at high temperatures*

[All concentrations are in grams per 1,000 grams of water]

Experiment	Temperature (°C.)	H ₂ SO ₄	Cuprous copper	Cupric copper	Total copper
49	200	25	-----	-----	0.008
132	250	22	3.4	.26	3.66
138	300	38	35.4	1.7	37.1
139	350	24	44.4	4.6	49.0

The total copper dissolved must also be a function of the concentration of acid at each temperature, and in order to arrive at some idea of this relationship the mass-law constants for equations (16) and (17) were computed separately. The constants, omitting the solids and water, as usual, and neglecting ionization, are as follows:

$$K_{16} = \frac{[\text{Cu}_2\text{SO}_4]^3}{[\text{H}_2\text{SO}_4]^4} \quad (26)$$

$$K_{17} = \frac{[\text{CuSO}_4]^3}{[\text{H}_2\text{SO}_4]^4} \quad (27)$$

The results are given in Table 3.

TABLE 3.—*Mass-law constants for reactions (16) and (17)*

[Concentrations are in gram-molecules per 1,000 grams of water]

Experiment	Temperature (°C.)	[H ₂ SO ₄]	[Cu ₂ SO ₄]	[CuSO ₄]	K ₁₆	K ₁₇
49	200	0.25	5×10 ⁻³	1.2×10 ⁻³	-----	-----
132	250	.22	0.025	0.0041	6.7×10 ⁻³	3.0×10 ⁻³
138	300	.39	.258	.0264	0.75	7.8×10 ⁻³
139	350	.24	.324	.0729	3.0	3.5×10 ⁻³

³³ Lewis, G. N., and Randall, Merle, *Thermodynamics*, p. 362, McGraw-Hill Book Co., 1923.

Table 3 clearly shows that both reactions (16) and (17) go further as the temperature rises. It was found, however, that the sulphuric acid was reduced only to about the same concentration at each temperature studied. Both the cuprous and cupric copper increase with rising temperature, but the cuprous is decidedly in excess at the high temperatures. In fact, at 350° the concentration of the cuprous sulphate exceeds that of the sulphuric acid present.

So far as the writer has been able to determine, reaction (16) can not be reversed, although the sulphuric acid is never entirely consumed. Reaction (17), however, appears to be partly reversible, and much study has been devoted to it, the results of which will be presented later. This reaction was given by Pickering³⁴ for certain experiments made by him to show the action of concentrated sulphuric acid on copper, but generally his results were represented by equation (18). In his experiments sulphur dioxide, if formed, was allowed to escape at atmospheric pressure. In the writer's experiments, on the other hand, weaker acid was used, and the products were confined in closed tubes. Under these circumstances the quantity of sulphur dioxide formed is very small, being generally scarcely enough to determine (experiment 132). In fact, it has been shown that sulphur dioxide and cupric sulphate react, as described in experiments 61 and 124, or at lower temperatures reaction (18) is simply reversed, according to qualitative tests (experiments 46 and 47). Copper will not consume all the available sulphuric acid in dilute solutions, which, from the preceding facts, appears to be due to the accumulation of cupric salt, sulphur dioxide, and perhaps even water itself—all substances that tend to reverse the action.

Doubtless the reactions might also be explained as caused by certain small concentrations of hydrogen, but the final results would not be changed.

Concentrated hydrochloric acid dissolves copper markedly, forming hydrogen and cuprous chloride, which is fairly soluble in the acid or other chloride solutions. The more dilute acid solutions dissolve a little copper. Thus, half-normal acid, containing 18.7 grams per liter, when heated with copper to 165° for 17 hours contained copper equivalent to 0.7 gram per liter (experiment 52). The results of Ipatief have already been mentioned.

Solutions of calcium chloride have been studied because such solutions are now found in the deep levels of the copper mines in Michigan.

³⁴ *Op. cit.*, p. 11. See also Cundall, J. T., and Fairgrieve, M. McC., The action of sulphuric acid on copper: *Chem. Soc. Jour.*, vol. 105, p. 60, 1914.

A concentrated solution of calcium chloride, specific gravity 1.5, containing approximately equal parts of water and calcium chloride, after heating with copper to 175° for 20 hours gave the equivalent of 0.07 gram of copper per liter (experiment 55). On the theory that this result was caused by the partial hydrolysis of calcium chloride into hydrochloric acid and lime, a similar experiment was performed with small quantities of silica and ferric oxide present also. After 54 hours heating at 190° the copper found in the solution was equivalent to 0.19 gram per liter.

Dilute sulphuric acid which is sufficiently concentrated to dissolve ferric oxide forms in the presence of ferric oxide acid ferric sulphate, which dissolves copper rapidly, the iron being reduced to the ferrous state and the solution becoming blue from the cupric sulphate.

Hydrochloric acid under the same circumstances also dissolves copper. In one experiment at 90° (experiment 57) the equivalent of 1.3 grams of copper per liter was found.

Copper is soluble in solutions of ammonium nitrite at ordinary temperature.³⁵ It is also appreciably soluble in cyanide solutions in the presence of air, but these two solvents need not be considered in geochemical studies. It is more or less attacked and dissolved by fused caustic soda at 350° C. and above.

Cuprous sulphide is somewhat soluble in solutions of alkali cyanides. It is also slightly soluble in solutions of ammonium sulphide or ammonium carbonate. It can also be brought into a colloidal condition by water containing hydrogen sulphide. Colloidal solutions have been suggested as possible aids in forming some ore deposits, the escape of gas being suggested as the cause of precipitation.³⁶ The writer has prepared many colloidal suspensions of cuprous sulphide but has generally found them too unstable to pass through filter papers or layers of powdered minerals (experiment 86). They are also coagulated by ferric oxide (experiment 89).

It has already been indicated that if sulphur dioxide and oxygen are components of magmatic emanations, then at certain temperatures sulphuric acid and soluble copper compounds may be present.

Hydrochloric acid is well known as a volcanic emanation. It is formed when hydrogen acts on the heated chlorides of the copper and iron groups, or when sulphuric acid acts on chlorides, and also from the decomposition of calcium chloride and magnesium chloride at high temperatures. To assume that the last source might account for the origin of hydrochloric acid in Michigan is no stretch of the

³⁵ Dhar, N. R., Einwirkung von Metallen, wie Kupfer und Zink, auf eine wässrige Lösung von Ammoniumnitrit: Zeitschr. anorg. Chemie, Band 119, p. 174, 1921.

³⁶ Tolman, C. F., jr., and Clark, J. D., The oxidation, solution, and precipitation of copper in electrolytic solutions and the dispersion and precipitation of copper sulphides from colloidal suspensions, with a geological discussion: Econ. Geology, vol. 9, p. 559, 1914. For the rôle of absorption in the genesis of ores see Kohler, E., Zeitschr. prakt. Geologie, vol. 11, p. 49, 1903.

imagination, for concentrated solutions of calcium chloride occur in the present deep mine waters, and the writer has actually heated some rock from one of the lower levels of the Calumet & Hecla lode and obtained water followed by hydrochloric acid.

The temperature at which calcium chloride begins to decompose in the presence of moisture is not known exactly. It is probably over 300°. Magnesium chloride, on the other hand, shows a tendency to decompose around 180°, which may explain the absence of magnesium chloride in the deep mine waters.

Although "alkaline sulphide solutions" have long been considered the normal type of deep mineralizing solutions, the waters that have been collected and tested probably do not exactly represent magmatic emanations but rather mixtures of these emanations with large proportions of circulating waters, generally very dilute and frequently not even hot, which in passing through long rocky channels become at least neutral if not alkaline.

In a single experiment (79) liquid sulphur dioxide could not be seen to dissolve any cuprous sulphide at ordinary temperature or at 64°, although Prescott and Johnson state that liquid sulphur dioxide dissolves sulphur.

Copper sulphate is soluble in cold water to the extent of 210 grams to the liter at 25° C., the solid phase being $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. This solubility increases regularly up to about 105°, where the solid phase becomes $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, and on further increase of temperature the solubility changes very slightly. The addition of sulphuric acid decreases the solubility of cupric sulphate markedly at all temperatures. On account of its significance for the problem in hand the writer made some determinations of the solubility in rather concentrated solutions of sulphuric acid at 200° C., with the results shown in the following table:

TABLE 4.—*Solubility of cupric sulphate in sulphuric acid at 200° C.*

Volume of solution (cubic centimeters)	Weight of solution (grams)	H_2SO_4 (grams)	H_2O (grams)	CuSO_4 (grams)
1,000	1,727	1,615	104	8
1,000	1,690	1,344	294	52
1,000	1,649	1,205	365	81

Metallic copper reacts with all cupric solutions to form more or less cuprous salt. The proportion of cuprous to cupric salt varies with the salt, with the concentration, and with the temperature; the relations for the sulphate at different temperatures are indicated in Table 1.

On account of the possible connection between solutions of copper and calcium chloride in the Lake Superior region the writer determined the solubility of cuprous chloride in such solutions at 25° C. (experiments 149-155). This solubility is very considerable when the concentration of calcium chloride is high, resembling the behavior with ferrous chloride and certain other salts. The data on solubility are given in Table 13 on page 69. The determinations might well be extended to higher temperatures. That such solutions deposit copper on dilution is shown in experiment 52a.

TRANSPORTATION OF COPPER

It is obvious that a number of the solutions referred to in the preceding pages could serve as transporting agents. This alone, however, can not explain deposits of copper; it should also be shown that precipitation is a logical final step.

To illustrate this point it may be said that cold dilute solutions can carry cupric sulphite or, what is the same thing, cupric sulphate and sulphur dioxide. Such solutions deposit copper on warming. But as it is necessary to assume that ascending solutions would be hot at the start, this particular reaction seems inapplicable to account for the deposition of copper. The same may be said of the simple hypothesis of precipitation caused by ferrous compounds acting on ascending solutions,³⁷ for ferrous compounds are just as likely to occur at depth, and how could the copper have got away from them? Another factor is needed to complete such a hypothesis.

The transfer of copper from hot to cold regions is the particular problem for consideration here. Such a transfer is possible where sulphates are present and rests on the formation and subsequent decomposition of cuprous sulphate. The transfer would of course be much increased by convective currents. It seems entirely logical to assume that some metallic copper is deposited in this way in nature, especially where the temperature gradient is high.

The quantity of copper deposited by a single cooling of a hot solution of the kind just referred to is rather small. Larger quantities have been obtained in laboratory experiments by maintaining a continuous circulation between hot and cold points by means of closed circuits or the use of large tubes favorable to convective circulation. In nature there usually can be considered only a single movement of a solution or diffusion, in the strict sense, through relatively narrow channels.

³⁷ Smyth, H. L., On the origin of the copper deposits of Keweenaw Point: Science, vol. 3, p. 251, 1896.

Diffusion is generally held to be too slow a process to account for the formation of most ores, but there appear to be circumstances under which it might have some effect. It appears difficult to suppose that the Lake Superior copper has collected into lodes by diffusion from small particles extensively disseminated in the traps. There is little if any reason to assume any concentration or temperature gradient toward the lodes as they are situated at present, and consequently none to assume concentration by diffusion from the source mentioned.

If diffusion from depth is postulated it seems necessary to suppose that such diffusion was restricted to fairly continuous water-filled channels; otherwise the copper would have been more widely distributed horizontally. The amount of diffusion possible in such channels can easily be approximated by making certain simple assumptions.

For example, let it be assumed arbitrarily that on account of differences in temperature the concentration of copper falls from 40 grams per liter to a trace within a vertical distance of 2 miles. Let it also be assumed that copper in solutions such as we are now considering will diffuse at the same rate as sodium chloride under similar conditions, that the average temperature was 200° C., and that all the copper which diffused was deposited. Then, according to the usual laws of diffusion,³⁸ the results are as set forth in the following table:

TABLE 5.—*Diffusion of copper in aqueous solutions*

Period	Concentration gradient (gram-equivalent per centimeter)	Cross section (square centimeter)	Temperature (°C.)	Quantity diffused (gram-equivalents)
1 day.....	1	1	18	1.06
1 day.....	1	1	200	5.6
1 day.....	0.000008	1	200	.000045
1 year.....	.000008	1	200	.016
2,900 years.....	.000008	1	200	46

The quantity 46 gram-equivalents, or 3.2 pounds, is sufficient copper to yield a column of "ore" half a mile high and 1 square centimeter in cross section, carrying 0.6 per cent copper. Under the conditions assumed in the calculation it would require 2,900 years for 3.2 pounds of copper to cross a square centimeter section. The richness of the ore deposit would therefore depend simply on the size of the available channels as related to the extent in height and cross section of the zone in which deposition occurred.

³⁸ Lewis, W. C., A system of physical chemistry, vol. 1, p. 428, Longmans & Co., 1916.

The calculations were made on the assumption of a uniform concentration gradient. Actually the gradient would probably be much steeper near the region of high temperature. For this reason the period calculated is most likely a minimum, and the maximum may be much greater. The process of diffusion would also doubtless be somewhat complicated by absorption of the dissolved constituents by the channel walls. However, the figures show the probable importance of the phenomenon of diffusion and also the desirability of learning as much as possible concerning the concentration of copper in various solutions at high temperature.

An actual movement of solutions from the hot region to the cool region would serve the purpose just as well as diffusion, provided that sufficient copper in solution can be postulated and that appropriate chemical reactions can be given to explain the deposition of copper, and the rate of transfer might be much more rapid than it could be by diffusion.

PRECIPITATION OF COPPER

It should be noticed first of all that hot acidified cuprous sulphate solutions, which can be considered cupric sulphate solutions saturated with copper, deposit copper on cooling. This fact is shown by many experiments in the literature, especially the so-called hot and cold tube experiments of Foerster and Seidel,³⁹ Richards, Collins and Heimrod,⁴⁰ and Stokes.⁴¹ It is immaterial how the cuprous sulphate is produced. For example, it may result from the action of cupric sulphate on chalcocite (experiments referred to on p. 36). Attempts to obtain the deposition of copper on cooling solutions of cuprous sulphate in the presence of cuprous chloride were not very successful, however, as basic salts and cuprite formed instead, but it is believed that this was because hydrochloric acid was driven into the vapor phase during heating of the tubes (experiments 135*a* and 135*b*). The experimental conditions could not be framed to agree exactly with the probable natural conditions. The effect of sodium chloride has not been sufficiently studied to say that it wholly prevents the deposition of copper from these solutions on cooling, but it at least lessens such deposition greatly, as the cuprous sulphate merely forms cuprous chloride and sodium sulphate.

³⁹ Foerster, F., and Seidel, O., *Zur Kenntniss der Elektrolyse von Kupfersulfatlösungen*: *Zeitschr. anorg. Chemie*, Band 14, p. 120, 1897.

⁴⁰ Richards, T. W., Collins, E., and Heimrod, G. W., *The electrochemical equivalents of copper and silver*: *Am. Acad. Proc.*, vol. 35, p. 124, 1899.

⁴¹ Stokes, H. N., *Experiments on the solution, transportation, and deposition of copper, silver, and gold*: *Econ. Geology*, vol. 1, p. 645, 1906.

Another general reaction less often referred to is the precipitation of copper from cuprous salt solutions by dilution.⁴² Particularly solutions containing cuprous chloride dissolved in hydrochloric acid or other chlorides, such as calcium and sodium chloride, and in equilibrium with copper, precipitate copper when diluted with water (experiment 52a). One is strongly tempted to conclude that some of the "mass" copper in fissures in the Lake Superior mines may have originated in this way at places where concentrated cuprous solutions mingled with more dilute waters.

Small flakes of copper may also be observed as the result of diffusion in capillary spaces or through semipermeable membranes under certain conditions.⁴³ If a concentrated solution of alkali sulphide is poured into a solution of cupric sulphate with as little stirring as possible the flocs of copper sulphide become more or less coated with metallic copper in the copper solution. This result is no doubt due to electrolytic action in which a circuit is formed, so that an electric current passes through the precipitate and returns through the solution, reducing copper ions to copper at one point and oxidizing sulphide ions to polysulphide at another point. Electric activity is probably responsible for some of the treelike growths and filaments of copper and silver in nature, but it would be foolish to attempt to explain thus all these occurrences. The electrolytic action depends on the passage of a current through solutions or moist rocks, and hence the oxidations and reductions involved may occur at points more or less separated. Many interesting results may be observed by anyone who will take the trouble to set up the combinations, when pieces of sulphide ore or strips of various metals are suspended at the boundary line of two dissimilar solutions, one being oxidizing and the other reducing. The difficulty of applying the observations, as well as lack of space, however, compels us to pass to the more usual phenomenon of chemical reaction.

In addition to the reactions already cited are those involving ferrous compounds, which have been repeatedly given in the literature to explain the origin of metallic copper.⁴⁴

Nearly all chemists who have described the reduction of copper salts by ferrous salts leave the inference in the reader's mind that only a little copper was obtained in their experiments, but that

⁴² Abegg's Handbuch, Band 2, abt. 1, p. 581, 1908.

⁴³ For references, see Wells, R. C., U. S. Geol. Survey Bull. 548, p. 8, 1914.

⁴⁴ Pumpelly, Raphael, The paragenesis and derivation of copper and its associates on Lake Superior: *Am. Jour. Sci.*, 3d ser., vol. 2, pp. 188-198, 243-258, 347-355, 1871 (especially p. 353). Stokes, H. N., Experiments on the solution, transportation, and deposition of copper, silver, and gold: *Econ. Geology*, vol. 1, p. 648, 1906. Fernekas, Gustave, Precipitation of copper from chloride solutions by means of ferrous chloride: *Econ. Geology*, vol. 2, p. 580, 1907. Lane, A. C., Keweenaw series of Michigan: *Michigan Geol. and Biol. Survey Pub.* 6, p. 847, 1911. Lindgren, Waldemar, *Mineral deposits*, p. 399, 1913.

enough was obtained to show that it might be formed that way in nature.

Thus Knop obtained only a mirror on the glass vessel in the course of time.⁴⁵ Wibel⁴⁶ could not repeat the experiment, but obtained traces of copper at 210° C. Braun obtained a "partial deposition." Hunt⁴⁷ states, however, that an excess of ferrous chloride converts one-third of the copper of cuprous oxide to metal. He also states that an excess of ferrous oxide or ferrous carbonate reduces all the copper of cupric chloride to metallic copper.

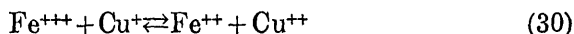


The experiment described by Stokes, starting with cupric and ferrous sulphate, was repeated by the writer (experiment 14) and yielded some copper on cooling, after heating at 200° for about 3 hours.

The equilibrium involved here is apparently the well-known one between ferric and cuprous salts on the one hand and ferrous and cupric salts on the other. For example,



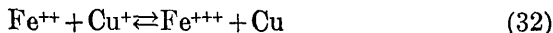
or as ions



Reasoning based on E. M. F. measurements leads to the expression for the equilibrium constant

$$\frac{[\text{Cu}^{++}][\text{Fe}^{++}]}{[\text{Cu}^+][\text{Fe}^{+++}]} = 10^{10} \quad (31)$$

In other words, the reaction with soluble salts lies very largely toward the right, but in neutral or alkaline solutions, because ferric hydroxide is much less soluble than ferrous hydroxide, the equilibrium may be displaced toward the left, when a second reaction occurs, forming metallic copper, thus:



The formation of the copper, however, may conceivably occur on account of the accumulation of cuprous ions, thus:



⁴⁵ Knop, A., Ueber die Kupfererz-Lagerstätten von Klein-Namaqualand und Damara-land; ein Beitrag zur Entwicklungs-Geschichte der Kupfer-Erze: Neues Jahrb., p. 514, 1861. (Also especially p. 543.)

