XXXVII.—*The Interaction between Copper and Sulphuric Acid.*

By Cecil William Rogers.

The reactions which occur between copper and sulphuric acid have been investigated by Berzelius (" Traité de Chimie," IV, p. 324), Barruel (*J. Pharm.*, 1834, **20**, 13), Maumené (*Ann. Chim. Phys.*, 1846, **18**, 311), Calvert and Johnson (J., 1866, **19**, 438), Pickering (J., 1878, **33**, 122), Baskerville (*J. Amer. Chem. Soc.*, 1895, **17**, 904), van Deventer (*Chem. Centr.*, 1905, **1**, 992), and Sluiter (*ibid.*, p. 903).

Berzelius noticed that a black residue formed during the reaction, which could be oxidised by nitric acid, and was of the opinion that it was the sub-sulphate. He made no analyses of the substance. Barruel found that the action could take place at the ordinary temperature if sufficient time was allowed. He held that sulphur dioxide was first formed which attacked the copper with the formation of cuprous sulphide and cupric oxide, the latter then dissolving in the excess of acid to form the sulphate. He also made no analyses of the supposed sub-sulphide. Maumené suggested that more than one reaction proceeds at the same time, and introduced the idea of two primary reactions with a number of secondary reactions. One of these primary reactions led to the formation of sulphur dioxide and cupric sulphate; the other to the production of cuprous sulphide as one resultant, which, in consequence of the secondary reactions, became oxidised through the stages Cu_2S; $CuO,2Cu_2S$; $CuO,2CuS$; CuO,CuS; to CuO. Calvert and Johnson carried out a few experiments on the relative effect of concentrated and dilute acid at temperatures between 130° and 150°. They observed the formation of cuprous sulphide, which they considered was due to free sulphur combining with the metal. They made no analyses, but gave the following reasons for their opinions : (1) No hydrogen sulphide is evolved, (2) no sulphur is volatilised, (3) the analogy between this reaction and that of sulphuric acid upon tin.

Pickering carried out a thorough examination of the subject in all its aspects and concluded that there were two primary reactions and two secondary reactions, the latter being dependent on the second primary reaction. He gave the following equations :

A. *Primary Reactions.*

(1) $Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O$,

which was supposed to depend on the formation of nascent hydrogen.

(2) $5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O$.

B. *Secondary Reactions.*

(1) $Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O$.
(2) $CuS + 2H_2SO_4 = S + CuSO_4 + SO_2 + 2H_2O$.

He stated that the primary reactions may occur either alone or together; that the metal is attacked at all temperatures from 19° upwards, the extent of the action increasing with rise in temperature; that very little gas was observed below 130°, and none at all insoluble in water; and that a deposit of sulphur was formed in the neck of the vessel either before or after the complete dissolution of the metal. He showed that no hydrogen sulphide was evolved, and he was the first to point out that the black residue in the flask consisted solely of copper and sulphur in the proportions required by the formula Cu_2S. From his observation that the ratio of $Cu_2S/CuSO_4$, expressed in terms of the copper content, decreased with diminishing temperature, and that the maximum ratio obtainable in the case of the second primary reaction was 2 : 3, he attempted to ascertain the temperature at which this reaction should go on alone. In this he was not successful, although approximations were obtained with the concentrated acid at 80° and with dilute acid at 130°. In no case was a ratio greater than 2 : 3 observed. He gave a number of reasons to show that the sulphide could not be formed either by the action of nascent hydrogen, hydrogen sulphide, or by the direct action of free sulphur on the metal.

Baskerville also carried out a series of experiments in which most of his work was in accord with that of Pickering. He gave the same equations, but differed in the detail of the operation of the primary reactions. He held that the first primary reaction predominates at all temperatures between 0° and 270° and that the proportion of material conforming to the second primary reaction increases from 0° to 100°, and then decreases from 100° to 270°. Below 100°, the primary reactions alone take place, the secondary reactions becoming evident at the higher temperatures with prolonged action, although even then, with short time, evidence of the operation of only the primary reactions was found.

It is to be noticed that neither Pickering nor Baskerville took any account of the sulphur formed during the reactions beyond recording its formation and tracing its origin to the decomposition of the sulphides. They ignored altogether the possible influence it might have had on the results of their experiments, especially at the higher temperatures. Both are agreed that two primary reactions take place. The present work was undertaken to examine this question of two primary reactions, to discover reasons for the different views expressed upon their influence at various temper atures, and to ascertain the effect, if any, of the liberated sulphur upon the final result of the action.