⁴⁶ Biddle, H. C., The reduction of copper by solutions of ferrous salts: Am. Chem. Jour., vol. 26, p. 377, 1901.

⁴⁷ Hunt, T. S., Contributions to the chemistry of copper: Am. Jour. Sci., 2d ser., vol. 49, p. 154, 1870.

The latter reaction is known to be displaced strongly to the right on cooling and seems to be the fundamental reaction that explains the deposition of copper by cooling alone.

Experiments 159 and 160, referring to equation (32) and also described elsewhere,⁴⁸ show conclusively that copper is deposited in visible crystals when the neutralization necessary to bring about reaction (32) in chloride solutions is made to occur slowly, even without any cooling. When sulphates are used no copper has up to the present been observed to deposit before cooling begins.

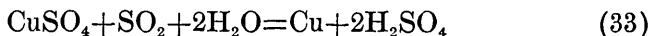
Potassium fluoride appears to have the same effect as alkalinity in bringing about the deposition of copper in mixtures of cupric and ferrous salts, according to Müller.⁴⁹

Deposition by ferrous compounds would seem to afford a possible explanation for the origin of native copper wherever acid copper-bearing solutions entered rocks carrying ferrous compounds, where the solutions were neutralized to the point at which ferric oxide would be precipitated. This explanation is not applicable, however, where ferric oxide appears to have been reduced and dissolved concomitant with the deposition of the copper, as is indicated in the Michigan deposits.

Mellor⁵⁰ gives an extensive bibliography referring to the many ways in which metallic copper can be formed from its compounds by reduction with organic substances, metals, and different reagents, especially at high temperatures, but very few of these ways could have any application to geochemical processes. Field evidence indicates that carbonaceous matter has precipitated metallic copper in some natural occurrences, however.

Let us now consider certain ways in which copper may be deposited chemically when some of the compounds involved contain sulphur in other forms than sulphate.

When a dilute solution containing cupric sulphate and an excess of sulphur dioxide is heated between 100° and 150° C. beautiful crystals of copper are deposited (experiments 46 and 47).



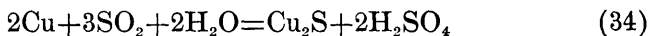
Cupric sulphite yields the same result as the sulphate. If, however, the temperature is raised to a point between 150° and 250° the copper first formed is more or less converted into cuprous sulphide (experiment 61). We have already seen that cuprous sulphide is formed when sulphuric acid acts on copper above 200°. Copper,

⁴⁸ Wells, R. C., Reaction between ferrous salts and cuprous salts: *Am. Jour. Sci.*, 5th ser., vol. 8, pp. 428-433, 1924.

⁴⁹ Müller, Erich, Ueber die reduzierende und oxydierende Kraft von Eisensalzen: *Zeitschr. Elektrochemie*, Band 14, p. 76, 1908.

⁵⁰ Mellor, J. W., *Inorganic and theoretical chemistry*, vol. 3, p. 10, Longmans, 1923.

when heated with a solution of sulphur dioxide at 200° to 230° (experiments 48, 59, and 60), is also converted into cuprous sulphide, probably according to the reaction



Now in this reaction the presence of ferric oxide decreases or prevents the formation of the sulphide, doubtless because the sulphur dioxide is consumed in reducing the ferric oxide (experiment 60). This experiment furnished the first concrete evidence found that the presence of ferric oxide could explain the persistence of copper, whereas in its absence chalcocite would be formed. Suppose that copper were first formed by any reaction whatever; a subsequent accession of sulphur dioxide would convert the copper into sulphide except where protected by the presence of ferric oxide.

If in the action of sulphur dioxide on cupric sulphate (experiment 61), there had been an excess of cupric sulphate instead of sulphur dioxide, the result would have been somewhat different. Under these circumstances less sulphide of copper is formed in the interval between 150° and 250°, and copper is the principal solid product (experiment 124). The products depend on whether sulphur dioxide or cupric sulphate is in excess: an excess of sulphur dioxide forms some chalcocite; an excess of cupric sulphate forms chiefly copper, unless too much sulphuric acid is present (experiment 128).

These somewhat confusing results are evidently explained by differences of temperature, the proportions of the substances taken, and reversibility of the reactions involved.

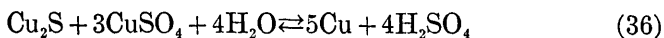
Thus, reaction (33), which proceeds to the right under the conditions mentioned, is the reverse of the one given by Pickering for the generation of sulphur dioxide by the action of concentrated sulphuric acid on copper.

Again, the reaction written for experiment 58,



is practically the reverse of that which explains the results of experiment 61.

Finally, if we multiply equation (33) by 5 and add it to equation (35) we obtain



which is the equation that has been found to explain most nearly the formation of copper from cuprous sulphide. Equation (36) is the reverse of equation (17), which represents in part the action of copper on sulphuric acid. We shall return to this reaction presently.

FORMATION OF NATIVE COPPER THROUGH OXIDATION OF SULPHUR BY FERRIC COMPOUNDS

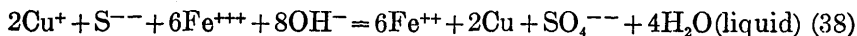
HYPOTHETICAL REACTIONS

The hypothesis that native copper has been formed through oxidation of sulphur by ferric compounds, which has been advocated with confidence by the geologists of the Calumet & Hecla Consolidated Mining Co., is, in simplest terms, that the copper was brought to its present position in a solution from which it would have been deposited as sulphide in the absence of hematite, but owing to the presence of the ubiquitous hematite the sulphur was oxidized, so that metallic copper was deposited instead.

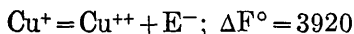
In its simplest form this conception might be expressed by the following reaction:



The thermal effect of this reaction at ordinary temperature is calculated to be an absorption of 38,700 calories, which is not encouraging for the reaction. Supposing the reaction to be entirely an ionic one, it may also be written



It is possible to evaluate the difference in free energy between the factors and products of this reaction by the methods outlined by Lewis and Randall,⁵¹ and the result is the very favorable diminution of free energy of 253,914 calories when all of the substances are present in their standard states. This calculation is based on one value not found in Lewis and Randall:



It must be noted at once, however, that the insolubility of the compounds involved greatly alters the situation, and according to the computations of the writer, the reaction can not be expected to take place under ordinary conditions, except in alkaline solutions and when the sulphate concentration is low.

The details of the calculation are as follows:

If $\Delta F^\circ = -253,914$ it is calculated that $\log K_{298} = 186$, and K , the equilibrium constant at ordinary temperature, is consequently 10^{186} . That is:

$$K = \frac{[\text{Fe}^{++}]^6 [\text{SO}_4^{--}]}{[\text{Cu}^+]^2 [\text{S}^{--}] [\text{OH}^-]^8 [\text{Fe}^{+++}]^6} = 10^{186} \quad (39)$$

⁵¹ Lewis, G. N., and Randall, Merle, Thermodynamics, p. 596, McGraw-Hill Book Co., 1923.

Now $[\text{Cu}^+]^2 [\text{S}^{--}]$, the solubility product of Cu_2S , is 2.2×10^{-47} , according to Trümpler.⁵²

Lamb⁵³ gives $[\text{Fe}^{++}] [\text{OH}^-]^2 = 9.8 \times 10^{-15}$, and Müller⁵⁴ gives $[\text{Fe}^{+++}] [\text{OH}^-]^3 = 1.1 \times 10^{-36}$.

On substituting in equation (39) the values of $[\text{Fe}^{++}]$ and $[\text{Fe}^{+++}]$ obtained from their solubility products, also 2.2×10^{-47} for $[\text{Cu}^+]^2 [\text{S}^{--}]$, and solving, we obtain

$$K = 2.4 \times 10^{178} \frac{[\text{SO}_4^{--}]}{[\text{OH}^-]^2} \quad (40)$$

If $[\text{SO}_4^{--}]$ is ten-thousandth molal, corresponding to the solubility of barium sulphate, we have

$$\text{For neutrality, } K = 2.4 \times 10^{188}$$

$$\text{For } 0.00001 \text{ N OH}^-, K = 2.4 \times 10^{184}$$

$$\text{For } 0.001 \text{ N OH}^-, K = 2.4 \times 10^{180}$$

A comparison of these values with that for equilibrium, $K = 10^{186}$, shows that it is only in the alkaline solutions that the reaction can be expected to occur, as already stated. Experiments with alkaline solutions, however, did not yield any conclusive results on account of experimental difficulties. The conditions of ionization and concentration in "magmatic solutions" above 300° still remain largely speculative and might be considerably different from those assumed above.

The calculations were not completed until after a good many experiments had been made, which was just as well, perhaps, because it was found that a certain amount of copper could be formed, even in acid solutions, from the above-named substances by virtue of other reactions. Reaction (37) is merely illustrative, and there are several other possibilities.

Instead of preparing solutions of cuprous sulphide of workable concentration in the laboratory it was necessary to use the solid. Until more is known about the character of the natural solutions carrying "copper sulphide" it seems necessary to postulate rather large quantities of solution, but this difficulty is clearly not insuperable, because in nature, in many parts of the world, copper sulphide has evidently been extensively transported in solution to form ore deposits. Obviously experimental conditions can seldom conform to natural conditions in all respects.

It appears possible to test the hypothesis under scrutiny by field evidence also. A good many localities where it seems to explain the

⁵² Trümpler, G., Zur Kenntnis des Elektromotorischen Verhaltens von Metallverbindungen mit Elektronenleitung: Zeitschr. physikal. Chemie, Band 99, p. 9, 1921.

⁵³ Lamb, A. B., The potential of iron calculated from equilibria measurements: Am. Chem. Soc. Jour., vol. 32, p. 1218, 1910.

⁵⁴ Müller, Erich, Ueber die reduzierende und oxydierende Kraft von Eisensalzen: Zeitschr. Elektrochemie, Band 14, p. 76, 1908.

facts, in addition to those in the Lake Superior district, have already come to light. In studying the origin of native copper in the red sandstone of Corocoro Steinmann concluded that ferric oxide has inhibited the deposition of copper sulphide and favored the deposition of copper.

STEINMANN'S EXPERIMENT

As further support for the conclusion above cited an experiment was made by L. Gassner under Meigen's direction, given in Steinmann's article, in which precipitated copper sulphide and ferric hydroxide were allowed to act on each other in the presence of calcium carbonate.⁵⁵

Gypsum was formed, and apparently a ferrous compound, but nothing is stated to show that metallic copper was one of the products.

This experiment has been repeated and studied very carefully under different conditions.

It has been found that when the reacting substances are carefully freed from soluble sulphates and when air is wholly excluded the quantity of sulphur oxidized in a couple of weeks, even at 92°, is extremely small (experiment 38). Nor were any better results obtained at 300° under the simple conditions recorded in experiments 44 and 45. Experiment 50 resembles experiment 38*b*, with 23 days' heating.

The striking changes observed when the solutions had an acid reaction, however, as in experiment 38*d*, were deemed worthy of further study. This phase of the problem is discussed in a later part of the paper.

ACTION OF SULPHIDE WATERS ON FERRIC OXIDE

Waters containing sulphides of the alkalis or alkaline earths convert ferric oxide into pyrite under certain conditions,⁵⁶ at least when the sulphides are in excess. Just what the results would be when ferric oxide is in excess does not seem to have been investigated with care. Some suggestions may be drawn from the experiments described in this paper that involve cuprous sulphide. In the Lake Superior district the sulphides of iron seem to be even rarer than chalcocite, and any hypothesis for the copper that involves sulphur as one

⁵⁵ Harry Rosenbusch Festschrift, p. 360, 1906.

⁵⁶ Doelter, C., *Synthese und Zusammensetzung des Pyrrhotin*: Min. pet. Mitt., vol. 7, p. 535, 1885-86. Allen, E. T., and Crenshaw, J. L., *Effect of temperature and acidity in the formation of marcasite (FeS₂) and wurtzite (ZnS)—a contribution to the genesis of instable forms*; Microscopic study by H. E. Merwin: Am. Jour. Sci., 4th ser., vol. 38, p. 427, 1914.

of the constituents would seem to require that the sulphur must have been almost completely oxidized and removed at some stage of the process. As will be shown later the most plausible theory to fit these requirements is that the sulphur was oxidized to sulphate or other soluble compounds and thus removed from the field of action.

Acid solutions in the presence of an excess of ferric oxide oxidize even cuprous sulphide, and considerable study has been given to the possible relations involved in such combinations.

FERRIC OXIDE, COPPER SULPHIDE, AND ACID

Mixtures of ferric oxide and copper sulphide are attacked by acids with results that depend on a number of factors. Ferric oxide is apparently attacked first, and further action resembles in many respects that produced by soluble ferric compounds. The marked tendency of ferric salts to hydrolyze, however, especially at high temperatures, is a significant feature of the problem. More and more acid is required to maintain appreciable quantities of ferric iron in solution as the temperature rises.

EQUILIBRIUM BETWEEN FERRIC OXIDE AND ACIDIFIED SOLUTIONS OF FERRIC SULPHATE

The composition of acidified ferric sulphate solutions that can remain in equilibrium with ferric oxide has been determined over a wide range of concentration and temperature by Posnjak and Merwin.⁵⁷ The figures given in Table 6 have been interpolated graphically from their data for the purpose of showing the content of ferric oxide of such solutions up to 4 per cent SO_3 .

TABLE 6.—Content of ferric oxide of acid ferric sulphate solutions in equilibrium with Fe_2O_3 , expressed in per cent

Temperature (°C.)	0.5 per cent SO_3	1.0 per cent SO_3	1.5 per cent SO_3	2.0 per cent SO_3	4.0 per cent SO_3
50.....	^a 0.2	^a 0.5	^a 0.9	^a 1.3	^b 2.6
75.....	^a .1	^a .3	^a .8	^a 1.3	^c 2.5
100.....	^a .03	^b .2	^c .5	^c .91	^d 2.1
140.....	^d Trace.	^d .01	^d .04	^d .2	^d 1.2
200.....	^d Trace.	^d Trace.	^d .02	^d .04	^d .4

^a Solid phase, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

^b Solid phase, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ (?).

^c Solid phase, $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$.

^d Fe_2O_3 .

⁵⁷ Posnjak, E., and Merwin, H. E., The system $\text{Fe}_2\text{O}_3\text{—SO}_3\text{—H}_2\text{O}$: Am. Chem. Soc. Jour., vol. 44, p. 1965, 1922.

The tendency toward hydrolysis is clearly shown by Table 6.⁵⁸ It is evident that a solution of ferric sulphate, of any such acidity as shown in the table, which is in equilibrium with ferric oxide at a high temperature, will dissolve much more of it on cooling. This fact offered a practical difficulty in the experimental work, as solutions in equilibrium with ferric oxide at a high temperature would acquire more ferric salt on cooling and thus perhaps dissolve a little copper if any had been formed. It seemed best not to attempt to work with ferric oxide in excess under such conditions.

The work of Posnjak and Merwin seems to show that the ferric salt in equilibrium with a solution saturated with ferric sulphate and containing considerable sulphuric acid at temperatures above 200° C. would probably be the basic salt, $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$; and the maximum concentration of iron in the solution would be less than 3 per cent of Fe_2O_3 for 10 to 50 per cent SO_3 . But quantities far less than this would oxidize sulphides.

BLEACHING ACCOMPANYING COPPER

The red rock of the Calumet conglomerate and the amygdaloidal lodes is noticeably bleached near the copper. Geologists have found that the bleached areas contain a lower percentage of total iron, especially of ferric iron, than the near-by unbleached rock.

This is apparently a widespread phenomenon that requires explanation. Either the solutions that brought in the copper were able to reduce hematite or the copper has done it; in either event the ferrous compounds thus formed have been removed. That the deposition of copper may not invariably accomplish bleaching is suggested by a few occurrences of copper in contact with unbleached rock, and by the fact that in one of Stokes's experiments at 200° he obtained hematite and copper side by side.⁵⁹ But it seemed desirable to obtain further experimental evidence on this point.

Solids, such as ferric oxide and copper, can of course affect each other only through the agency of solutions in contact with them that serve as media for the transportation of the reacting elements. But ferric oxide is one of the most insoluble oxides known, if we judge from its behavior in the fractional precipitation of hydroxides.⁶⁰ Neutral and alkaline solutions do not dissolve enough of it to give a test with thiocyanates, and the writer has found that the solution must have an acidity as great as $\text{pH}=5.5$ permanently to dissolve enough to respond to the test.

⁵⁸ See also Wells, R. C., The electrical conductivity of ferric sulphate: *Am. Chem. Soc. Jour.*, vol. 31, p. 1027, 1909.

⁵⁹ *Econ. Geology*, vol. 1, p. 648, 1906.

⁶⁰ Wells, R. C., The fractional precipitation of some ore-forming compounds at moderate temperatures: *U. S. Geol. Survey Bull.* 609, p. 25, 1915.

While making the above tests the writer also noted the marked tendency of ferric oxide to go into a colloidal solution around pH=5.4 (experiment 11). Thomas and Frieden⁶¹ have indicated the value pH=5.0 for the same phenomenon.

Experiments on the modification of aqueous solutions by metallic copper were made by Fischer,⁶² who showed that metallic copper will come into equilibrium (equation 19) with a cupric sulphate solution under certain conditions in a few hours. It seemed desirable to investigate whether copper could affect ferric oxide in this way.

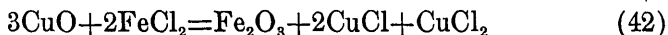
In neutral or alkaline solution no action could be detected (experiment 5). In the presence of carbon dioxide the results were inconclusive (experiment 39). With ferric sulphate, however, action began at once (experiment 12) and the ferric salt was largely reduced with accompanying solution of copper—that is, acid solutions caused a reaction to occur rapidly.

Some experiments were also made to see if cuprous salts are able to reduce ferric oxide. In alkaline or even neutral solutions no significant action could be detected (experiments 2, 3, 4).

The reaction which might be expected here may be written



Not only did the experiments fail to show that such a reaction occurs to any significant extent, but essentially the reverse reaction was found to occur with ease by Hunt,⁶³ who gives the equation



Here the cupric compound is only partly reduced to cuprous salt, but the whole of the ferrous salt is oxidized to ferric. The progress of the reaction is facilitated by the presence of NaCl to dissolve the CuCl formed.

Biddle also states that from an emulsion of ferrous and cupric hydroxides, after long standing, crystals of cuprous oxide can be separated.⁶⁴

In the presence of acids, on the other hand, noticeable reaction occurs (experiment 145), and the results are very similar to those

⁶¹ Thomas, A. W., and Frieden, A., Ferric salts as the "solution link" in the stability of ferric oxide hydrosol: *Am. Chem. Soc. Jour.*, vol. 45, p. 2529, 1923.

⁶² Fischer, Franz, Die chemische Uebertragbarkeit der Metallpotentiale und der chemische Lösungsdruck der Metalle: *Zeitschr. physikal. Chemie*, Band 52, p. 55, 1905. Earlier experiments are given by Abel, E., Über das Gleichgewicht zwischen den verschiedenen Oxydationsstufen desselben Metalles: *Zeitschr. anorg. Chemie*, Band 26, p. 361, 1901.

⁶³ Hunt, T. S., On the general metallurgical method of Messrs. Whelpley and Storer: *Am. Jour. Sci.*, 2d ser., vol. 43, p. 305, 1867; also somewhat more fully in *Contributions to the chemistry of copper*: *Idem*, vol. 49, p. 153, 1870.

⁶⁴ Biddle, H. C., The reduction of copper by solutions of ferrous salts: *Am. Chem. Jour.*, vol. 26, p. 377, 1901.

in which copper is used. The soluble ferric salt formed by solution of ferric oxide in the acid is rapidly reduced to ferrous salt with accompanying oxidation of the cuprous salt.

RESULTS WITH AN EXCESS OF ACID

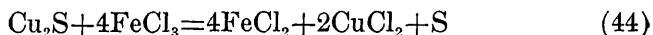
In order to hasten the investigation a number of experiments were tried with ferric sulphate and ferric chloride in place of ferric oxide and acid.

The results obtained depended on whether the copper sulphide or the ferric salt was in excess.

With the ferric salt in excess, experiment 11, for example, shows that the cuprous copper is quickly oxidized even at ordinary temperature.



But conjointly with this reaction some of the sulphide sulphur is also oxidized to free sulphur, the reaction for which would be



In experiment 101 sulphur was observed as a product soon after the components were mixed and warmed slightly. On heating to a higher temperature covellite became visible. The further possible reactions involved in this experiment are given with the discussion of the analytical results.

In experiment 102, in which Cu_2S was decidedly in excess, cuprous chloride crystallized whenever the tube was cooled, indicating still another reaction:



Lastly, there is the possibility of the oxidation of free sulphur to sulphur dioxide or sulphuric acid or both. Many hints are found in the literature that sulphuric acid may be formed in experiments such as those under consideration, especially at 170° or higher. Stokes⁶⁵ found that at 100° ferric sulphate oxidizes about 17 per cent of the sulphur of marcasite and about 60 per cent of that of pyrite to sulphuric acid. He found that an excess of pyrite or marcasite reduces ferric salts essentially to the ferrous condition. The reaction occurs very slowly in the cold but fairly rapidly at the boiling temperature.

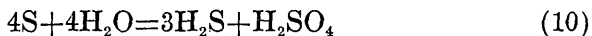
Experiment 95 shows that practically no sulphate is formed by the action of ferric chloride on cuprous sulphide at ordinary temperature in the course of a few weeks. In fact, Vogt⁶⁶ found that ferric chloride in acting on chalcocite produced only a trace of sulphate in several years at ordinary temperature.

⁶⁵ Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 15, 1901.

⁶⁶ Posepny, Franz, The genesis of ore deposits, 2d ed., p. 677, 1902.

At higher temperatures, however, the production of sulphate begins to take place. Experiment 9, at 110°, can be explained only by assuming that some sulphuric acid was formed, starting with ferric oxide and cuprous sulphide in an acid solution, although all the sulphur was not oxidized in 42 hours.

The necessity of this action at high temperatures may be deduced from the fact that sulphur reacts with water thus:

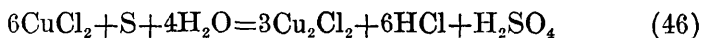


Experiment 100 shows that copper salts are converted to sulphides by sulphur in the presence of water at 200°.

Equation (43) therefore represents only an intermediate stage in the final result, as indicated more fully in experiment 101; and, on the other hand, in experiment 102, in which there was a large excess of cuprous sulphide, very little sulphuric acid was formed even at 200°, the oxidizing action of the ferric salt being used up in the easier or quicker reactions.

The oxidation of free sulphur by ferric sulphate was studied in experiments 18, 19, 20, and 21, which show that sulphur reduces ferric sulphate very slowly at ordinary temperature, increasing in rate up to 200°, at which temperature the action is complete in a few hours with concentrated solutions but either incomplete or slower with dilute solutions.

Wardlaw and Pinkard⁶⁷ state that sulphur is without effect on cupric chloride when boiled with it for four hours, except in the presence of concentrated hydrochloric acid, when the following reaction occurs:



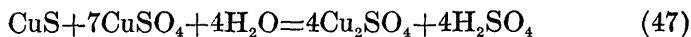
Experiment 100 shows that covellite is formed at 200° under certain conditions.

CUPRIC SULPHATE AND COVELLITE

It has been shown conclusively by Zies, Allen, and Merwin⁶⁸ that covellite and cupric sulphate react thus:



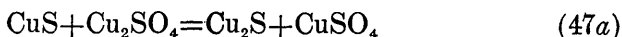
These authors further suggest that this final result is attained in two stages, one of which is



⁶⁷ Wardlaw, William, and Pinkard, F. W., The oxidizing properties of sulphur dioxide, pt. 3: Chem. Soc. Jour., Trans., vol. 121, p. 218, 1922.

⁶⁸ Zies, E. G., Allen, E. T., and Merwin, H. E., Some reactions involved in secondary copper sulphide enrichment: Econ. Geology, vol. 11, p. 429, 1916.

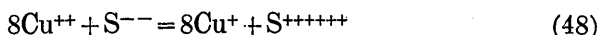
and the other is the formation of the less soluble Cu_2S at the expense of CuS by the cuprous sulphate formed by equation (47), thus:



As the chemical tendencies that start reaction (47) are of special interest in the present problem it is helpful to analyze them somewhat more fully. Any general tendencies thus established will be helpful in interpreting other similar reactions. Some of the constituents in the reaction—for example, sulphate ions—appear on both sides of the equation and are therefore probably of only incidental consequence. On the other hand, copper obviously changes its stage of oxidation, one atom of sulphur is oxidized from the sulphide stage to sulphate, and all the hydrogen of the water appears as sulphuric acid.

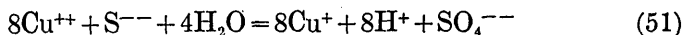
THEORY OF THE REACTION

The ionic reactions that appear to be involved are:



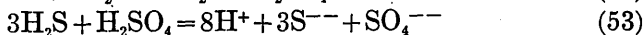
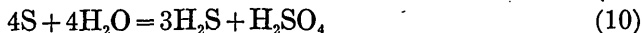
Equation (48) is an oxidation-reduction reaction and expresses the simultaneous reduction of the cupric copper to cuprous and the oxidation of the sulphide sulphur to sulphate sulphur. The next equation expresses the common possibility that the constituents of water participate in a reaction as ions. Equation (50) expresses the process whereby the somewhat hypothetical sulphur and oxygen ions shown assume the more stable form of a sulphate ion with no net change of electrification.

On cancellation and addition the three preceding equations give



which is the simpler ionic form of equation (46a).

The above changes might also be expressed in the following way:

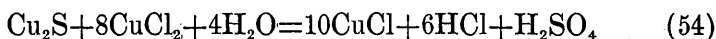


which by cancellation and addition yield the same result as before. In this method of interpretation the sulphur is viewed as being oxidized first from the sulphide stage to free sulphur, which then reacts with water according to equation (10), the equilibrium studied by Bichowsky.

Equation (48) itself probably summarizes more than one reaction, as the sulphur is assumed to pass directly from its lowest to its highest valence. On account of the presence of cupric ions and hydrogen ions in excess it is obvious that the concentrations of S^{-} and O^{--} available for reactions (48) and (50) must be very small indeed.

APPLICATION TO CHALCOCITE

The theory developed above, as indicated more particularly by equation (51), was found to be applicable to chalcocite as well as to covellite, especially at higher temperatures. Thus in experiment 109, which employed cupric chloride and which was run for 1 day at 200°, cupric ions oxidized a small quantity of the sulphide ions of the chalcocite to sulphuric acid. The equation is believed to be:



Many other experiments made by the writer show the same tendency. For example, in experiment 131 the action was continued for 2 days at 250° with complete oxidation of the sulphur.

The reverse reaction, evidence for which was sought experimentally, is clearly more difficult. Thus, in experiment 85 cuprous chloride was not oxidized by dilute sulphuric acid in the course of one day's heating at 300°. In experiment 134 cuprous sulphide was heated 4 days with dilute sulphuric acid with very slight consequences, if any. However, the action of more concentrated sulphuric acid even at 200°, as shown by experiment 58, appears to involve the oxidation of both cuprous and sulphide ions as well as the reduction of the sulphate, the sulphur from both sources reaching the intermediate form corresponding to SO_2 .

CUPRIC SULPHATE AND CHALCOCITE

RESULTS OF EXPERIMENTS

That some copper appears to be formed when cupric sulphate acts on cuprous sulphide at 200° is stated by Zies, Allen, and Merwin⁶⁹ and has been verified by the writer (experiment 66), but as the quantity of copper was always relatively small a number of variations in the conditions were tried to see if the yield of copper could be increased. The quantity previously obtained might have been formed merely on cooling from the cuprous sulphate produced in the reaction.

Increasing acidity seemed to lessen the simultaneous formation of basic copper sulphate (experiments 67 and 62), but too much acid

⁶⁹ Op. cit., p. 430.

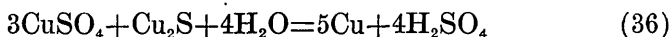
also seemed to lessen the yield of copper (experiment 64). No basic salt was obtained under certain conditions when the experiment was performed in a silica tube at 300° (experiment 122). The yield of copper improved as higher temperatures were employed (experiment 127) and the greater the proportion of cupric sulphate (experiment 125).

If we attempt to analyze the probable mechanism of this change, as was done for covellite, we find that reaction (51) is clearly involved. This reaction must produce 8 Cu⁺ for every S removed.

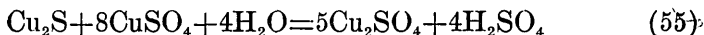
If, then, Cu is removed from solution, thus,



the following equation would result:



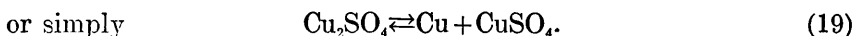
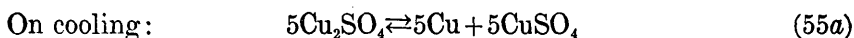
The same result is obtained without the use of the ionic form of expression, thus:



which on addition give equation (36).

The numerous experiments made to establish this reaction (114, 115, 116, 117, 122, 123, 125, 127, 128) are described in detail at the end of this paper and in the accompanying tables. The results obtained by analyzing the contents of the tubes after cooling satisfied equation (36) fairly well, but the question arose whether any of the copper was formed at the high temperatures. In order to throw light on this question a device was arranged for withdrawing the sealed tubes from the furnace for brief examination without cooling them off appreciably (experiment 136). Although it was impossible to examine the tubes much above 250° or at very close range, copper could not be observed. On the other hand, its deposition from the resulting solutions on cooling was conspicuous and easily seen.

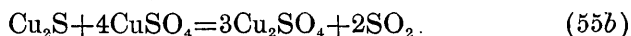
It seems probable, therefore, that the production of copper in the tubes is the result of two separate reactions:



The net result is expressed by equation (36). The cupric sulphate is not entirely consumed when chalcocite is present in excess, so that obviously an equilibrium is involved, and it would seem that reac-

tion (55) should be reversible. We know that when copper dissolves in sulphuric acid some chalcocite is formed, but experiment 85 gave no grounds for believing that cuprous salts will reduce sulphuric acid. Equation (19) is known to be reversible, but we have already concluded that no copper is produced at, say, 250°. It must consequently be assumed for the present that a small concentration of some other product not identified in the analyses, such as hydrogen or sulphur dioxide, presumably put a stop to the reaction.

The following possible intermediate reaction may be worthy of consideration:



Such a reaction might account for the somewhat variable results actually obtained in verifying reaction (36) and might well be studied further. Sulphur dioxide was not identified as a prominent constituent in any of the final solutions, but in some of them a slow increase of sulphate seemed to occur on standing after the tubes were opened, which may possibly have been due to small amounts of sulphur dioxide, or also possibly to traces of thionic acids which were not tested for. In experiment 132*a*, involving the action of copper on sulphuric acid, a very small amount of sulphur dioxide was found in the final solution.

If equation (55) is reversible, it might be possible to apply the mass law to it, which would give, with the usual omission of the solids and water, ionization being neglected,

$$K = \frac{[\text{Cu}_2\text{SO}_4]^5 [\text{H}_2\text{SO}_4]^4}{[\text{CuSO}_4]^8} \quad (56)$$

This constant was evaluated roughly by making the assumption that the copper that was formed came from the cuprous sulphate present when hot, as indicated by equation (19), thus giving a measure of the concentration in the hot solution of cuprous sulphate and allowing the cupric concentration to be evaluated by difference. The results are shown in Table 7.

TABLE 7.—*Apparent equilibrium constant for reaction (55)*

[Concentrations in gram-molecules per 1,000 grams of water]

Experiment	Temperature (°C)	[Cu ₂ SO ₄]	[H ₂ SO ₄]	[CuSO ₄]	K ₅₅
114.....	250	0.118	0.56	1.14	8.8×10 ⁻⁷
116.....	250	.134	.52	1.27	4.6×10 ⁻⁷
117.....	250	.098	.48	.52	9.2×10 ⁻⁸
115b.....	300	.21	.59	1.09	2.5×10 ⁻⁸
115c.....	300	.28	.63	.95	8.1×10 ⁻⁸
122.....	300	.36	.31	.75	5.1×10 ⁻⁸
123.....	300	.21	1.53	.81	1.2×10 ⁻⁸
125.....	300	.82	1.06	3.55	1.7×10 ⁻⁸
127.....	350	.63	.51	.28	1.9×10 ⁻⁸

The results in Table 7 indicate that reaction (55) proceeds more and more to the right as the temperature rises. By comparing the ratios of cuprous to cupric copper in Tables 7 and 1 it seems clear that the solutions referred to in Table 7 could not have been saturated with metallic copper at the temperature of heating, but only became so on cooling.

As the tubes were generally allowed to cool in the heater, which sometimes required several hours, there may have been a slight shift of the equilibrium represented by equation (55) from the state obtained at higher temperatures, but this shift was evidently not enough to prevent the solution becoming saturated with copper on cooling. The higher the temperature at which the mixture was heated the greater the proportion of cuprous copper, and accordingly the higher the temperature at which the solution became saturated with copper on cooling and the more metallic copper deposited.

It would appear that at some higher temperature, not yet realized experimentally, the solution might become saturated with metallic copper in virtue of reaction (55), and then reaction (36) would be realizable at that temperature. As previously stated, the net result of heating and cooling conforms fairly well with the requirements of reaction (36), in so far as it occurs, as shown by Table 12. In experiment 127 about 75 per cent of the cuprous sulphide taken was used up and more metallic copper was formed than the cuprous sulphide taken, owing to contribution from the cupric sulphate.

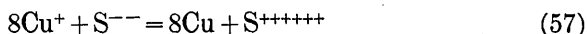
EFFECT OF SULPHURIC ACID

With considerable sulphuric acid present in experiment 64 no copper could be detected after 2 days' heating at 200°, whereas without initial acid in experiment 110 a little copper was formed. Experiments 122 and 123 were run at 300°—one with no initial acid, the other with considerable acid. The copper formed with no initial acid (and only slightly more cupric sulphate) was practically twice the quantity formed in the other way. Lastly, as shown by experiment 138, sulphuric acid alone with copper reverses the reaction, dissolving copper to form cuprous sulphide, cuprous sulphate, and cupric sulphate until the concentration of the sulphuric acid is reduced to a definite relation to that of the cupric sulphate.

A few experiments were tried with substances present intended to use up the sulphuric acid as fast as formed, but no striking yields of copper were thus obtained (experiments 108 and 111).

CUPROUS CHLORIDE AND CHALCOCITE

It appeared to be important to determine whether cuprous salts can oxidize sulphides. No oxidation was obtained by means of cuprous chloride at 200° or 250° (experiments 69 and 126). This result seems to rule out the possibility of the following reaction, accounting for the formation of metallic copper:



In short, as far as the experiments have shown, cuprous salts do not oxidize the sulphur of chalcocite. The action is limited to the cupric salts.

THEORIES PROPOSED TO ACCOUNT FOR THE DEPOSITION OF NATIVE COPPER FROM ASCENDING SOLUTIONS

Owing to the number of conditions that are unknown because they have left little if any record, it is difficult to frame a picture complete in all details of the exact way in which native copper has formed in nature through changes that can be linked to ascending solutions. Certain suggestions can be offered, however, which are based on the studies recorded in this paper and supported by them. Obviously, these suggestions do not exhaust the possibilities, especially as neither alkaline solutions nor solutions above 300° C. have been studied to any great extent. The results are such as could be obtained with workable solutions and the apparatus available. They are sufficient, however, both to supplement and to modify previous theories.

So far as shown positively by experimental laboratory evidence, copper can be deposited by solutions assumed to be ascending—that is, solutions being cooled, diluted, or reacting with surface rocks—in the ways set forth below.

DEPOSITION BY COOLING

Hot rising solutions carrying cuprous sulphate are gradually cooled and as they cool will deposit metallic copper. The presence of chlorides, however, seems greatly to lessen if it does not entirely prevent this action.

DEPOSITION BY DILUTION

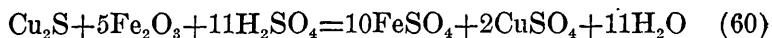
Solutions carrying considerable cuprous chloride, by virtue of its large solubility in certain brines and other concentrated solutions, deposit a small fraction of the copper as free metal on being gradually diluted. This mode of origin may account for some of

the "mass" copper in the Lake Superior mines, where cross fissures have permitted the intermingling of the concentrated brines with more dilute solutions.

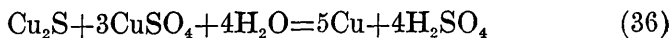
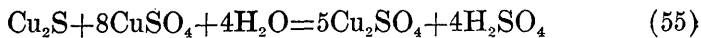
DEPOSITION BY FRACTIONAL OXIDATION OF COPPER SULPHIDE

The formation of metallic copper by oxidation of the sulphide, as practiced in smelting, has been alluded to early in this paper. Analogous reactions have been given in the literature based on oxidation by atmospheric oxygen, cupric salts, and ferric salts. Much of the work described in this paper concerns oxidation by ferric iron, or rather, inasmuch as that appears to involve the formation of ferrous and cupric salts, oxidation by cupric salts. The stages by which ferric oxide may be viewed as acting on a sulphide solution are as follows:

Hot acid solutions containing copper and sulphur, assumed for the sake of simplicity to be equivalent in their chemical activity to acid solutions carrying cuprous sulphide, meet ferric oxide. The acid is decreased by solution of some ferric oxide. The ferric salt thus formed exerts an oxidizing influence, which is, however, at once balanced by the reducing action of cuprous sulphide, with the production of ferrous sulphate and cupric sulphate, as indicated by the following reactions



If there is available a further quantity of cuprous sulphide in solution, its presence, the decrease of acidity, and the formation of water, ferrous sulphate, and cupric sulphate would all favor the reactions



The second of this pair of reactions may possibly occur at a very high temperature but has not yet been realized experimentally. However, the first reaction yields cuprous sulphate, which deposits copper on cooling. The consumption of cuprous sulphide in these ways would obviously leave less of it to be deposited as the solution cooled, whereas copper would still be deposited on cooling. Conditions favoring the deposition of copper would be an initial high temperature, the reduction of acidity to the point where no more ferric oxide would be attacked or the local exhaustion of the ferric oxide by solution and reduction as outlined, and lastly cooling and dilution of the initially heated solutions. In this way the sulphur

would make its exit as ferrous sulphate. A reaction that embraces all the steps mentioned would be:



A qualitative verification of the possibility of such a reaction in the presence of an excess of sulphuric acid is recorded in experiment 119.