EXPERIMENTAL.

The purest electrolytic copper foil obtainable and concentrated sulphuric acid (A.R.) were used. The foil was cut into pieces 3 × 1·6 cm., one piece only being used in each experiment.

The apparatus consisted of a reaction tube, about 6 inches long, furnished with two tapped side tubes for the admission of an inert gas and the removal of the gaseous products, and a ground glass stopper from which the copper was suspended on a fine glass thread. Sufficient acid was employed to cover the metal completely when in the tube, the acid being maintained at the required temperature by means of a suitable bath for at least $\frac{1}{2}$ hour before the introduction of the metal. A current of purified carbon dioxide was passed through the tube throughout an experiment, this creating an inert atmosphere, effectively removing the gaseous products, and keeping the surface of the metal fairly clean. The sulphur dioxide evolved, which was the only gaseous product of the reactions, was absorbed either by iodine or potassium permanganate. The amount of copper used was found by weighing the strip before and after an experiment, and the copper as sulphate was estimated as cupric oxide.

The Completed Action.—It is stated that at 270° the reaction represented by the equation

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O$$

proceeds alone. A series of experiments carried out at 270° furnished evidence which, while supporting the above equation in so far as the final result is concerned, showed that this is not the only action which occurs. The complete conversion of the metal into the sulphate takes place within a few seconds of the introduction of the metal, and the gas is evolved with such rapidity that the copper is carried to the upper portion of the acid. Further, before the flood of gas commences, there is an appreciable interval, during which the surface of the metal becomes covered with a black deposit. This deposit is practically entirely acted upon at the conclusion of the experiment except for such very small particles as are carried out of the liquid by the upward rush of gas and deposited on the sides of the reaction vessel. The acid itself quickly assumes a blue colour and white crystals may be observed to fall continuously from the surface of the metal. The crystalline deposit at this temperature is always quite white and free from the grey tints found in that formed at lower temperatures. On examination under the microscope it is found to consist of a large number of imperfectly formed crystals together with a few tabular crystals, the whole being characteristic of anhydrous copper sulphate when crystallised from the concentrated acid at the same temperature. The examination of the crystalline deposits obtained at different temperatures will be dealt with in a later section. The following results are typical of those obtained at this temperature :

No.	Cu used.	SO_2 found.	Cu as $CuSO_4$.	Cu as sulphide.	Sulphur.	Acid.
1	0·2692	0·2618	—	Trace	Trace	Slightly brown
2	0·4649	0·4333	—	,,	,,	Brown
3	0·4450	0·4208	—	,,	,,	Slightly brown
4	0·4920	0·4841	0·4820	,,	,,	,, ,,
5	0·4929	0·5016	0·4631	,,	,,	Red
6	0·5012	0·5126	—	None	None	Colourless

The sulphur dioxide was estimated by absorption in iodine solution and titration of the excess iodine by thiosulphate. The low values for the copper sulphate are due to the fact that the anhydrous salt was filtered off before analysis, the 2—3% of copper which remained in solution thereby being left out of account. That copper still remains dissolved in the acid may be shown by the addition of a saturated solution of potassium bromide, when a dark, amorphous precipitate of the anhydrous bromide is thrown down. The excess of sulphur dioxide in experiments (5) and (6) is probably due to the dissociation of the acid itself; both experiments were prolonged for some time after the action had ceased. The lower values in some of the other cases are due to incomplete collection of the total sulphur dioxide owing to the closure of the experiments within a few seconds of the cessation of the reaction.

An interesting point arises in connexion with experiment (5). After the action had ceased, the reaction tube and its contents were allowed to cool slowly during several hours, and the acid liquid was then bright red. The crystalline deposit was quite normal when viewed under the microscope, and the abnormal colour may be ascribed, perhaps, to the colloidal condition of traces of sulphur remaining in solution. This suggestion is supported by the fact that after several weeks the acid deposited a small quantity of sulphur and became brown; the sulphur redissolved on shaking, producing a reddish-brown solution. All attempts to reproduce this effect met with failure.

Since traces of both sulphur and sulphide were met with at 270°, the reaction temperature was raised, but in the majority of cases both persisted. This circumstance, together with the darkening of the metallic surface before the evolution of gas commences, points to the conclusion that the simple equation is not sufficient to explain the action even at this high temperature, and that the formation of sulphide and the subsequent liberation of sulphur are probably steps in the series of reactions involved.

The Black Deposit.—The black deposit was therefore carefully investigated. Trial experiments showed that it is produced most abundantly between 100° and 130°. The material for examination was prepared by immersing a large piece of the metal in the acid, a current of carbon dioxide being passed continuously. When the metal became coated, it was removed and at once plunged into thoroughly boiled water, beneath which the deposit was removed. The metal, after thorough cleansing and drying, was then returned to the acid, these operations being repeated until sufficient material had accumulated. Although the temperature range is most favourable to the rapid formation of the sulphidic matter, it also happens that the acid reacts with it fairly quickly, so that the actual amount of material collected is comparatively small. At lower temperatures, the rate of reaction is too slow for the rapid collection of the sulphidic matter.

The deposit was transferred from the water to a small platinum funnel, thoroughly washed with boiled water, dried, and weighed. Any sulphur present was extracted with carbon disulphide. The material was then treated with hot, concentrated nitric acid until no further action took place, the residual sulphur being weighed. The sulphur was removed by ignition from the funnel, which was weighed once more as a check. The copper and the oxidised sulphur in the filtrate from the nitric acid treatment were then estimated as cupric oxide and barium sulphate, respectively.

A large number of analyses of this type were carried out, and in every case the total percentage of copper and sulphur was about 100. There can be little doubt that the black residue consists entirely of copper and sulphur. The ratio of copper to sulphur, however, varied considerably, even in specimens collected from the same piece of metal and the same acid for different analyses; but the proportions always exhibited values between those required for cuprous sulphide and cupric sulphide, being nearer to the former than to the latter. It appears, therefore, that the first product is cuprous sulphide, which is then decomposed partly into cupric sulphide. The following table shows results obtained by the method of analysis given above :

Temp.	Cu %.	S %.	Total %.
100°	78·72	21·49	100·21
110	75·44	25·32	100·76
110	77·43	22·11	99·54
120—125	72·54	30·36	103·20
125	73·77	25·67	99·44
132	78·29	21·56	99·85

Cu_2S requires Cu, 79·86; S, 20·14% and CuS requires Cu, 66·48; S, 33·52%. No oxysulphides were obtained in any of these experiments.

The Secondary Reactions.—Experiments were then carried out with the two sulphides prepared by ordinary laboratory methods with the object of ascertaining the mode of decomposition of these substances in contact with the concentrated acid. Cupric sulphide was allowed to react with the acid at the required temperature until all had disappeared. The sulphur dioxide evolved was absorbed by iodine solution. A current of carbon dioxide was passed to assist in the removal of the sulphur dioxide, and to provide an inert atmosphere. The crystalline deposit was examined microscopically and found to be characteristic of cupric sulphate, and to contain inclusions of undecomposed sulphide. For the estimation of the copper, both the crystalline deposit and the acid liquid were taken, since some sulphate remained in solution. The sulphur dioxide evolved was, in general, in excess of that required by the equation given below, the excess increasing up to a definite maximum with rise in temperature and with the duration of the experiment. This can only have been due to the sulphur set free during the reaction, some of which reacted with the acid, while some was volatilised and condensed in pale yellow crystals of the β-form on the cooler parts of the reaction tube. The volatile material, on being heated on a microscope slide covered by a small glass dome, underwent all the changes characteristic of the effect of heat on sulphur. Small portions heated with free access of air gave the unmistakable odour of sulphur dioxide and reduced potassium dichromate. From the data given in the table below, it is evident that the cupric sulphide reacts with the acid according to the equation.

$$CuS + 2H_2SO_4 = SO_2 + CuSO_4 + S + 2H_2O,$$

and that the sulphur reacts with more acid:

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

Temp.	CuS used.	CuO as $CuSO_4$.	SO_2 found.
100°	1·486 g.	1·225 g.	1·152 g.
110	2·465	1·975	1·763
120	2·613	2·142	2·435
130	1·753	1·449	1·861
140	3·792	3·097	3·471
160	1·937	1·595	3·912 (prolonged action)
170	1·642	1·348	3·536 ,, ,,

That cuprous sulphide reacts with sulphuric acid to produce cupric sulphide was established by the change of composition of the black sulphide after immersion in the acid for various periods, the acid being diluted considerably to stop the action. Sulphur invariably made its appearance after a time. The experiments were made in pairs at different temperatures, one of each pair being stopped after a short time, the other carried on for some considerable time, especially at the lower temperatures, the rate of reaction being very slow. The original composition of the black sulphide was 79·81% Cu, 20·58% S in the two experiments at 60° and 79·82% Cu, 20·10% S in the others. The final compositions were :