This is essentially the theory advanced by the geologists of the Calumet & Hecla Consolidated Mining Co. to account for the deposition of native copper rather than copper sulphide in the Lake Superior district, where ferric oxide has apparently been the oxidizing agent. It appears that laboratory evidence supports this hypothesis under certain conditions, the principal experimental limitation being the necessity of working in acid solutions. As it is obvious that every natural condition could not be reproduced in the laboratory it would probably be unwise to claim that acidity is a necessary condition for the reaction, but it is the only key the writer has found to start the chain of reactions noted. In fact, all the theories here proposed permit the use of solutions of at least sufficient acidity to carry significant quantities of dissolved copper. It is only fair to state that on account of experimental difficulties solutions of mild acidity, such as those containing large quantities of carbon dioxide or hydrogen sulphide under great pressure, have not yet been thoroughly studied.

DEPOSITION BY NEUTRALIZATION AND REDUCTION

Deposition of metallic copper by the reduction of compounds of oxidized copper by hydrogen has been referred to above (p. 7) and need only be mentioned here. On the other hand, reduction of copper compounds by ferrous compounds is the theory that has long been most generally held to account for the formation of native copper in the Lake Superior district, without much regard to whether the cupriferous solutions ascended or descended. The necessary reactions for this process, as elucidated by Biddle, Stokes, Fernekes, Lane, and others, involve the removal of ferric oxide from solution along with the copper, a feature which the present study has purposely wished to avoid, if possible, in accordance with the field evidence, which shows that the copper is generally found where the ferric oxide has been dissolved from the accompanying rocks. A brief discussion of the chemistry of this process accompanies equations (28) to (32).

This mode of forming native copper can obviously not be left out of consideration entirely, because of the common association of ferrous and copper compounds, and it might be viewed as an adjunct

to any theory in which such mixtures are involved. On it Smyth based his theory of the deposition of copper from ascending solutions, which the writer has ventured to supplement with the processes of neutralization and cooling. Neutralization is suggested in order that the initial solutions can be assumed to have been not very alkaline, so that appreciable concentrations of copper salts and ferrous salts could be present in them. If the initial solutions were alkaline in the presence of ferrous compounds it is difficult to see how significant quantities of copper could have been transported. Cooling is suggested as logical in ascending solutions. But as has been shown under the preceding heading cooling alone will cause the deposition of copper from acid solutions containing cuprous and ferrous sulphates. On the other hand, ferrous compounds in acid solutions will precipitate copper as the solutions are neutralized, even without cooling.

COMPARISON OF THE THEORIES

In applying the theories presented above to various districts the essential conditions of each district must be considered and the choice made accordingly. The first two theories are so general that they might apply almost anywhere, and they take no account of the chemical character of the gangue or the rocks penetrated by the solutions. The third theory seems to fit the Lake Superior district best in that the specific influence of ferric oxide in the rocks is taken into account in determining the character of the copper mineral deposited. The fourth theory is to a certain extent the opposite of the third in that oxidized copper compounds are assumed to be reduced to metal, whereas in the third theory sulphide solutions are assumed to have been fractionally oxidized.

Each of the theories assumes a different kind of solution: the deposition of copper is brought about in the first by cooling a cuprous sulphate solution, in the second by dilution of a cuprous chloride solution, in the third by oxidation of a cuprous sulphide solution, and in the fourth by reduction of any oxidized copper compound. Possibly some of these different processes may have gone on simultaneously or successively in some places.

EXPERIMENTS

Experiment 1.—Ferric oxide and cuprous sulphide. Initial weights: Cu_2S 0.159 gram, Fe_2O_3 0.480 gram, NaCl 1.0 gram, H_2O 10 grams. These substances were placed in a tube which was drawn out, evacuated, sealed off, and heated in a steam bath at about 92°C . for 13 days. No visible metallic copper was formed.

Experiment 2.—Ferric oxide and cuprous chloride. About 1 gram of CuCl was placed in a tube with 0.1 gram Fe_2O_3 , 2.1 grams NaCl , and 6 cubic centi-

meters H_2O . After evacuating and sealing the tube it was heated at 110°C . for 1 hour. The solution was then tested by indicators and found to be acid to methyl red but not to methyl orange, indicating a pH value of about 4. The iron found in the solution was negligible, not more than 0.005 milligram.

Experiment 3.—The same substances were used in experiment 3 as were used in experiment 2 with the addition of 2 grams of metallic copper and were heated at 150°C . for 5 hours. On cooling, some of the cuprous chloride recrystallized, and some thick treelike growths of recrystallized copper had apparently formed on the ends of the copper wires. A few scattered flakes of copper were also visible at various points in the tube. Not more than a trace of iron could be detected in the solution, but a very small amount, equivalent to about 3 milligrams FeO , as nearly as could be determined, appeared to exist in the ferrous condition in the solid. The color of the solid remained red. Repetitions of this experiment did not always yield metallic copper, and the crystals of copper that were observed may have resulted from the etching of the wires. See experiments 10, 31, 69, 126, 163, 164, and 165 for similar data.

Experiment 4.—The same substances as those used in experiment 3 except the NaCl were heated at 200°C . for 17 hours. The solid remained red; no blue color appeared in the solution. The solid was extracted with ammonia, after which it was heated with hydrochloric acid; the solution then gave no test for ferrous iron with potassium ferrocyanide.

Experiment 5.—Ferric oxide and copper. Some clean copper in the form of wire was heated with a suspension of ferric hydroxide in a sealed tube at 110° for five hours. No change was visible. Heated at 200° for three hours, neither copper nor iron could be detected in the solution.

Experiment 6.—Several solutions of different hydrogen-ion concentrations, buffered by mixtures of acetic acid and ammonium acetate, were shaken with well-washed ferric hydroxide, with the following results after long standing:

Ferric hydroxide dissolved

pH	Reaction with KSCN	Character of solution
4.0	Strong.....	Clear.
4.6	do.....	Do.
5.2	do.....	Slightly colloidal.
5.3	Weak.....	Do.
5.4	do.....	Strongly colloidal.
5.5	Very faint.....	Slightly colloidal.
5.9	None.....	Clear.

Experiment 7.—Ferric oxide and sulphur dioxide. About 0.04 gram Fe_2O_3 in the form of hydroxide was sealed in a tube with 0.75 gram of NaHSO_3 and 5 cubic centimeters H_2O . Heated to 100° 4 hours; only 0.0023 gram of Fe was found in the solution. The solid was not tested.

Experiment 8.—Ferric oxide and hydrogen sulphide. About 0.05 gram Fe_2O_3 was sealed in a tube with H_2S . An immediate darkening occurred. Heated 15 hours at 100° ; some films of pyrite were formed; the rest of the material remained black FeS .

Experiment 9.—Ferric oxide, cuprous sulphide, and sulphuric acid. Initial weights: Cu_2S 0.02 gram, Fe_2O_3 0.08 gram, H_2SO_4 1.91 grams=1.03 cubic centimeters, and H_2O 3.97 cubic centimeters. Tube evacuated, sealed, and heated 3 hours at 110° . The solution was then pale green, and some ferric oxide had been dissolved. A little ferric oxide remained after 20 hours. After 42 hours the residue was inconsiderable but appeared to contain a few droplets of sul-

phur and a few black specks. Found in solution: FeSO_4 0.0889 gram, CuSO_4 0.0356 gram. Molecular ratios:

$$\frac{\text{FeSO}_4 \text{ formed}}{\text{Cu}_2\text{S taken}} = 7.1, \quad \frac{\text{CuSO}_4 \text{ formed}}{\text{Cu}_2\text{S taken}} = 1.8$$

The CuSO_4 formed is approximately equivalent to the copper of the cuprous sulphide, but the FeSO_4 , estimated by titration with KMnO_4 , is greater than that required by both of the following reactions:



Apparently, therefore, some of the sulphur was also oxidized at the expense of the ferric salt. As the oxidation of S to SO_3 by Fe_2O_3 would yield 6FeO an equation may be written to express the reaction on the assumption that all of the sulphur is so oxidized.

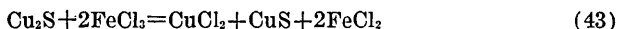


Actually only 7FeSO_4 was produced under the conditions described, as some of the sulphur was left in the free state.

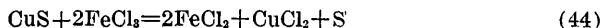
Equation 60 requires the following weights of substances: Cu_2S 1.00 gram, Fe_2O_3 5.02 grams, H_2SO_4 6.77 grams.

Experiment 10.—Initial weights: CuCl 1.5 grams, NaCl 2 grams, H_2O 6 cubic centimeters. Heated at 150° for 3 hours. At the conclusion of the experiment the tube was tilted while hot from its original position so that the solution would drain from the solid previous to cooling, and analysis showed that the solution must have contained at 150° about 19 per cent of CuCl and 16 per cent of NaCl .

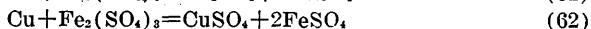
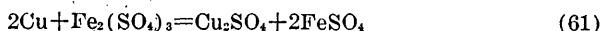
Experiment 11.—Cuprous sulphide and ferric chloride. Weights taken: Cu_2S 0.10 gram, FeCl_3 0.532 gram, H_2O 50 cubic centimeters, in an atmosphere of CO_2 , at room temperature. After 15 minutes' shaking 5 cubic centimeters was withdrawn and titrated, showing 33 per cent of the iron as ferrous. At 17 hours 44 per cent was ferrous. After 3 days 51 per cent was ferrous, cupric copper was obviously present in solution, and the solid had a blue tint suggesting CuS . The first reaction is probably



But as the ferrous salt produced was greater in amount than that which corresponds to this reaction some of the sulphide must also have been oxidized in addition, possibly as follows:



Experiment 12.—Copper and ferric sulphate. Initial weights: Copper 0.87 gram, solution 3 cubic centimeters, containing 0.0765 gram $\text{Fe}_2(\text{SO}_4)_3$ and 0.153 gram H_2SO_4 . Action began immediately, giving a blue solution. Heated over night in a steam bath, a slight flocculent precipitate appeared which eventually turned dark. The blue color was estimated colorimetrically at about 0.3 normal CuSO_4 . After standing several months at room temperature the solution was titrated with KMnO_4 , giving apparently 0.0498 gram Fe'' . Dissolved $\text{Cu} = 0.0284$ gram. The following reactions were assumed:



By making a few simple corrections for the Cu' and Fe'' content corresponding to equation (61) the following values were obtained for equation (62): Cu''=0.0275 gram, Fe'' calculated from Cu'' 0.0498 gram, Fe'' found 0.0482, in good agreement with the written equation. The Cu' content was calculated from Cu'' by Abel's equation.⁷⁰ As the ferric sulphate was not all reduced it is assumed that an equilibrium was obtained in which the ferrous salt greatly predominated over the ferric.

Experiment 13.—Ferric oxide, cuprous sulphide, and sulphuric acid. Initial weights: Cu₂S 0.02 gram, Fe₂O₃ 0.08 gram, H₂SO₄ 5 cubic centimeters of 0.5 normal acid. Considerable reaction in 6 hours at 178°. Some blue grains appeared and some sulphur. Solution pale blue. Heated 17 hours more at 141°; most of the solids dissolved. Tube stood in drawer for 7 months; the insoluble flakes were brilliantly colored, purple and lavender, and some ferric oxide remained.

Experiment 14.—Repetition of Stokes's experiment.⁷¹ Initial weights: FeSO₄·7H₂O 0.5 gram, CuSO₄·5H₂O 0.5 gram, KHCO₃ 0.05 gram in a separate tube, dissolved later, H₂O 5.0 cubic centimeters. Heated on steam bath 6 hours; no copper. Heated at 200° for 3 hours. Some copper was visible on cooling, also a black mineral, probably hematite, and a red substance, which may have been either Fe₂O₃ or Cu₂O.

Experiment 15.—Initial weights: Cu₂S 0.02 gram, Fe₂O₃ 0.08 gram, H₂SO₄ 0.06 gram, FeSO₄·7H₂O 0.5 gram. Heated at 186° for 17 hours; no copper. Heated at 200° for 20 hours; a few specks of copper around the rim. Heated at 200° for 2 days more; considerable copper around the rim. The results of further experiments similar to this one are summarized in Tables 8 and 12, on pages 66-68.

Experiment 16.—Initial weights: Cuprous sulphide 0.08 gram, ferric oxide 0.02 gram, H₂SO₄ 0.01 gram=0.80 cubic centimeter of 0.256 normal acid. Some CuSO₄ was formed before the tube was sealed. Heated at 250° for 2.5 hours. Both Fe₂O₃ and Cu₂S remained. Green and yellow films were conspicuous on the walls of the glass tube, and at one point a few small bright particles of metallic copper. The solution had become alkaline. This experiment shows that ferric sulphate oxidizes cuprous copper faster than it does sulphur, especially at low temperatures.

Experiment 17.—Initial weights: Chalcocite 0.16 gram, hematite 0.16 gram, NaCl 1.0 gram, KHCO₃ 0.05 gram, H₂O 5.0 gram. Heated at 183° for 17 hours; no visible effects; solution strongly alkaline.

Experiment 17a.—Initial weights: Cuprous sulphide 0.08 gram, ferric oxide 0.02 gram, NaHSO₄ 0.03 gram dissolved after sealing tube, H₂O 10 grams. Heated at 250° for 1 hour; solution was very pale blue, containing a trace of Cu but no Fe, and was practically neutral (pH about 7.7). A little cuprite as a stain above the solution.

Experiment 18.—Ferric sulphate and sulphur. Taken: 2 cubic centimeters of a solution containing 0.383 gram Fe₂(SO₄)₃, 0.026 gram H₂SO₄, 0.03 gram S, and 1.0 gram H₂O. Initial iron as ferric sulphate 0.0430 gram. Heated 5½ months at 92° in a sealed tube. Found 0.0020 gram iron as ferrous sulphate.

Experiment 19.—Same as experiment 18 except for dilution to 17 cubic centimeters. Found 0.0025 gram iron as ferrous sulphate.

Experiment 20.—Taken: Fe₂(SO₄)₃ 0.383 gram, H₂SO₄ 0.026 gram in 2 cubic centimeters of solution, S 0.03 gram. Heated at 200° for 17 hours. The ferric

⁷⁰Abel, E., Über das Gleichgewicht zwischen den verschiedenen Oxydationstufen desselben Metalles: Zeltschr. anorg. Chemie, Band 26, p. 397, 1901.

⁷¹Stokes, H. N., On pyrite and marcasite: U. S. Geol. Survey Bull. 186, p. 44, 1901.

color disappeared. Some sulphur remained. A little Fe_2O_3 and a little FeS formed. The solution was still acid and pale green. Found FeSO_4 with KMnO_4 equivalent to 0.359 gram $\text{Fe}_2(\text{SO}_4)_3$. The solution showed only a trace of ferric iron with KSCN .

Experiment 21.—Same as experiment 20 with 10 cubic centimeters H_2O . Results similar to those of experiment 20 except that more sulphur remained, partly in drops and partly coating the glass beneath the solution. The coating was brownish on the inside. Titration showed FeSO_4 equivalent to 0.140 gram $\text{Fe}_2(\text{SO}_4)_3$, or about 37 per cent of that taken.

Experiment 22.—Sulphuric acid and sulphur. Initial weights: H_2SO_4 0.063 gram diluted to 5 cubic centimeters, S 0.0103 gram, Na_2SO_4 0.0912 gram. Heated at 190° for 18 hours; the solution smelled of H_2S but gave only 0.0012 gram H_2S on analysis.

Experiment 23.—Cupric sulphate and sulphur. Initial weights: CuSO_4 0.1596 gram, NaHSO_4 0.24 gram, S 0.0480 gram, H_2O 5 cubic centimeters. Heated at 210° for 19 hours; much Cu_2S formed and most of the sulphur was used up. Only 0.0176 gram copper remained in solution.

Experiment 24.—Ferric oxide and sulphur. Initial weights: About 0.215 gram $\text{Fe}(\text{OH})_3$ and 0.0215 gram sulphur. Heated at 210° for 5 hours; some pyrite formed but was a dirty yellow, not bright. The solution was alkaline and free from iron; apparently contained no SO_2 , but on acidifying precipitated sulphur and consumed KMnO_4 equivalent to 0.019 gram FeO . Residue seemed to show some ferrous salt present.

Experiment 25.—The purpose of experiment 25 (Steinmann's experiment)⁷² was to allow precipitated ferric hydroxide and copper sulphide to act on each other in the presence of calcium carbonate. After heating at 92° for a week the solution gave positive tests for calcium and SO_4 with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and BaCl_2 , but as the ferric hydroxide used was not free from sulphate results are not conclusive. The residue extracted with HCl gave a test for ferrous iron, but the inconclusiveness of this test is pointed out in experiment 38d. The test is described further in experiments 36 and 38a.

Experiment 26.—Ferric oxide and sodium sulphide. The addition of sodium sulphide to a suspension of ferric oxide seemed to produce very little effect at first, but on heating a black colloidal solution resulted.

Experiment 27.—Ferrous sulphide and ferric oxide. Certain solutions were mixed in quantities to yield FeS and $\text{Fe}(\text{OH})_3$ in the proportion of one molecule of each. The mixture was heated at 130° for 16 hours. A white deposit appeared and a colloidal greenish solution. Red color was absent. After long standing, the solution was clear, the sediment was greenish, but the coating on the tube was white. The tube was considerably attacked. After opening the tube the solution was found to contain an excess of Na_2S but no SO_4 . The white deposit was not sulphur but probably residue from the glass. Thiosulphate could not be detected. The green sediment, which did not seem to dissolve in dilute HCl , gave an apparent content of 7.6 per cent of ferrous iron, 17.5 per cent ferric iron, and a little sulphur. Possibly it could be termed greenalite.

Experiment 28.—The same mixture used in experiment 27 with some CuSO_4 in addition, on heating at 280° for 4 hours yielded a clear solution with a dark precipitate. Small specks in the precipitate suggested covellite, pyrite, bornite, and sulphur, but most of the solid was black and amorphous. The tube was not much attacked.

⁷² Harry Rosenbusch Festschrift, p. 360.

Experiment 29.—Similar to experiment 9. Weights: Cu_2S 0.159 gram, Fe_2O_3 0.32 gram, H_2SO_4 0.29 gram, H_2O 7 cubic centimeters. Heated at 172° for 22 hours; much Fe_2O_3 was still undissolved; the solution was blue. Heated at about 175° for several days; the Fe_2O_3 gradually disappeared, but not the blue color. After several days' heating at 230° the remaining sulphide assumed a blue tint suggesting covellite, and apparently a few specks of copper were deposited on cooling.

Experiment 30.—Experiment 30 resembled experiment 25 but was inconclusive on account of traces of sulphate in the ferric oxide used.