Temp.	60°.	80°.	100°.	120°.	160°.
% Cu	75·71; 72·23	74·55; 69·64	76·82; 68·92	74·73; 68·51	76·22; 70·61
% S	24·18; 27·72	24·86; 30·02	22·81; 30·82	25·60; 30·72	23·51; 28·64

Sulphur dioxide was evolved continuously, but quantitative measurements were not made. Where a crystalline deposit was obtained, this was examined microscopically and found to be cupric sulphate. It thus appears that the cuprous sulphide decomposes into cupric sulphide with the simultaneous formation of cupric sulphate and sulphur dioxide according to the equation

$$Cu_2S + 2H_2SO_4 = CuS + CuSO_4 + SO_2 + 2H_2O,$$

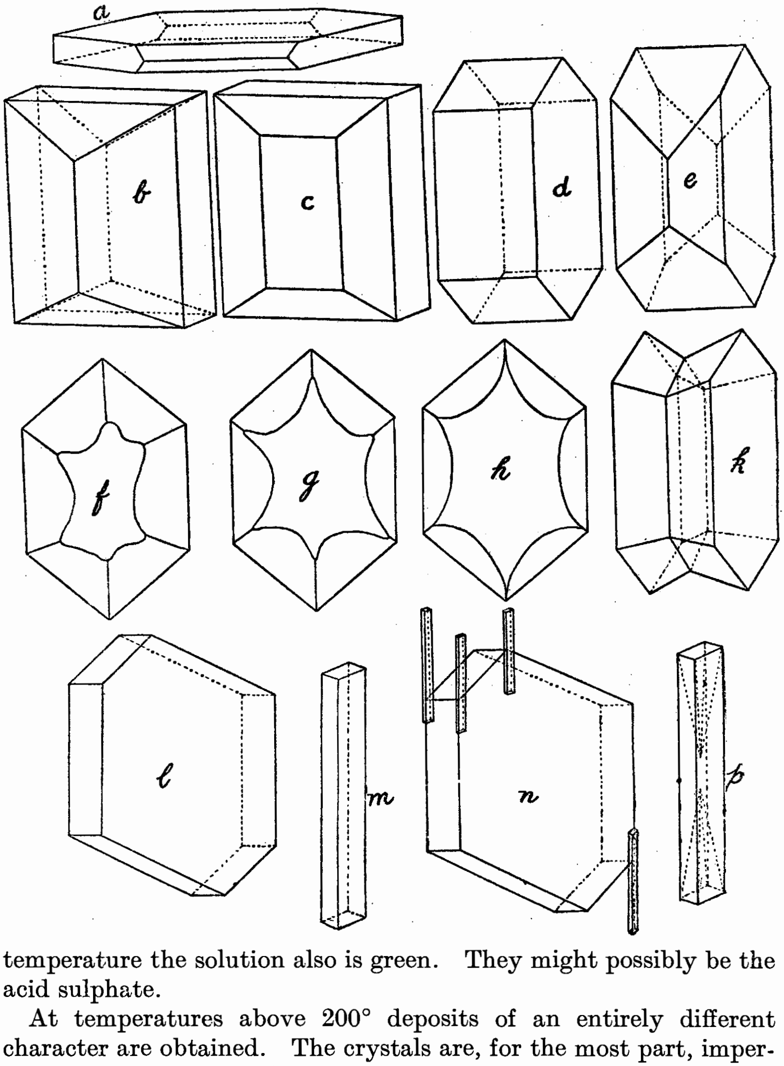
and that the cupric sulphide so formed then reacts with the acid in the manner already described.

The Crystalline Deposit.—This has been stated by previous investigators to be anhydrous cupric sulphate, but as no means of identification were given, and owing to the possibility of the hydrolysis of a more complex substance on the addition of water, and the varying nature of some of the results obtained, it was thought necessary to examine the substance further. For this purpose the microscope was employed.

Except when prepared at the higher temperatures, above 200°, and even then, only when kept at this temperature for some time, under which conditions the substance is fairly soluble, producing a green solution, the deposit is never white; it is generally of a dingy grey appearance. This is due to the fact that it contains a quantity of the two sulphides, the particles of which have served as nuclei round which the crystals have formed, thus protecting them from further attack by the acid. If such a deposit be treated with acid at a temperature higher than that at which it was formed, some of the crystals will dissolve, and the sulphides thus liberated will react with the acid in the usual manner. The employment of sufficient acid to dissolve the whole of the deposit results in the formation of a perfectly white, sulphide-free product on cooling.

At temperatures up to about 200° the crystalline deposit consists almost entirely of crystals belonging to the rhombic system, being combinations of the pinacoids, prism, and macrodome. Typical crystals are shown in the diagram (types a, b, c, d, and e). These are transparent and colourless, and frequently contain inclusions of sulphide. Twinning is not of common occurrence except in the case of type a. There are, in addition to these rhombic crystals, others which appear to be monoclinic, are green, grouped, few in number, and are formed chiefly at 130° and above, at which temperature the solution also is green. They might possibly be the acid sulphate.

FIG. 1.



At temperatures above 200° deposits of an entirely different character are obtained. The crystals are, for the most part, imperfectly developed, and of the rhombic crystals, only those of type d reach full development. Types a, b, c, and e are absent. Various intermediate stages in the growth of type d may be found in abundance, the earlier stages being represented by crystals with one fully developed hexagonal face, partial development of the corresponding parallel face, growth being greatest in the regions opposite to the angles of the hexagon, these faces being united by six inclined planes (types f, g, h). Continued growth of the irregular face leads ultimately to the formation of a hexagonal face corresponding to that originally present, the two being now united by twelve inclined planes and presenting the appearance of k. Subsequent growth fills up the hollows to produce the perfect crystal. The mode of formation appears to resemble that of the crystals of the alkali halides. In addition to these imperfect forms, there are a large number of monoclinic crystals, tabular parallel to the ortho axis (1). These are well developed. On cooling the solution obtained at these temperatures, no further deposition of rhombic crystals takes place; instead, long slender prisms make their appearance below about 180° (m). The prisms grow either on the monoclinic crystals just mentioned, or singly, or, occasionally, in groups. They appear to belong to the triclinic system, although their arrangement parallel to the orthopinacoid when growing on the monoclinic plates suggests that they also might be monoclinic (n). Many of them are hollowed out from the position of the basal pinacoid faces inwards, presenting the appearance of p. Copper sulphate pentahydrate, specially prepared for the purpose, was dehydrated either by heat, or by immersion in concentrated sulphuric acid for some days. The anhydrous substance, prepared in either manner, in solution in the concentrated acid below 180°, deposits nothing but the prismatic crystals previously mentioned. If, however, the solution is prepared at, say, 160°, so that it will become saturated at a considerably lower temperature, and is then set aside out of contact with moisture, nothing deposits from it for some time, but when crystallisation does set in, the rhombic crystals are formed to the exclusion of the long, slender prisms. This process may require two or more days for its completion.

At temperatures above 200° the crystals obtained showed all the characteristics of those prepared by the action of the acid on the metal. It was found, further, that neither carbon dioxide nor sulphur dioxide exerted any influence on the type of crystal developed at any temperature, and that no sulphur dioxide was evolved on heating the crystals with the acid. There can be little doubt, therefore, that the crystalline deposit obtained by heating the acid with the metal is anhydrous cupric sulphate; moreover, it appears that the anhydrous salt is at least dimorphous, and possibly trimorphous.

The Primary Reaction.—Both Pickering and Baskerville were agreed that two primary reactions take place. It would seem rather unusual, however, for two substances to react in two totally different ways at the same temperature unless one of them be metameric. Of the reactants concerned, the acid is the only one which could fulfil this condition, and there is no evidence to show that it does actually exist in more than one form. Hence it is to be expected that only one primary reaction could take place. Further, both Pickering and Baskerville state that below 130° the evolution of gas is very slow, and that only at this temperature do bubbles of gas make their appearance. If the acid acted on the metal directly with the production of sulphur dioxide, it would be expected that bubbles of gas would be observable with ease at much lower temperatures, as in the case of zinc with dilute sulphuric acid. Even if the zinc and the acid be highly purified, the bubbles may be readily detected, although the action is slow. This again points to the possibility that the gas does not arise from the direct action of the acid on the metal, and that two primary reactions do not, in fact, take place.

If a piece of the purest electrolytic copper foil be totally immersed in the concentrated acid which has been heated to, and maintained at, a given temperature in an atmosphere of carbon dioxide for about $\frac{1}{2}$ hour before the introduction of the metal, the following observations may be made :

At 50°. The first visible product of the interaction is a film on the metal, of a brownish hue, the formation of which is indicated by the loss of lustre of the metallic surface. This film gradually leaves the surface of the copper, the whole of which it covers, and it is then seen to be of almost the same shade as the metal itself. It remains suspended in the acid, being slowly moved about by the convection currents, and may be observed to change its colour to yellow and then to disappear—dissolve in the acid—colouring the latter yellow also. After this cycle of changes has proceeded for some time the acid becomes opalescent. No gas bubbles can be observed on the surface of the metal, yet sulphur dioxide is undoubtedly formed after a time.