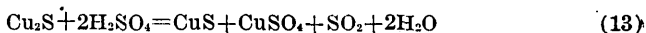
Experiment 31.—Continuation of experiment 10. Weights: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 3.5 grams, NaCl 3.5 grams, Cu 3.5 grams, H_2O 6 cubic centimeters. Heated 3 hours at 250° and tilted hot. Much CuCl crystallized. Apparently Cu_2O was formed. Some crystals of copper were visible on the wire near the lower end of the tube. An approximate determination of the CuCl presumably dissolved in the hot solution gave about 780 grams per liter.

Experiment 32.—Action of hematite on chalcocite in fused sodium bisulphate. Weights: Hematite 0.32 gram, chalcocite 0.16 gram, $\text{Na}_2\text{S}_2\text{O}_7$ 1.0 gram. Heated to 340° in a glass tube in CO_2 . SO_2 was evolved, a little sulphur sublimed, and apparently some CuS remained, with much Fe_2O_3 . Considerable CuSO_4 was formed. In the water extract KMnO_4 gave an equivalent of 0.022 gram FeO .

Experiment 33.—Effect of SO_2 on cupric hydroxide. Five cubic centimeters of a saturated solution of SO_2 was added to 5 cubic centimeters of a suspension of cupric hydroxide in a tube with CO_2 atmosphere. Red crystals soon formed, probably $\text{CuSO}_4 \cdot \text{Cu}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. Heated to 125° ; metallic copper deposited. The experiment was repeated several times. The solution was more or less blue.

Experiment 34.—Experiment 34 was a continuation of experiment 32; the same weights of the same substances were taken in a sealed tube with CO_2 . Heated at 300° for 1 hour; the red color disappeared. The residue was dark but not black. Some magnetite was formed. The solution was found to contain 0.125 gram FeO and 0.0495 gram copper.

Experiment 35.—Chalcocite and sulphuric acid. Initial weights: Butte chalcocite 0.259 gram, H_2SO_4 (concentrated) 1.0 gram. Heated at 132° for 16 hours; no significant changes noted. Heated at 250° for 4 hours; some small crystals, needles and plates, appeared. On cooling and opening much SO_2 under pressure was noted; the residue contained a blue product, probably covellite. Some of the solution was sealed up and heated to 150° , with the production of a few centigrams of covellite. Pickering's equation for this reaction is



Further study is recorded in experiment 58, in which no sulphide of copper remained.

Experiment 36.—A blank test similar to experiment 25, but omitting Cu_2S , after heating one week revealed the presence of some sulphate in the ferric hydroxide being used. For the continuation see experiment 38a.

Experiment 37.—Experiment 37 was a continuation of experiment 35, with no further conclusions.

Experiment 38a.—Steinmann's experiment, continued from experiment 25. Some ferric hydroxide was prepared from sulphate-free reagents and washed until it began to become colloidal. Some of the suspension, 20 cubic centimeters = 0.15 gram Fe_2O_3 , was mixed with 0.05 gram CaCO_3 . After long digestion at 90° the solution gave no test for sulphate.

Experiment 38b.—A mixture similar to that used in experiment 38a, with about 0.15 gram of precipitated copper sulphide, which had been washed until nearly colloidal, was placed in a tube, which was sealed after the air had been thoroughly removed by a vacuum pump. After 17 days' heating at 92° the solution gave a trace of SO_4 equal to only 0.2 milligram.

Experiment 38c.—In experiment 38c the same procedure was employed as in experiment 38b, using pure Cu_2S , with practically the same result.

Experiment 38d.—The purpose of experiment 38d was to produce considerable carbon dioxide in the tube in addition to the substances named in experiment 38b by introducing hydrochloric acid in a small tube which could be overturned later. Weights taken: Fe_2O_3 0.60 gram, Cu_2S 0.30 gram, CaCO_3 0.68 gram, HCl 0.24 gram, H_2O 6.0 cubic centimeters, volume of tube 24 cubic centimeters. Heated 4 days at 145°. Results: Iridescent particles which may have been copper, Cu_2O , or Fe_2O_3 ; covellite; anhydrite. The results are largely due to the fact that a strong acid was injected into the mixture. Simple tests show that such an acid dissolves some of the ferric oxide, forming, say, ferric chloride, which is then quickly reduced by sulphides to ferrous chloride. A mixture of ferric oxide and copper sulphide extracted with warm dilute hydrochloric or sulphuric acid yields a solution containing soluble ferrous and copper compounds. Hence Gassner's conclusion that a ferrous compound was formed in the Steinmann experiment is not justified by the evidence, although it may be correct, as he extracted the residue with acid.

Experiment 39.—A suspension of ferric oxide was sealed in a tube containing a quantity of clean copper wire in the presence of carbon dioxide. After being heated 12 days at 92° the residue was tested for ferrous iron by extracting with dilute hydrochloric acid and adding potassium ferrocyanide. A faint but distinct indication of ferrous iron was obtained. No ferrous iron could be detected in the solution, however. No copper could be detected in the solution.

Experiment 40.—Precipitation of copper by ferrous sulphate. Weights: Cu_2S 0.1 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.25 gram, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.25 gram, Fe_2O_3 0.1 gram, CaCO_3 0.5 gram, HCl (in a separate container tipped after sealing tube) 0.36 gram, H_2O 5 cubic centimeters. A little CO_2 escaped before the tube was sealed. Heated at 205° for 2 days; the solution was colorless; much CaSO_4 and abundant copper formed. Fe_2O_3 remained.

Experiment 41.—Similar to experiment 40. Weights: Cu_2S 0.1 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.25 gram, Fe_2O_3 0.1 gram, FeCO_3 0.5 gram, HCl 0.30 gram, H_2O 6 cubic centimeters. Heated at 150° for 2 days; the solid was a brilliant mixture of blue, yellow, and red; the solution blue. Heated at 190° for 1 day more; no Cu was noted but apparently CuS .

Experiment 42.— Fe_2O_3 and Cu_2S . Initial weights: Fe_2O_3 0.33 gram, Cu_2S 0.11 gram, H_2O 10 cubic centimeters. Tube filled with CO_2 . Heated at 195° for 18 hours; the solution gave no test for copper or iron but a slight test for SO_4 '. The solid was extracted with oxalic acid, which gave a solution showing a little ferrous iron but no copper. Extracting with HCl gave both copper and ferrous iron in solution.

Experiment 43.—Hematite and Cu_2S . Initial weights: Hematite 0.48 gram, Cu_2S 0.16 gram, H_2O 5 cubic centimeters. Tube filled with CO_2 . Heated at 210° for 18 hours. The solution was strongly alkaline. It gave no tests for iron or copper but showed SO_4 '. The insoluble matter extracted with oxalic acid gave a test for copper but none for ferrous iron. Hydrochloric acid extracted copper but no ferrous iron. The last two experiments require verification by means of blank tests to insure that the reagents were reliable and that no oxidation by the atmosphere could have occurred.

Experiment 44.—Ferric oxide and cuprous sulphide at 300° C. Initial weights: Fe_2O_3 0.24 gram, Cu_2S (prepared by heating copper sulphide in hydrogen at 600° for an hour and found by analysis to be Cu_2S) 0.0796 gram, H_2O 5 grams, and CO_2 to displace air. The experiment was first tried in glass tubes, which were heated in an iron bomb containing water to equalize the pressure within the tubes, but the glass tubes were so badly attacked and decomposed that the results were useless. Silica tubes were then substituted for the glass. At first these were placed in larger glass tubes containing water, as the first tubes available were rather thin. However, the alkaline solution formed from the glass also attacked the silica. Later strong silica tubes were obtained and heated directly in the steel bomb with water to equalize the pressure. Heated in silica tubes at 300° for 2 hours; no visible change. Heated at 300° for 3 days; no visible change, except that some of the silica formed a colloidal solution and some was deposited at the bottom of the solution. Cu_2S remained unchanged. No sulphate was formed.

Experiment 45.—Initial weights: Fe_2O_3 0.080 gram, Cu_2S 0.1592 gram, H_2O and CO_2 as in experiment 44. Results same as those in experiment 44.

Experiment 46.—Action of sulphur dioxide on cupric sulphate solutions at 160° C. Initial weights: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.79 gram = 0.2 gram Cu, SO_2 aq. 2.9 cubic centimeters = 0.19 gram SO_2 , H_2O 1.0, air about 5 cubic centimeters. Warmed to 100°; spangles of copper became visible. Heated to 160° for 1 hour; SO_2 used up 0.14 gram, Cu precipitated 0.125 gram.

Experiment 47.—Similar to experiment 46. Initial weights: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.79 gram, SO_2 0.30 gram in 4.75 cubic centimeters. Heated for 1 hour at 160°. Copper estimated still in solution from color, 0.04 gram. Heated at 200° a moment, then 19 hours at 160°. Solution still blue, but the copper had a black film on it.

Experiment 48.—Action of sulphur dioxide on copper. Weights: Copper 2.9530 grams, SO_2 5 cubic centimeters = 0.305 gram. Heated at 145° for 21 hours; a few brownish flocs suggesting a sulphide. Heated for 21 hours more; same result. Heated at 217° for 42 hours; a lot of black sediment. SO_2 remaining, 0.020 gram; used, 0.285 gram; SO_2 formed = 0.125 gram H_2SO_4 . Copper remaining, 2.8434 grams; changed to Cu_2S , 0.1096 gram.

Experiment 49.—Action of dilute sulphuric acid on copper. A little copper was heated with 10 cubic centimeters 0.5 normal sulphuric acid in a sealed tube free from air to 200° for 42 hours. No color could be detected in the solution, and the copper remained bright. Analysis gave 0.08 milligram in the solution, equivalent to 8 milligrams per liter. See experiment 138 for results at 300°.

Experiment 50.—Resembled 38b. Initial weights: Fe_2O_3 about 0.15 gram in the form of a suspension, CaCO_3 0.05 gram, H_2O 25 cubic centimeters. Air boiled out. Cu_2S added, 0.15 gram. CO_2 was passed for 1 hour, and tube was sealed without interrupting stream of CO_2 . Heated at 92° for 23 days. Practically no sulphate formed. Residue warmed with dilute HCl , filtered off; the solution showed ferrous iron and cupric salt but no sulphate.

Experiment 51.—Experiment 51 was similar to the preceding experiment. Initial weights: Fe_2O_3 0.08 gram, Cu_2S 0.1592 gram, CaCO_3 1.27 grams, HCl (in inner tube) 0.92 gram. Volume of tube 26.5 cubic centimeters. Heated at about 150° for 17 days; considerable black and some purple precipitate formed. No further significant changes were noted during the course of 27 days further heating. No metallic copper was observed.

Experiment 52.—Action of copper on hydrochloric acid. Taken: 10 cubic centimeters 0.5 normal acid, 3.0 grams copper wire, in tube with atmosphere of CO_2 . Heated 2 days at 150°, then 17 hours at 165°. Some of the copper

was dissolved and reprecipitated on one end of the wires. The solution, after cooling, gave the equivalent of 0.70 gram copper per liter.

Experiment 52a.—An apparatus, shown in Figure 1, was arranged by which a concentrated solution of cuprous chloride, dissolved in strong calcium chloride, could be diluted with pure water, all in an atmosphere of CO_2 . Only a few drops were mixed every few days by allowing some of the mixture to escape while first water and then cuprous chloride entered the long tube in which mixing occurred. During the course of six months a noteworthy deposit of crystals of copper formed where the first dilution occurred. Cuprous chloride was also deposited. At the second point of dilution these phenomena were less conspicuous. A long copper wire had been placed in the tube to see

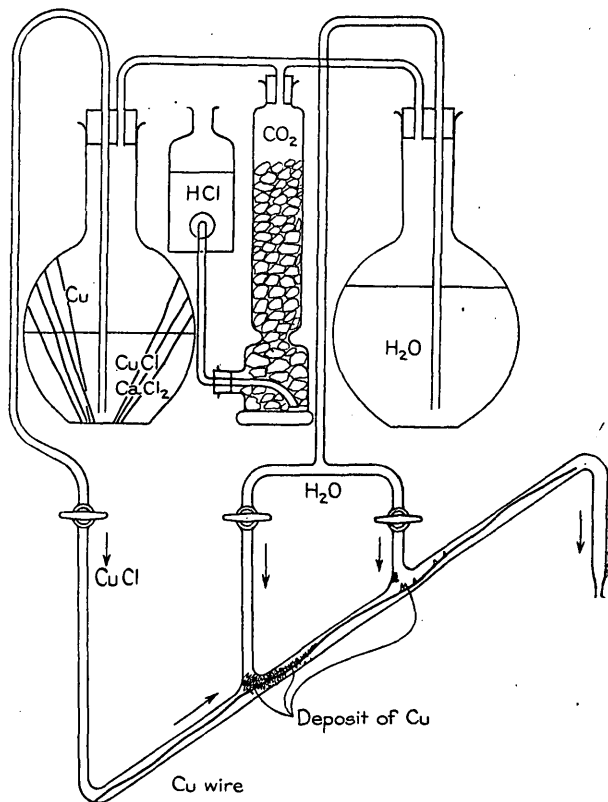


FIGURE 1.—Apparatus used in experiment 52a

if any electrolytic transfer would occur, but the results appeared to be due entirely to the dilution of the concentrated solution.

Experiment 53.—Copper and mine water from 81st level, Red Jacket shaft, Calumet & Hecla mine, depth 4,900 feet, collected August, 1921. Some metallic copper was heated with 20 cubic centimeters of this water at 92° in a glass tube for 3 months. Copper found in solution 0.2 milligram, equivalent to 0.01 gram per liter.

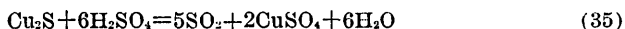
Experiment 54.—Experiment 54 was similar to the preceding one, with an atmosphere of CO_2 . Heated at 150° for 40 days; 15 cubic centimeters of the solution gave 1.8 milligrams of copper equivalent to 0.12 gram per liter.

Experiment 55.—Solubility of copper in calcium chloride brine (equal parts CaCl_2 and H_2O). Heated at 175° for 20 hours and filtered hot; the solution gave the equivalent of 0.07 gram of copper per liter.

Experiment 56.—Similar to preceding. Initial weights: $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ 15.0 grams, H_2O 12.0 grams, Cu 3.0 grams, Fe_2O_3 0.2 gram, SiO_2 0.2 gram. Heated at 200° about 2 days; the solution gave the equivalent of 0.19 gram of copper per liter.

Experiment 57.—Solubility of copper in the presence of acid and Fe_2O_3 . Initial weights: Fe_2O_3 0.2 gram, HCl 0.1 gram, H_2O 15.0 cubic centimeters; copper in excess. Heated at 90° for 3 days; the solution gave 0.042 gram of iron in the ferrous state and 0.017 gram copper=1.3 gram per liter.

Experiment 58.—Repetition of experiment 35. Initial weights: Cu_2S 0.250 gram, H_2SO_4 (boiled) 1.50 grams. Heated in an evacuated sealed tube at 200° for 4 days; the Cu_2S disappeared. Volume of tube 9.3 cubic centimeters. Pale-blue crystals, probably a sulphate of copper, perhaps $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$, formed. Opened under iodine solution, the SO_2 formed was estimated by titration to be 0.32 gram after allowing for the iodine liberated from the KI by the CuSO_4 . The following equation is suggested:

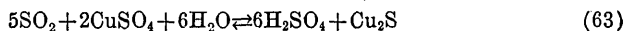


This demands 0.50 gram SO_2 calculated from the weight of Cu_2S taken, which is somewhat larger than the SO_2 found. A little SO_2 may have escaped when the tube was opened, however, as the pressure was considerable, and some iodine solution had to be added while the SO_2 was being absorbed, whereas the iodine solution should have been in excess.

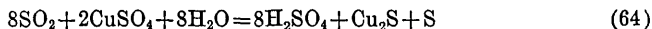
Experiment 59.—Similar to experiment 48. Initial weights: Cu 1.999 grams, SO_2 2 cubic centimeters=0.1830 gram, H_2O 3.0 cubic centimeters. Heated 4 days at 225° ; considerable Cu_2S formed. SO_2 remaining, 0.029 gram; $\text{SO}_4^{''}$ formed, 0.0770 gram. Apparently 0.0009 gram of sulphur was also formed.

Experiment 60.—Similar to preceding, with the addition of 0.46 gram Fe_2O_3 . Heated for 4 days at 225° ; only a little Cu_2S formed. No SO_2 remained. FeSO_4 , 0.214 gram. Sulphur, none. Solution neutral.

Experiment 61.—Sulphur dioxide and cupric sulphate. Initial weights: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.100 gram, SO_2 5 cubic centimeters=0.158 gram, a little CO_2 . Volume of tube 9.6 cubic centimeters. Heated at 225° for 4 hours, the copper first deposited became coated with Cu_2S . Heated at 225° for 5 days, much Cu_2S was formed and in one end of the tube droplets of sulphur. Sulphur found, 0.0084 gram. No H_2S or copper. Trace of SO_2 . Reaction acid. SO_4 found, 0.2082 gram. Two reactions probably occur:



and



Experiment 62.—Action of cupric sulphate on cuprous sulphide. Initial weights: Cu_2S 0.080 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.500 gram, H_2SO_4 0.200 gram, H_2O 5 cubic centimeters. Heated at 230° for 1 day; showed numerous flakes of copper on cooling. The second day a very small quantity of an insoluble white salt appeared which was observed in several similar experiments and is believed to be formed by attack of the glass.

Third day, no appreciable change. The results of analyses of the solid residue and final solution obtained are given in Tables 8 and 9. These determinations were made by Prof. Glenn V. Brown, of Bucknell University, to

whom the writer wishes to express his appreciation for the attention given by him to possible sources of error in the analytical work. Professor Brown also analyzed the products obtained in experiments 69, 101, 102, 104, 108, 110, 114, 115, 116, 117, 121, 123, 125, 127, 128, 132b.

Experiment 63.—Qualitative experiment. A mixture of CuS with a solution containing FeSO_4 , CuCl_2 , and HCl was heated at 130° for 15 hours. Cu_2S and CuCl were formed. No further change was noted after heating at 200° for two days.

Experiment 64.—Experiment 64 resembled experiment 62 except in the use of 0.69 gram of H_2SO_4 . Two days' heating at 200° produced no metallic copper. Four days' further heating some months later, at 300° , yielded considerable copper on cooling.

Experiment 65.—Similar to experiment 62, but with CaCl_2 present. (See Table 8.) Heated at 200° for 1 day; no copper formed, but the color of the solution disappeared, and CuCl may have been precipitated in the CaSO_4 present.

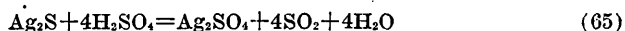
Experiment 66.—Action of cupric sulphate on cuprous sulphide, continuing experiment 62. Initial weights: Cu_2S 0.080 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.250 gram, H_2O 5.0 cubic centimeters. Heating at 150° two hours caused the precipitation of considerable basic salt. Heated at 200° ; no copper was observed the first day, but some appeared the second day, also possibly Cu_2O . The third day there was more Cu_2O , and all the other constituents were still present. The same result the next day, possibly CuO in addition. Some sulphide was still present. The tube was accidentally broken at this stage, and contents lost.

Experiment 67.—Similar to experiment 66, except with 0.500 gram $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 0.100 gram H_2SO_4 in a total volume of 5 cubic centimeters. Heated at 200° . A little copper and basic salt appeared the first day on cooling; somewhat more copper the second day. After 9 days there was no further visible change. The crystals of copper were easily observable with a lens.

Experiment 68.—Copper introduced with the other reagents. Initial weights: Cu_2S 0.08 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.50 gram, H_2SO_4 0.23 gram, Cu 0.066 gram, H_2O about 5.0 centimeters. Heated at 200° for 1 day; considerable copper appeared as beautiful crystals, on cooling, on the surface of the solution. Heated 24 hours more; even more copper was recrystallized and the wire was about half gone.

Experiment 69.—Will cuprous salts oxidize cuprous sulphide? Initial weights: Cu_2S 0.08 gram, CuCl 0.20 gram, Cu 0.10 gram, H_2O 5.0 cubic centimeters. Heated 6 days at 200° ; a little Cu_2O was formed and a little copper was apparently dissolved and reprecipitated on the glass and throughout the solution. No SO_4^{--} was formed. For the results at 250° see experiment 126.

Experiment 70.—Action of H_2SO_4 on Ag_2S . Initial weights: Ag_2S 0.50 gram, H_2SO_4 (concentrated) 2.0 cubic centimeters, H_2SO_4 (1-1) 0.4 cubic centimeters. Heated at 92° , some gas was formed. Heated at 200° for 20 hours; some Ag_2S still remained. The tube showed the presence of SO_2 on opening. The solution gave a precipitate of Ag_2SO_4 on dilution. Found in the solution: SO_2 0.11 gram, Ag 0.1772 gram. Possible reaction:



Experiment 71.—Uncompleted.

Experiment 72.—Will FeSO_4 act on Cu_2S to produce copper? Weights: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.50 gram, Cu_2S 0.02 gram, H_2O 4.78 cubic centimeters. Heated

at 200° 6 days; no significant change was noticed. Some months later the tube was heated 3 days more at 250° without any results.

Experiment 73.—Action of dry cupric chloride on cuprous sulphide. Weights taken: CuCl_2 0.270 gram, Cu_2S 0.159 gram. Sealed in a vacuum and heated to 500° C. for 20 minutes. The mixture melted. Some sulphur sublimed into the ends of the tube. The melt was dark in the center and brown around the edges. Heated again 30 minutes. The melt was clear to brownish black in transmitted light. The sulphur found by extraction with CS_2 was 0.0070 gram. According to this result only part of the materials reacted, and on dissolving the residue in ammonia much Cu_2S appeared which had not been attacked. The ratio of copper to chlorine in the soluble part showed that about 36 per cent of the copper was in the form of cuprous chloride. These findings support the view that as far as the materials reacted the reaction was



Experiment 74.—Action of sulphur dioxide and hydrogen on copper at 900° C. About 10 grams of copper in the form of a bundle of small wires was heated gradually to 900° during the course of 80 minutes in a stream of gas consisting of about 2 volumes hydrogen to 1 volume sulphur dioxide. Water was formed, but no hydrogen sulphide could be detected in the outgoing gas. After cooling and opening the tube the copper was seen to be converted into beautiful crystals of the sulphide for about a seventh of its length. The crystals were black, blue, brass-colored, lavender, and pale green, very well crystallized, and had apparently been very nearly if not wholly melted. A little bunch of crystals terminated the end of each wire.

Experiment 75.—Will SO_2 convert Cu_2S to copper? Weights: Cu_2S 0.02 gram, SO_2 as dry gas 0.10 gram. Volume of tube 9 cubic centimeters. Heated at 92°, 150°, 200° for 1 day each; no copper was formed.

Experiment 76.—Will SO_2 reduce Fe_2O_3 ? Weights: Fe_2O_3 0.020 gram, SO_2 as dry gas 0.100 gram. Heated a day at 92°; no change was visible. Heated a day at 150°; the color turned to buff. Heated a day at 200°; no further change. On opening several months later SO_2 was still present under pressure, but the Fe_2O_3 was not all reduced. In fact, on washing out the SO_2 with H_2O , dissolving in H_2SO_4 , and titrating with KMnO_4 only 0.0020 gram FeO was found.

Experiment 77.— SO_2 and Cu_2S with Fe_2O_3 . Weights: Cu_2S 0.020 gram, Fe_2O_3 0.04 gram, SO_2 0.024 gram, H_2O 5.0 cubic centimeters. Heated at different temperatures, finally at 250° for 6 days; no copper was observed.

Experiment 78.—Similar to experiment 77. Weights: Cu_2S 0.02 gram, Fe_2O_3 0.13 gram, SO_2 0.04 gram, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5 gram, H_2O 5.0 cubic centimeters. Heated at 200° 2 days; no copper was observed. The solid remained red.

Experiment 79.—Action of liquid sulphur dioxide on cuprous sulphide. Half a gram of SO_2 was condensed into a tube, previously evacuated, containing 0.02 gram Cu_2S , and sealed off. No action could be observed on standing or after the tube was heated 24 hours at 65° C.

Experiment 80.—Action of liquid dioxide on ferric oxide. Ferric oxide was also treated as described in experiment 79. The red color turned slightly paler, somewhat buff, but by no means disappeared.

Experiment 81.—Attempt to increase the action of Cu_2S by increasing its solubility. Initial weights: Cu_2S 0.02 gram, KCN 0.05 gram, Fe_2O_3 0.04 gram, H_2O 5.0 cubic centimeters, SiO_2 0.02 gram. No change resulted after heating at

92° for a day. On heating one day at 200° a dirty black precipitate formed, the Fe_2O_3 was no longer visible, and after long standing a few extremely faint indications of metallic copper were observed. On heating to 250° a year later the tube exploded. Old tubes are apparently considerably weaker than new ones.

Experiment 82.—Behavior of colloidal Cu_2S . Some CuCl was precipitated with H_2S . After washing by decantation about 8 times with water containing H_2S a colloidal solution resulted. Fe_2O_3 was precipitated and washed until it was more or less colloidal. (See experiment 6.) Equal volumes of these two colloidal solutions were mixed and sealed in an atmosphere of CO_2 , and the mixture was heated at 92° for 15 days. A green sediment formed, and the solution cleared completely. This result can probably be ascribed to the action of the CO_2 and also to the coagulating effect of one colloid on the other.

Experiment 83.—Initial weights: Fe_2O_3 0.0028 grams, colloidal Cu_2S 15 cubic centimeters. Heated in CO_2 at 200° for 1 day; the red oxide disappeared and a few black flocs were formed. On further heating the tube broke.

Experiment 84.—Action of colloidal Cu_2S on Fe_2O_3 . A long tube in the form of a siphon 6 millimeters in diameter was filled with hematite and Fe_2O_3 , and through it was caused to pass very slowly a colloidal solution of Cu_2S , which was protected by an atmosphere of CO_2 . In the course of some months certain stains that suggested chalcopyrite, bornite, covellite, and, it is barely possible, copper resulted, but the amounts were extremely small and could not be readily observed. The most noticeable effect was that the colloidal Cu_2S was precipitated and retained by the hematite, so that the outflowing solution was clear.

Experiment 85.—Action of cuprous salts on sulphuric acid. Initial weights: CuCl 0.5119 gram, H_2SO_4 5 cubic centimeters of 0.5 normal acid. Heated at 300° for 1 day; the resulting solution was not noticeably blue, and therefore no significant quantity of cuprous copper could have been oxidized. More or less cuprite formed on the inner glass tube in which the CuCl had been introduced, showing the marked attack that the solution made on the poorer grade of glass. From the fact that no cupric salt was formed it may be concluded that no sulphuric acid was reduced.

Experiment 86.—Similar to experiment 84. Fifteen grams of commercial cuprous chloride was placed in a liter bottle with about 500 grams of copper shot. The bottle was filled with distilled water previously freed from air and shaken about an hour, in order to bring the copper salt into equilibrium with copper, thus making it chiefly cuprous chloride. The precipitate which formed was allowed to settle out. The resulting solution was decanted into another bottle and saturated with hydrogen sulphide. A colloidal suspension of cuprous sulphide resulted which remained suspended indefinitely. When the excess hydrogen sulphide was displaced by passing a stream of carbon dioxide through the solution for an hour, the stability of the suspension was lessened to such an extent that it showed a zone of settling in the course of a few days. When some of the suspension containing carbon dioxide was allowed to flow slowly through a tube filled with coarsely powdered hematite, the resulting solution was entirely clear. It contained principally ferrous bicarbonate, not more than a trace of copper, and no sulphide or sulphate. Indistinct tarnishings on the hematite seemed to resemble chalcopyrite in places and metallic copper in other places, but, as in experiment 84, these products could not be positively identified. The experiment was terminated by stoppage of the tube caused chiefly by coagulation of the suspension.

Experiment 87.—The experiment was started with 2.0 grams of CuCl , and procedure was as in experiment 86. The sulphide was precipitated by exactly 200 cubic centimeters of H_2S gas. The Cu_2S that formed flocculated to such an extent that the solution was not used further.

Experiment 88.—Not completed.

Experiment 89.—Fifteen grams of commercial CuCl was treated as in experiment 86 until the solution was saturated with H_2S . This solution remained in complete suspension for 4 days, when some suspended ferric oxide was mixed with it. The suspended particles began to flocculate at once, and the solution became gradually clear. A few shiny yellow scales resembling chalcopyrite appeared in the precipitate, but these were not separated or positively identified.

Experiment 90.—Some copper wire was heated in a current of dry SO_2 at 500° for half an hour. Scarcely any tarnish appeared on the copper. When the SO_2 was moist, however, the copper was well blackened in half an hour.

Experiment 91.—Action of air on Cu_2S at 500° . A weighed quantity, 0.1000 gram, of Cu_2S gained 0.0469 gram after heating 3 hours at 500° . The product, based on a determination of its content of sulphur, was $\text{CuO} \cdot \text{CuSO}_4$. Sulphur found, 13.2 per cent as demanded by the written formula. Soluble in dilute HCl .

Experiment 92.—Carbon monoxide and Cu_2S at 500° . Apparently no action.

Experiment 93.—Attempt to prepare colloidal cupric sulphide. A solution containing 1 gram of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 500 cubic centimeters was mixed with a solution of 0.187 gram of Na_2S in 500 cubic centimeters. After 2 days a considerable quantity of black copper sulphide had precipitated, and the solution above was greenish yellow.

Experiment 94.—Similar to experiment 93. Three solutions were prepared, each containing 1 gram of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a liter. Hydrogen sulphide gas was added to each, 38, 76, and 152 cubic centimeters, respectively. Precipitates began to coagulate in all the bottles very soon after the gas was introduced and settled out completely in the course of a few days. The results were not comparable with those in experiment 86.

Experiment 95.—Action of ferric chloride on cuprous sulphide at ordinary temperature. Initial weights: Cu_2S 0.500 gram, FeCl_3 0.0500 gram, HCl 0.005 gram, H_2O 50 cubic centimeters. The air was pumped out of the solution and replaced with carbon dioxide. The first day the yellow color was replaced by a blue-green color. The addition of KSCN gave a red color and a white precipitate, possibly CuSCN . No sulphate had formed. At the end of a week the iron in solution was about 89 per cent in the ferrous state, as shown by titration with KMnO_4 . After 52 days a similar result was obtained, and still practically no sulphur had gone to the sulphate condition.

Experiment 96.—Ferric oxide and cuprous sulphide. Similar to experiment 9. Weights: Fe_2O_3 0.192 gram, Cu_2S 0.063 gram, H_2SO_4 0.222 gram, H_2O 0.208 cubic centimeter. Heated at various temperatures up to 300° ; no copper was observed. The quantity of H_2O was too small to be thoroughly in contact with all the substances.

Experiment 97.—Action of H_2SO_4 on copper. Acid of specific gravity 1.42 developed no visible color on heating a week with copper at 90°C .

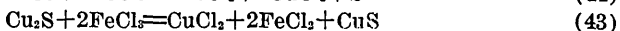
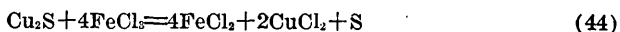
Experiment 98.—Action of FeCl_3 on Cu_2S . Weights: Cu_2S 0.100 gram, FeCl_3 0.022 gram, H_2O 5.0 cubic centimeters. Heated at 200° for 17 hours; some Fe_2O_3 was deposited in thin flakes, ferrous salt was produced equivalent to 0.0067 gram FeO , also a little SO_4^{--} , and a possible trace of copper. The weakness of this experiment is that the Fe_2O_3 becomes more soluble on cooling,

and the ferric salt thus formed would tend to dissolve any copper precipitated, if the Cu_2S did not reduce the ferric salt fast enough.

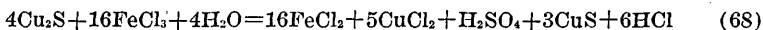
Experiment 99.—Initial weights: Cu_2S 0.100 gram, FeCl_3 0.022 gram, HCl 0.175 gram, H_2O about 5 cubic centimeters. Heated at 200° for two days; beautiful black crystals formed, probably recrystallized Cu_2S , not more than traces of SO_4 or sulphur. Ferrous iron in solution equivalent to about 0.006 gram FeO . Cupric and ferric salts present. For repetition see experiment 101.

Experiment 100.—Sulphur and cupric chloride. Initial weights: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.85 gram, S 0.64 gram, H_2O 5.0 cubic centimeters. On heating at 200° for 17 hours the blue color of the solution had disappeared. After three days' heating there was abundant copper sulphide, blue, lavender, purple, and black.

Experiment 101.—Ferric chloride and cuprous sulphide. Initial weights: Cu_2S 0.240 gram, FeCl_3 0.325 gram, HCl 0.200 gram, H_2O to a volume of 5 cubic centimeters. The yellow color began to change to green immediately on mixing, and on warming to 90° sulphur appeared in the course of an hour. Heated at 200° for two days; the solution was still slightly yellow, the solid somewhat purple and blue, suggesting covellite. After the solution was heated four days more there was no further visible change except an increase in the quantity of covellite. Analysis then showed in the precipitate Cu 0.0946 gram, S 0.0343 gram, and, in the solution, SO_4 0.0378 gram. The results can not be reconciled with any simple single reaction. It is believed that all the following reactions occurred either simultaneously or in succession.



Or, by combining (44), (10), and (67) to eliminate sulphur one obtains

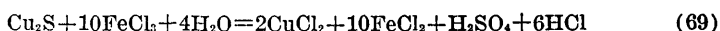


Analysis of the products seems to show that about half of the precipitate was unchanged Cu_2S , so that on this basis 0.175 of the original Cu_2S reacted. The requirements of equation (68) are then as follows:

Quantities required for equation (68) and quantities found

	Calculated	Found
	Gram	Gram
Cu as CuS	0.053	0.043
S as CuS026	.021
SO_4 in solution.....	.026	.038

These results indicate that another reaction must have taken place to a small extent, forming H_2SO_4 without the simultaneous production of CuS . This reaction was probably some such reaction as the following:



Adding equations (68) and (69) we obtain (quite arbitrarily)



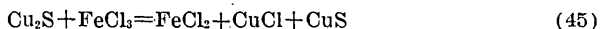
Assuming that 0.175 gram of Cu_2S reacted we have by equation (70) the quantities shown in the following table:

Quantities required for equation (70) and quantities found

	Calculated	Found
	Gram	Gram
Cu as CuS.....	0.042	0.043
S as CuS.....	.021	.021
SO ₄ '' in solution.....	.042	.038

Apparently the net result is approximately a combination of equations (68) and (69).

Experiment 102.—Action of Cu₂S in excess on FeCl₃. Initial weights: Cu₂S 0.300 gram, FeCl₃ 0.150 gram=1.41 cubic centimeters of stock solution, HCl 0.195=1 cubic centimeter of stock solution, H₂O in addition 2.5 cubic centimeters. Heated at 200° for 1 day. Some covellite was formed, also cuprous chloride, which separated on cooling. The solution was still very pale yellow. Probable reaction:



Heated 5 days longer at 200°. The covellite became gradually less noticeable. The yellow element in the color of the solution did not seem to disappear entirely. Final result: Total sulphur in precipitate, 0.0592 gram (taken as Cu₂S 0.0603 gram); SO₄'' in solution 0.0033 gram.

Experiment 103.—Initial weights: Cu₂S 0.16 gram, CuCl 0.50 gram, CuCl₂ 0.12 gram, FeCl₃ 0.033 gram, HCl 0.39 gram, H₂O about 4.0 cubic centimeters. Heated at 150° for 1 day and at 200° for 1 day; no visible changes. When heated at 250° the tube exploded.

Experiment 104.—Copper and sulphuric acid. Initial weights: Cu 0.5 gram, H₂SO₄ 0.50 gram, H₂O 2.85 cubic centimeters. Volume of tube 12 cubic centimeters. Heated at 250° for 3 days. Some of the copper recrystallized on cooling; in fact, only a little of the original wire remained. Cu₂S and CuSO₄ were formed. Heated 2 days more; the copper mostly recrystallized on cooling. Analysis of products is given in Tables 9 and 10. From later work discussed on pages 15 and 37 it is inferred that theoretically all the copper taken in this experiment should have dissolved at 250°—that is, if the sulphuric acid was not too greatly reduced by the reaction to be effective.

Experiment 105.—Effect of Cu₂O. Initial weights: Cu₂S 0.16 gram, Cu₂O 0.429 gram, H₂O 5.0 cubic centimeters. Heated at different temperatures, finally 2 days at 250°; no visible copper.

Experiment 106.—Same as experiment 105 with 0.05 Fe₂O₃ in addition. Heated finally 4 days at 250°; no visible copper.

Experiment 107.—Cu₂S and Fe₂(SO₄)₃. Weights: Cu₂S 0.30 gram, Fe₂(SO₄)₃ 0.192 gram, H₂SO₄ 0.513 gram, H₂O 5.0 cubic centimeters. Heated at 150° for 2 days; no visible change except that the solution turned blue. Heated at 250° for 2 days; no copper deposited on cooling.

Experiment 108.—Cuprous sulphide, cupric sulphate, and cuprous oxide. Initial weights: Cu₂S 0.08 gram, CuSO₄.5H₂O 0.38 gram, Cu₂O 0.28 gram, H₂O 5 cubic centimeters. Heated at 200° for 1 day; a little copper formed, solution still blue. Heated another day; a little bright-green basic salt formed. The precipitate was now analyzed. Sulphur found 0.0151 gram, originally taken as cuprous sulphide 0.0160 gram, which shows that a little of the sulphur of the cuprous sulphide had been oxidized.

The experiment was repeated, using Cu₂S 0.106 gram, CuSO₄.5H₂O 0.50 gram; otherwise as above. Heated to 300° for 4 days. A little copper and a green

basic salt were formed. Both Cu_2S and Cu_2O remained. The solution was moderately blue. Two years later no basic salt was visible; Cu_2S , Cu, and Cu_2O remained.

Experiment 109.—Cupric chloride and cuprous sulphide. Initial weights: Cu_2S 0.08 gram, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.26 gram, H_2O 5.0 cubic centimeters. Heated at 200° for 1 day; found in solution as sulphate 0.0027 gram = 0.0080 SO_4'' . About 17 per cent of the sulphur in the chalcocite was oxidized by heating at 200° for 1 day. Cuprous chloride was suspected as another product of the reaction. (See further experiment 131.)

Experiment 110.—Oxidation of chalcocite by cupric sulphate. Initial weights: Cu_2S 0.08 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.375 gram, H_2O 5.0 cubic centimeters. Heated at 200° for 1 day; a very little copper formed, also a green basic salt. Heated 1 day more. Analyzed. Found 0.0160 gram of sulphur in precipitate, identical with sulphur taken as Cu_2S . Practically no acid in the solution. The reaction had scarcely started.

Experiment 111.—Cuprous sulphide, cupric sulphate, and sodium acetate. Initial weights: Cu_2S 0.08 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.50 gram, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ 0.72 gram. Heated for 2 days at 200° ; a little copper was formed and a large quantity of a red salt which was not determined. The blue color of the solution practically disappeared.

Experiment 112.—Oxidation of Cu_2S at 200° . (See Table 8.) Four days' heating at 200° gave a bare trace of copper on cooling.

Experiment 112.—Oxidation of Cu_2S at 200° . (See Table 8.) Four days' end. Weights as given in Table 8; the solution was dilute. Heated for 6 days with one end in furnace supposed to yield 250° , the other end water-cooled. No copper. The acidity was unchanged. Evidently the reaction did not progress appreciably, probably because 250° was not attained.

Experiment 114.—Similar to experiment 62, but more CuSO_4 was taken. Weights in Table 8. Heated at 250° for two days. A measurable quantity of copper deposited on cooling. Results of analyses in Tables 9 and 12.

Experiment 115a.—Tube broke.

Experiments 115b and 115c.—Heated at 300° for four days and six days respectively. Weights and analyses shown in Tables 8-12. Experiments at temperatures above 250° were made by inclosing the tubes in an iron bomb with water inside to equalize the pressure on the tubes.

Experiment 116.—Similar to experiments 115b and 115c; heated 56 days at 250° . (See Tables 8-12.)

Experiment 117.—Effect of FeSO_4 . (See Tables 8-12.)

Experiment 118.—Run in a silica tube. Initial weights: Cu_2S 0.32 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 1.500 grams, H_2SO_4 0.10 gram, H_2O 4.96 centimeters. Heated 11 days at 350° ; a little copper appeared on cooling. Not analyzed.

Experiment 119.—Ferric oxide, cuprous sulphide, etc. (See Tables 8-12.) Heated at 300° for 6 days. A little copper was deposited on cooling, and the solution was slightly blue.

Experiment 120a.—Action of sulphuric acid on Jena glass tubes. Exactly 5 cubic centimeters of 0.5 normal sulphuric acid was placed in a Jena glass tube, 22 centimeters long, 1 centimeter in internal diameter, and heated in a horizontal position at 200°C . for 20 days. Original H_2SO_4 0.1225 gram, remaining 0.0932 gram, neutralized 0.0293 gram. Some crystals formed on the inside of the tube which qualitative tests indicated to consist of SiO_2 , SO_4'' , Ca, and possibly K. There was not enough material to analyze. E. S. Larsen examined it microscopically and thought that three separate things were present; some basal hexagonal tablets, uniaxial (+) $\omega = 1.58$ and ϵ about 1.60, possibly an alunite; some skeletal prisms with n about 1.47; and some needles

with high index of refraction. Some of the crystals formed little radiating clusters, and some grew along the glass. The solution was found to contain SiO_2 0.0192 gram, Al_2O_3 0.0010 gram, CaO 0.0055 gram, MgO trace, K_2O trace, Na_2O not determined.

Experiment 120b.—Similar to preceding, in a tube 16 centimeters long, heated 11 days at 300° . Original H_2SO_4 0.1225 gram, remaining 0.1125 gram, neutralized 0.0100 gram, which is less than found in 120a. No crystals formed in the tube. The solution gave SiO_2 0.0067 gram, CaO 0.0010 gram, MgO trace, K_2O 0.0036 gram, Na_2O not determined.

Experiment 121.—Ferric sulphate and cupric sulphide. Resembled experiment 107. Initial weights and results shown in Table 8. Heated for 18 days at 200° ; solution slightly blue but no copper. Heated 11 days more at 300° ; some copper appeared on cooling. The sulphur of the solids was more than enough to form Cu_2S , so that either sulphur or CuS may also have been present.

Experiment 122.—Resembled experiment 118. A silica tube of volume about 15 cubic centimeters was used. (See Tables 8–12.) No acid was used; that formed in the reaction prevented any formation of basic salt, even at 300° .

Experiment 123.—Similar to experiment 122 but with H_2SO_4 present, also less CuSO_4 . The copper deposited on cooling was only about half that formed in experiment 123. (See Tables 8–12.)

Experiment 124.—Action of cupric sulphate on sulphur dioxide. Initial weights: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 2.00 grams, SO_2 0.222 gram, H_2SO_4 0.49 gram, H_2O 10.0 cubic centimeters. Heated at 250° for 1 day; apparently nothing but copper was formed. Heated 4 days more; in addition to the copper a trace of fine dark crystals, apparently either CuS or Cu_2S , was formed.

Experiment 125.—Resembled experiment 114 but with more CuSO_4 . Some of the CuSO_4 crystallized out on cooling. Details in Tables 8–12.

Experiment 126.—Resembled experiment 69. Initial weights: Cu_2S 0.10 gram, CuCl 0.20 gram, Cu 0.10 gram, HCl 0.20 gram, H_2O 5.0 cubic centimeters. Heated 2 days at 200° ; the CuCl recrystallized on cooling. Heated 5 days at 250° ; a very little copper was recrystallized and deposited as a red tint on some of the CuCl on cooling, especially at a certain zone near the end of the tube. No sulphate was formed.

Experiment 127.—Similar to experiment 122 but heated at 350° . Details in Tables 8–12. Silica tube.

Experiment 128.—Resembled experiment 49. Initial weights: Cu 0.50 gram, H_2SO_4 0.50 gram, H_2O 2.85 cubic centimeters. Heated 4 days at 350° ; considerable Cu_2S was formed. Some copper was recrystallized, but the results resembled in most respects those obtained by starting with Cu_2S and CuSO_4 . The acid was not all used up, but the copper may not have been present in sufficient amount. Details in Tables 8–12.

Experiment 129.—Neutralizing action of rock from the Leucite Hills, Wyo., supposed to be wyomingite, on sulphuric acid. Initial weights: Wyomingite 1.0 gram, HCl 0.5 gram, H_2O 5.5 cubic centimeters. Heated 2 days at 250° ; HCl then 0.150 gram; neutralized 0.350 gram. Potassium in solution as K_2O , 0.120 gram = 12 per cent of rock. The alkalis were apparently all dissolved. In fact, a little potassium may have dissolved from the tube, or the rock may have been orendite with approximately 12 per cent K_2O .

Experiment 130.—Neutralizing action of Jena combustion tubing, powdered and selected between 60 and 200 mesh. Quantity taken, 1.0 gram; H_2SO_4 0.100 gram, H_2O 6.96 cubic centimeters. Heated 2 days at 250° . H_2SO_4 was then 0.0684 gram; neutralized 0.032 gram.

Experiment 131.—Oxidizing action of cupric salts. Initial weights: Cu_2S 0.16 gram, CuCl_2 0.96 gram, H_2O 5.60 cubic centimeters. Heated 2 days at 250° ; the sulphur of the Cu_2S was completely oxidized to sulphate. A considerable quantity of CuCl crystallized out on cooling. The solution was a pale willow-yellow.

Experiment 132a.—Resembled experiment 49. Initial weights: Cu 0.50 gram, H_2SO_4 0.1225 gram, H_2O 4.96 cubic centimeters. Heated 4 days at 250° . The resulting solution was pale blue. A small quantity of copper was recrystallized and a trace of Cu_2S formed. The recrystallized copper, separated as well as possible, after correction for a trace of sulphide, was found to be 0.0050 gram. Copper in solution 0.0069 gram. The solution was boiled and a very small amount of SO_2 , 0.008 gram, found by collecting in KMnO_4 .

Experiment 132b.—A duplicate of the tube analyzed in 132a was heated 4 days more at 300° . Found: In the solid, copper 0.473 gram, sulphur 0.0065 gram, equivalent to 0.0323 gram Cu_2S ; in the solution, Cu 0.0225 gram, SO_4^{--} 0.1005 gram, acidity by titration equivalent to 0.078 gram H_2SO_4 . The results of calculation of the possible reaction, given in Table 12, do not conform very closely to the requirements of equation (17), which is the reverse of equation (36) expressing the action of cupric sulphate on chalcocite.

Experiment 133.—Similar to preceding experiment. Initial weights: Cu 0.127 gram, H_2SO_4 0.392 gram, H_2O 0.392 cubic centimeter. Volume of tube 14 cubic centimeters. Heated at 300° for 4 days; the copper was entirely recrystallized with the production of Cu_2S and CuSO_4 . In fact, the solution nearly all crystallized as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The products were not analyzed.

Experiment 134.—Similar to preceding experiment. Initial weights: Cu_2S 0.160 gram, H_2SO_4 0.196 gram, H_2O 7.93 cubic centimeters in all. Heated at 300° for 4 days; there was no visible change. On opening the tube no SO_2 could be detected by the smell, but on boiling the solution, absorbing the gas in water, and titrating with KMnO_4 , a possible trace of SO_2 was indicated.

Experiment 135a.—Effect of the presence of CuCl on reaction (36). Initial weights: Cu_2S 0.16 gram, CuSO_4 1.21 grams, CuCl 0.40 gram, introduced dry in separate inner tube, H_2O 5.0 gram. Heated at 300° for 4 days. The tube was considerably attacked. A bright-green salt was formed and possibly Cu_2O but no copper.

Experiment 135b.—Initial weights: Cu_2S 0.32 gram, CuSO_4 1.21 gram, CuCl 0.1996 gram, H_2SO_4 0.1225 gram, H_2O 4.96 cubic centimeters. Heated at 300° for 2 days. Some of the green salt formed, also very good crystals of Cu_2O , especially on the poorer glass of the inner tube, but only one or two small flakes of copper.

Experiment 136.—To see if the copper is formed by reaction (36) at the high temperature. Initial weights: Cu_2S 0.32 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 3.00 grams, H_2O 5.0 cubic centimeters. Heated at 250° for 15 hours and inspected while hot. The color was a dark green with a large quantity of basic salt, but no copper was visible. When heated 2 days more the quantity of basic salt had decreased, but no copper appeared. When heated 3 days more the basic salt was mostly gone. When heated 2 days more the solution was green, but no copper appeared. The tube was now allowed to cool in a sloping position. Crystals of copper appeared in the solution, which became blue. A little $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystallized, also a little green basic salt and a few octahedra of cuprite.

Experiment 137.—Similar to experiment 49. Initial weights: Copper 1.0003 grams, H_2SO_4 0.3691 gram, H_2O 4.88 cubic centimeters. Heated at 200° for 2 days; no visible color developed, but a trace of Cu_2S formed. When heated at 250° for 7 hours more a pale-yellowish color developed, with considerable Cu_2S . When heated 17 hours more the solution was faintly blue, and a few

specks of recrystallized copper appeared in the end of the tube, which was probably the coldest part; this shows how easily the copper migrates from warm to cold regions. When heated 1 day more the solution was a pale greenish blue. On cooling the solution deposited a lot of copper and became blue. Most of the Cu_2S was well crystallized, showing lathlike and feathery forms.

Experiment 138.—Similar to experiments 49 and 132 but heated at 300° . Initial weights: Copper 1.00 gram, H_2SO_4 0.3691 gram, H_2O 4.88 cubic centimeters. Heated at 300° for 2 days and cooled. Tube now contained Cu_2S , recrystallized copper, and CuSO_4 , estimated colorimetrically at 0.086 gram copper. Analysis: Copper recrystallized, corrected for Cu_2S , 0.0794 gram. Total copper in solid 0.9054 gram; total sulphur 0.0150 gram. Solution: Copper 0.0896 gram, SO_4'' 0.3180 gram. The calculations based on these determinations are given in Tables 1 and 11.

Experiment 139.—Similar to experiment 138 but heated at 350° in silica tube. Duplicates, one in silica, one in glass. The glass tube was much attacked but held. Weights: Copper 1.000 gram, H_2SO_4 0.3691 gram, H_2O 4.880 cubic centimeters. Heated at 350° for 2 days. The contents of the silica tube were analyzed. Solid: Recrystallized copper, corrected for Cu_2S , 0.0996 gram, total copper 0.8704 gram, total sulphur 0.0212 gram. Solution: Copper 0.1246 gram, SO_4'' 0.3005 gram. For calculations see Table 1.

Experiment 140.—Pyrite and copper in the presence of water. Uncompleted.

Experiment 141a.—Effect of high alkalinity. Weights: Fe_2O_3 0.768 gram, Cu_2S 0.064 gram, NaOH 5 cubic centimeters of solution of specific gravity 1.19. Heated at 200° for 3 hours; no visible changes occurred.

Experiment 141b.—Similar to experiment 141a. Weights: Fe_2O_3 0.764 gram, Cu_2S 0.064 gram, NaOH 5 cubic centimeters of solution 15.5 normal. Heated at 300° for 1 day. The tube cracked and was very much attacked, so that the results were not satisfactory. However, there were no evidences of copper or ferrous sulphate. Only on extracting with dilute acid was ferrous iron found, and this is explicable by the evidence of experiment 38.

Experiment 142.—Pyrrhotite and ferric oxide. Weights: FeS 0.088 gram, Fe_2O_3 0.64 gram, H_2O 5.0 cubic centimeters. Heated at 300° for 1 day; no soluble SO_4'' or Fe'' was formed. Hydrochloric acid of course gave some Fe'' , but no SO_4'' in the solid.

Experiment 143.—Ferric oxide and sodium sulphide. Initial weights: FeCl_3 equivalent to 0.897 gram Fe_2O_3 , NaOH 1.88 gram = 2.17 cubic centimeters of 15.5 normal NaOH , Na_2S 0.78 gram = 1 cubic centimeter of 2 normal Na_2S . Heated at 300° for 1 day. Some FeS was formed at once. The tube was much attacked. The inside of the tube was more or less covered by a greenish coating. No soluble SO_4'' or Fe'' found; in fact, the solution was faintly alkaline. The solution gave a white precipitate on acidifying with H_2SO_4 and consumed a small amount of KMnO_4 equivalent to 0.0034 gram FeO . No pyrite could be detected. The dry powder was slightly magnetic.

Experiment 144.—Ferric oxide and sulphur. Compare experiment 24. Weights: Fe_2O_3 0.500 gram, sulphur 0.05 gram, H_2O 5.0 cubic centimeters. Heated at 300° for 1 day; the solution contained considerable SO_4'' (not acid, hence probably K_2SO_4 from the glass) and a little Fe'' . The solid appeared to contain some sulphide, perhaps FeS or FeS_2 in the form of a slimy dull-gray powder not rapidly soluble in acid but of indistinct character under the microscope. Hydrochloric acid dissolved some ferrous compound, at least 0.0034 gram FeO . No residual sulphur could be detected.

Experiment 145.—Ferric oxide and cuprous chloride in acid solution. Weights: $\text{Fe}_2(\text{SO}_4)_3$ and $\text{H}_2\text{SO}_4=0.0765$ gram Fe_2O_3 and 0.1535 gram H_2SO_4 in 1 cubic centimeter of solution, H_2O 2.0 cubic centimeters, CuCl 0.3015 gram (in an inner capsule). The substances were not mixed until the air was very thoroughly pumped out and the tube sealed. After mixing the solution soon developed a blue color, estimated colorimetrically to be equivalent to 0.056 gram of cupric copper. Theory for complete reduction of the ferric salt 0.061 gram. Heated at 125° for 2 days; some Fe_2O_3 and possibly other hydrolytic products were deposited, and the solution became somewhat paler.

Experiment 146.—A blank test on the CuCl , treated as in the preceding experiment but without any ferric salt, gave no blue color. After heating at 125° for 2 days and cooling a very little copper deposited on cooling. No blue color was visible.

Experiment 147.—Gradual neutralization of a ferrous-cupric solution likely to deposit copper. Weights: H_2O 50 cubic centimeters, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.0278 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.250 gram, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ 1.09 grams. The material was sealed in a vacuum, the solids being in a separate tube. Mixed. A fine yellow precipitate soon began to form and in 15 minutes had flocculated. The solution was then somewhat greenish, and the precipitate gradually became the color of ferric hydroxide, verging slightly toward yellow. Heated at 100° for 4 hours and then cooled; the precipitate was decidedly red, although no particles of copper could be identified by any metallic appearance. The solution was nearly colorless, but after filtering off the precipitate in air it gave only 0.0050 gram iron and 0.0050 gram copper. When the solid was immersed in silver sulphate solution metallic silver was precipitated, but as cuprous oxide gives the same result this does not prove that metallic copper existed in the precipitate, and there is no evidence that it was present. The fact that ferric hydroxide appeared to be formed and that the precipitate reduced silver sulphate solution seems to show that the precipitate was a mixture of ferric and cuprous oxides or hydroxides.

Experiment 148.—Similar to experiment 147, but with twice as much ferrous sulphate and sodium acetate. The precipitate did not coagulate as quickly as that in experiment 147. The flask was heated very gradually up to 100° over the course of a week. The results were similar to those obtained in experiment 147 except that the color of the precipitate was much more yellow, hardly at all red, resembling freshly precipitated cuprous oxide. The solution gave 0.0062 gram iron and 0.0018 gram copper.

Experiments 149–153.—Solubility of CuCl in solutions of CaCl_2 at 25°C . The determinations were made in an atmosphere of nitrogen in the apparatus shown in Figure 2. It will readily be seen that water or calcium chloride solution could be freed from air and introduced into the tube or the saturated solution removed from it by connecting as desired, turning the proper stop-cocks, and allowing nitrogen from a cylinder of the compressed gas to pass as slowly or fast as desired. The precipitated CuCl was first well washed. The tube containing the mixture was then shaken from time to time and kept at constant temperature in the thermostat accurate to 0.1° . After settling, the clear solutions were decanted into a graduated cylinder and weighed. They were then analyzed by separating the copper as sulphide and determining it by electrolysis. The calcium was precipitated as oxalate and weighed as lime. The results are shown in Table 13.

Experiment 155.—This experiment was similar to experiment 14. Initial weights: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.5 gram, H_2O 5.0 cubic centimeters. The tube was observed from time to time during 24 hours while it

was being heated at 200°. No copper appeared, but some red substance, thought possibly to be cuprite, was formed. Copper appeared on cooling, however, but redissolved on heating. The experiment shows that the copper obtained in Stokes's experiment was probably precipitated by cooling and not by reaction at a high temperature.

Experiment 157.—This experiment was performed to neutralize the acidity gradually and thus to increase the quantity of Cu_2SO_4 formed. Initial weights: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.5 gram, wyomingite 0.2 gram, H_2O 5.0 cubic centimeters. After heating the tube at 200° for two days no copper was visible in the hot solution. The tube was then tilted and cooled slowly. When cold a considerable quantity of copper had separated from the solution, and no significant quantity of it could be seen in the solids, showing that the copper is not formed while hot, at least for a certain initial period.

Experiment 158.—Initial weights: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 0.5 gram, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.5 gram, Cu_2O 0.8 gram, H_2O 5.0 cubic centimeters. The tube after heating

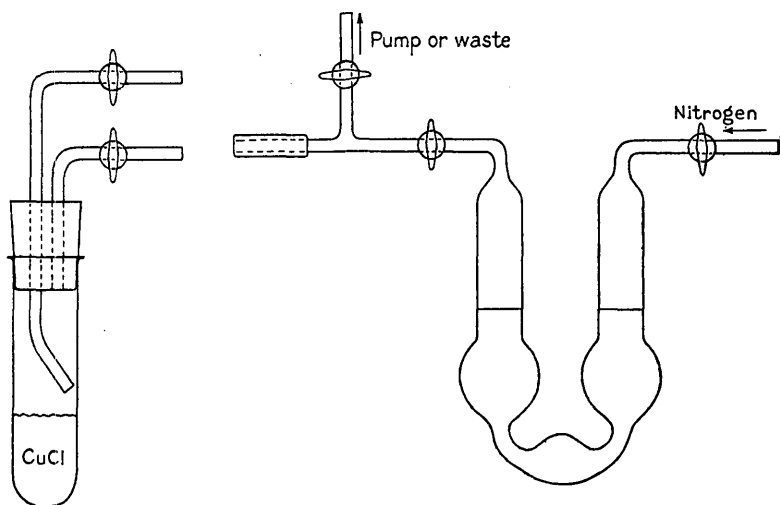
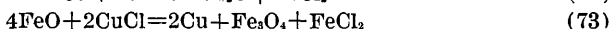
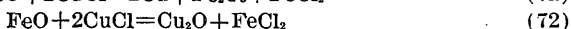
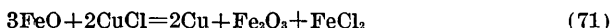


FIGURE 2.—Apparatus used in experiments 149-153

at 200° for two days showed no copper while hot, but after tilting the tube and cooling as in the previous experiment copper was observed in the solution and only a very few specks in the solid. Some feathery crystals were also present in the solution, but not definitely shown to be Cu_2SO_4 . There was not as much hematite in the solid as in the preceding experiment.

Experiments 159a-159g.—Reaction of CuCl on FeO at 100°. A ferrous chloride solution was made by immersing an excess of iron in hydrochloric acid, the solution being protected by an atmosphere of nitrogen. This solution was withdrawn quantitatively as desired and precipitated by an exact equivalent of caustic soda solution, also in an atmosphere of nitrogen. In most of the experiments saturated sodium chloride was used as a diluent to the extent of half the volume of the main solution. Similarly, cuprous chloride dissolved in a concentrated solution of sodium chloride was added to the suspension of ferrous oxide. All reactions were done at about 100° C. in a closed flask, the contents of which could be boiled in a slow stream of nitrogen. In experiment 159c the sodium hydroxide was added to the mixed ferrous and cuprous salts

instead of first precipitating the ferrous oxide. The data obtained are given in Table 14, in which the lines entered as "theory" are computed from the weights of FeO or CuCl taken, depending on which was in excess, according to equations (71), (72), and (73).



The precipitate formed in these experiments, after drying on filter paper in air, was strongly magnetic. This suggests that magnetite was one of the products, as indicated by equation (73).

The data in Table 14 show that equation (72) may be left out of consideration. Equation (71) evidently expresses the principal change, especially when CuCl is in large excess. At the same time, however, some magnetite appears to be formed, as expressed by equation (73), and this equation appears to be still better verified as the excess of CuCl is decreased, as would be expected.

In experiment 159f, a single blank test with cuprous chloride solution and metallic copper, a little metallic copper appeared to be dissolved in the usual procedure at 100°. Also, while equations (71) and (73) serve to represent the essential changes, there is a little too much iron dissolved, the cause of which is not clear, although it may be caused in part by hydrolysis of the cuprous chloride.

The results of the experiments are in harmony with the following facts: (1) Cuprous oxide is of the same order of solubility as ferrous oxide. (2) Ferric oxide is much less soluble. (3) The equilibrium



lies naturally toward the right but is displaced toward the left in alkaline or slightly acid solutions by the relatively much smaller solubility of ferric oxide.

According to the writer's computations from available electromotive-force measurements, the equilibrium constant for equation (74) at ordinary temperature is

$$\frac{[\text{Cu}^+][\text{Fe}^{++}]}{[\text{Fe}^{+++}]} = 5,000 \quad (75)$$

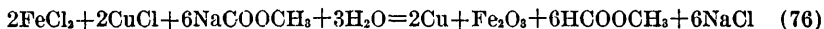
If the solubility products of $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, and CuOH at 25° are taken as 19.8×10^{-16} , 1.1×10^{-38} and 1.6×10^{-9} respectively, it is easily calculated that in solution as alkaline as $\text{Fe}(\text{OH})_2$ itself ferrous oxide should readily convert cuprous salts into metallic copper. As a matter of fact, however, ferrous chloride is formed, and this is even more favorable for the precipitation of copper. The final solution in experiment 159g, for example, contained ferrous chloride, 0.0042 molal, and cuprous chloride dissolved in sodium chloride, 0.0281 molal. The unknown ionic concentrations are $[\text{Cu}^+]$ and $[\text{Fe}^{+++}]$, the first depending on the existence of a complex ion and the second depending on $[\text{OH}^-]$ —that is, on the hydrogen ion concentration or pH value, and possibly on the existence of magnetite as a solid phase.

According to Bodländer and Storbeck⁷⁸ $[\text{Cu}^+]$ will be highest in the least saline solutions. Evidently, however, $[\text{Fe}^{++}]$ can be varied more widely than $[\text{Cu}^+]$.

⁷⁸ Bodländer, G., and Storbeck, O., Beiträge zur Kenntnis der Cuproverbindungen: Zeitschr. anorg. Chemie, vol. 31, pp. 1-41, 458-476, 1902.

Experiments 160a-160j.—Action of FeCl_2 on CuCl in solutions of regulated pH, or hydrogen ion concentration. The pH value was fixed by different proportions of acetic acid and sodium acetate. When ferrous chloride and cuprous chloride were introduced into such solutions, boiling in an atmosphere of nitrogen, no copper was precipitated if the pH value was initially less than about 5.0. Under certain conditions, shown more fully in Table 15, with a pH value of 5.2 a slight film, probably containing some copper, formed on the walls of the flask in the course of 2 hours boiling. The experiment was repeated with less sodium chloride present, but no crystals of copper could be detected. With a pH value of 5.38 and somewhat more sodium chloride, the deposit showed some small particles of ferric oxide, each surrounding a nucleus of minute crystals of copper visible with a lens.

Repetition of the experiment with more ferrous chloride and less cuprous chloride, in a flask that had a slight film remaining from the previous experiment, gave a deposit that showed under a lens or a microscope numerous crystals of copper, some spicules, some thick crystals showing triangular faces, most of them largely covered with iron oxide, which also adhered to the glass in the form of minute lumps and flocs without definite form. This iron oxide was not magnetic. The reaction that occurred here may be written



These experiments show that the use of ferrous hydroxide is not absolutely necessary for the deposition of metallic copper and also that copper is a recognizable product when the reaction is made to occur very slowly, and further that the deposition of copper is not dependent on cooling in the chloride solutions, as it seems to be in the sulphate solutions (experiments 155-158).

Experiments 161 and 162.—Unfinished.

Experiment 163.—This experiment was a repetition of experiment 3. The tube was heated at 150° for 25 hours. There were no signs of recrystallized copper on cooling.

Experiment 164.—Similar to experiment 31. Weights: CuCl 4.5 grams, NaCl 3.5 grams, Cu 2.0 grams, H_2O 6.0 cubic centimeters. This tube was sealed with some air in it, then heated to about 80° . Soon after, one of the wires was seen to be much attacked near one end so that it had the appearance of a bunch of crystals at that point and some crystals or fragments of copper were loose in the tube. It would therefore have been impossible to note any recrystallization of copper in this tube. When the tube was heated at 150° for 15 hours a little green basic salt formed, and much of the CuCl recrystallized on cooling. When the tube was heated at 175° for 5 hours and tilted while hot the green basic salt remained with the copper and had therefore not dissolved in the hot solution, but most of the CuCl had dissolved and recrystallized on cooling.

Experiment 165.—Similar to experiment 164, but 4.0 cubic centimeters of H_2O and 2 cubic centimeters of concentrated HCl were taken instead of 6 cubic centimeters of H_2O . When the tube was heated at 150° for 15 hours no recrystallized copper was observed on cooling. The solution was practically colorless. The tube was heated at 175° for 5 hours and tilted hot; about 95 per cent of the CuCl recrystallized, showing a solubility of approximately 700 grams of CuCl per liter in this solution at 175°C . No basic salt was formed. The CuCl was beautifully crystallized.

DEPOSITION OF NATIVE COPPER

TABLE 8.—*Substances taken and conditions of experiment*

[All weights in grams]

Experiment No.	Temperature (°C.)	Duration of experiment (days)	CuSO ₄	Cu ₂ S	H ₂ SO ₄	FeSO ₄	Fe ₂ O ₃	H ₂ O
a 15	200	2	-----	0.02	0.08	0.50	0.08	5.0
a 62	230	3	0.320	.08	.23	-----	-----	5.35
b 64	200	2	.320	.08	.69	-----	-----	5.69
b 65	200	1	.320	.08	None.	c 4.0	-----	5.2
a 66	200	6	.160	.08	None.	-----	-----	5.09
a 67	200	9	.320	.08	.10	-----	-----	5.26
b 72	200	6	-----	.02	-----	.273	-----	4.8
b 77	200	3	-----	.02	d .024	-----	.04	5.0
b 78	200	3	-----	.02	d .040	.50	.130	5.23
b 101	200	6	-----	.24	e .201	-----	f .325	2.0
b 102	200	6	-----	.30	e .195	-----	f .150	3.5
a 108	200	2	.243	.08	e .28	-----	-----	5.14
b 109	200	1	A .26	.08	-----	-----	-----	5.08
a 110	200	2	.24	.08	-----	-----	-----	5.13
a 112	200	4	.24	.08	.23	-----	-----	20.3
b 113	200	6	.24	.08	.23	-----	-----	30.3
i 114	250	2	1.919	.1600	.340	None.	None.	8.25
115b	300	4	1.919	.1600	.340	None.	None.	8.25
115c	300	10	1.919	.1600	.340	None.	None.	8.25
116	250	56	1.919	.1600	.340	None.	None.	8.25
117	250	8	.640	.1278	.340	.546	None.	6.06
119	300	6	None.	.1000	.444	None.	.192	5.00
120a	200	16	None.	None.	.1225	None.	None.	5.35
120b	300	11	None.	None.	.1225	None.	None.	5.35
121	300	11	None.	.1000	.742	None.	f .192	5.21
122	300	11	1.215	.3200	None.	None.	None.	5.69
123	300	11	.92	.32	.70	None.	None.	5.26
125	300	4	3.84	.500	.340	None.	None.	5.00
127	350	4	1.21	.16	None.	None.	None.	5.69
128	350	4	k .50	None.	.500	None.	None.	2.85
132a	250	4	k .50	None.	.1225	None.	None.	4.96
132b	300	4+	k .50	None.	.1225	None.	None.	4.96
138	300	2	k 1.00	None.	.3691	None.	None.	4.88
139	350	2	k 1.00	None.	.3691	None.	None.	4.88

a A trace of copper formed.

b No copper observed.

c CaCl₂.d SO₂.

e HCl.

f FeCl₃.g Cu₂O.h CuCl₂ · 2H₂O.

i Measurable copper formed in most of the succeeding experiments.

j Fe₂(SO₄)₃.

k Metallic copper.

TABLE 9.—*Analysis of solid residues*

[All weights in grams]

Experiment No.	Temperature (°C.)	Duration of experiment (days)	Total copper	Sulphur	Copper equivalent to sulphur	Metallic copper
62	220	6	0.0659			A little.
101	200	6	.0946	0.0343	0.1360	
102	200	6		.0592	.2347	
104	250	5	.1461	.022	.0872	0.0589
108	200	2		.0151	.0600	Trace.
110	200	2		.0160		Trace.
112	200	4				Trace.
114	250	2	.1422	.0211	.0838	.0584
115b	200	4	.1977	.0225	.0894	.1083
115c	200	10	.2120	.0157	.0623	.1497
116	250	56	.1695	.0260	.1031	.0664
117	250	8	.1372	.0255	.1014	.0358
119	300	6	.0530	.0101	.0402	.0128
121	300	11	.0500	.0143		Present.
122	300	11	.3405	.054	.214	.126
123	300	11	.276	.0515	.208	.068
125	300	4	.5033	.626	.248	.255
127	350	4	.2590	.0087	.035	.224
128	350	4	.2920	.0347	.1376	°.1544
132a	250	4	°.0067	.0004	.0017	°.0050
132b	300	4	.473	.0065	.0258	.0447
138	300	2	.9054	.0147	.0582	.847

° 0.3456 reacted.

° Copper recrystallized with a little sulphide.

°. Copper recrystallized.

TABLE 10.—*Analysis of solutions*

[All weights in grams]

Experiment No.	Copper	Total SO ₄ ''	H ₂ SO ₄ by titration	H ₂ SO ₄ by calculation
101		0.0378		
102		.0033		0.0034
104	0.1308	.4092	0.2104	
109			°.0080	
113			.23	
114	.6622	1.436	.3629	.450
115b	.6867	1.498	.4682	.478
115c	.6475	1.526	.5134	.560
116	.7330	1.512	.3617	.417
117	.2387		.2862	
120a			.0932	
120b			.1125	
121	.0165	.8809	.729	
122	.4008	.7704	.144	.174
123	.3425	1.2878	.777	.786
125	1.391	2.604	.509	.50
° 127	.329	.775	.263	.29
° 128	.1810	.4013	.1051	.129
132a	.0069	.1138		
132b	.0225	.1005	.078	.070
138	.0896	.3180		

° SO₄'' only.

° Silica tube.

TABLE 11.—*Calculation of weights that reacted, based on preceding data*

[All weights in grams]

Experiment No.	CuSO ₄ in final solution ^a	CuSO ₄ that reacted	Cu ₂ S in residue	Cu ₂ S that reacted	SO ₄ '' combined with copper in solution	Balance of SO ₄ ''	Equivalent weight of H ₂ SO ₄	H ₂ SO ₄ formed
102	-----	-----	0.2941	0.0059	-----	0.0033	0.0034	0.0034
108	-----	-----	.0750	.0050	-----	-----	-----	-----
114	1.665	0.255	.1048	.0552	0.996	.441	.450	.110
115b	1.725	.195	.1118	.0482	1.030	.468	.478	.138
115c	1.020	.293	.0780	.0820	.975	.550	.560	.220
116	1.841	.078	.1291	.0309	1.103	.409	.417	.077
117	.5998	.0402	.1267	.0333	-----	-----	-----	-----
122	1.005	.210	.268	.052	.604	.167	.170	.170
123	.860	.099	.260	.060	.515	.773	.789	.089
125	3.50	.30	.311	.189	2.10	.51	.52	.180
127	.773	.442	.044	.116	.495	.28	.29	.29
128	b. 455	b. 455	b. 172	b. 172	.274	.127	.129	b. 38
132a	.0169	b. 0158	b. 0021	b. 0021	.0100	.104	.106	b. 017
132b	.0565	b. 0565	b. 0323	b. 0323	.0340	.068	.070	b. 053
138	.2251	-----	-----	-----	.1335	.1825	.1862	b. 183

^a Including Cu₂SO₄.^b Formed.^c That reacted.TABLE 12.—*Molecular ratios of reacting substances*

Milligram-molecules

Experiment No.	Temperature (°C.)	CuSO ₄	Cu ₂ S	Cu	H ₂ SO ₄
114	250	1.60	0.347	0.920	1.12
115b	300	1.22	.30	1.70	1.40
115c	300	1.84	.515	2.36	2.25
116	250	.489	.194	1.05	.79
117	250	.252	.209	.564	-----
122	300	1.31	.33	1.98	1.73
123	300	.62	.38	1.06	.91
125	300	1.88	1.19	4.01	1.84
127	350	2.77	.729	3.52	2.95
128	350	2.85	1.08	5.44	3.88
132b	300	.35	.20	.76	.54

Molecular ratios

114	250	4.6	1	2.7	3.2
115b	300	4.1	1	5.7	4.6
115c	300	3.57	1	4.58	4.38
116	250	2.5	1	5.4	4.07
117	250	1	1	3	-----
122	300	4.0	1	6.0	5.3
123	300	1.6	1	2.8	2.4
125	300	1.6	1	3.4	1.5
127	350	3.8	1	4.83	4.06
128	350	2.6	1	5.02	3.6
132b	300	1.7	1	3.5	2.7
Theory for reactions (36) or (17)	-----	3	1	5	4

TABLE 13.—*Solubility of cuprous chloride in calcium chloride solutions at 25° C.*

[Concentrations in per cent by weight]

Experiment No.	Specific gravity of solution	CaCl ₂	CuCl
153	1.04	3.33	0.438
152	1.12	9.75	1.934
149	1.17	13.48	3.698
151	1.30	19.84	8.503
150	1.48	25.55	19.71

TABLE 14.—*Reaction of CuCl on FeO in aqueous solution at 100° C.*

[All weights in grams]

	Volume (cubic centimeters)	Fe taken as FeO	Cu taken as CuCl	Cu precipitated	Fe dissolved
Experiment 159b.....	139	0.141	0.324	0.092	0.074
Experiment 159d.....	196	.141	.444	.090	.047
Experiment 159f.....	200	.141	.444	.087	.047
Theory for equation (71).....		.141	.107	.107	.047
Theory for equation (72).....		.141	.321	.321	.141
Theory for equation (73).....		.141	.080	.080	.035
Experiment 159c.....	144	.141	.111	.081	.040
Theory for equation (71).....		.141	.107	.107	.047
Theory for equation (72).....		.049	.111	.111	.049
Theory for equation (73).....		.141	.080	.080	.035
Experiment 159e.....	200	.282	.160	.155	.080
		.211			
Theory for equations (71), (72), and (73).....		.070	.160	.160	.070
		.281			
Experiment 159f.....	187	* None.	.444	* .009	

* Metallic copper taken in excess in place of FeO.

* Cu dissolved.

TABLE 15.—*Reaction of CuCl and FeCl₂ at 100° in solutions of regulated pH value*

[Final volume of solution, 200 cubic centimeters]

Experiment No.	NaCl (grams)	Normal CH ₃ COOH (cubic centimeters)	Normal CH ₃ COONa (cubic centimeters)	pH at 25° C.	0.504 M FeCl ₂ (cubic centimeters)	0.926 M CuCl (cubic centimeters)	Results
160a.....	2.20	20.0	20.0	4.5	1.7	4.8	No precipitate.
160b.....	1.97	16.0	24.0	4.7	1.7	4.8	Do.
160c.....	1.50	8.0	32.0	5.20	1.7	4.8	Very slight precipitate after some time.
160d.....	2.08	5.0	35.0	5.38	2.0	5.0	A faint cloud appeared in 2 minutes, a considerable film on glass in 2 hours with small crystals of Cu.
160e.....	1.08	3.2	36.8	5.62	2.0	5.0	Precipitation began at once and was too rapid for the formation of many recognizable crystals of Cu.
160f.....	.43	5.0	35.0	5.45	5.0	2.0	Precipitation fairly rapid.
160g.....	.43	8.0	32.0	5.23	5.0	2.0	Precipitation but no crystals of Cu seen.
160h.....	.43	10.0	30.0	5.08	5.0	2.0	Do.
160i.....	1.30	12.0	28.0	4.93	5.0	2.0	No Cu in 2 hours.
160j.....	2.17	5.0	35.0	5.38	5.0	2.0	Visible crystals of Cu on walls of flask in 2 hours.

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