At 50—120°. On increasing the initial temperature the formation of the brown material takes place with increasing rapidity, as also the conversion of this into the yellow substance. No gas bubbles can yet be observed.

At 130—140°. At about 130° the same phenomena occur with great rapidity, and at the same time bubbles of gas make their appearance; but no bubbles are formed until a deposition of the film has taken place. The particles constituting the film at this temperature soon coalesce, the material then appearing black and forming a coating on the metal. The acid darkens owing to the suspended sulphide, but if the metal be removed it rapidly becomes clear again. Sulphur is deposited on the cooler parts of the apparatus.

The initial formation of the brown film could still be detected at temperatures above 140°. In every case there was an appreciable interval between the immersion of the metal and the appearance of the gas bubbles, which were never formed until the black sulphide had been produced. Hence the formation of sulphur dioxide is probably not due to the direct action between the acid and the metal. Support for this contention is found in the results of the following experiments.

A single piece of foil was totally immersed in the concentrated acid contained in one of the reaction tubes, the exit tube from which was connected by a series of T-pieces to absorption tubes in such a manner that any one of the latter could be put into communication with the reaction vessel directly, the change from one to another being made with the utmost facility. A current of carbon dioxide was passed throughout each experiment, the acid being heated to, and maintained at the required temperature for at least $\frac{1}{2}$ hour before the introduction of the metal. The sulphur dioxide evolved was absorbed in potassium permanganate.

Experiment 1. *At* 50°. Twenty c.c. of $N/50$-potassium permanganate were placed in each of three absorption tubes, each being connected in turn to the reaction vessel. Upon the removal of each tube 25 c.c. of 0·918 $N/50$-oxalic acid were added to its contents, and the volume of permanganate solution required for the titration of the excess of oxalic acid was measured. In all these experiments the reagents were delivered from over the same range of the burettes employed, this ensuring uniformity in the quantities of liquids taken. By blank tests it was found that 4·8 c.c. of the permanganate solution were required to titrate the excess of oxalic acid. The following results were obtained :

1. Removed after the expt. had proceeded for 5 mins. .... 4·8 c.c.
2. ,, ,, ,, ,, ,, 17 ,, ... 4·7 ,,
3. ,, ,, ,, ,, ,, 30 ,, ... 4·9 ,,

No film had yet formed.

Experiment 2. *At* 60°. The same piece of copper was employed with fresh acid, the remaining details conforming to those of Experiment 1.

1. Removed after the expt. had proceeded for 5 mins. .... 4·8 c.c.
2. ,, ,, ,, ,, ,, 19 ,, ... 4·9 ,,

The film had formed and was about to leave the surface of the copper.

Experiment 3. *At* 50°. The same piece of copper was used with fresh acid.

1. Removed after the expt. had proceeded for 5 mins. .... 4·8 c.c.
2. „ „ „ „ „ 50 „ .... 4·9 „

The film had just made its appearance.

3. Removed after the expt. had proceeded for 70 mins. .... 4·9 c.c.
4. „ „ „ „ „ 100 „ .... 5·0 „

These experiments, and others carried out in a similar manner, clearly indicated that the sulphur dioxide is not produced before the formation of the sulphide, but that after the formation of the latter the liberation of the gas commences. The varying time interval between the immersion of the metal and the appearance of the film is probably due to the nature of the metallic surface.

In order to test the above experiments and to gain additional evidence, another series was carried out with the solutions of permanganate and oxalic acid diluted to *N*/200, so that the oxalic acid became 0·918 *N*/200. The titrations were carried out in Nessler cylinders, the end-points being judged by comparison with similar cylinders containing known amounts of permanganate. By blank tests, it was found that 20 c.c. of permanganate with 25 c.c. of oxalic acid required 5·0 c.c. of permanganate to titrate the excess of oxalic acid.

Experiment 1. *At* 60°.

1. Removed after the acid had been heated for 45 minutes before the addition of the copper .... 5·0 c.c.
2. Removed 10 minutes after the addition of the copper .... 4·9 „
3. „ 36 „ „ „ „ „ .... 5·2 „

Film formation first observed at this point.

4. Copper removed after 90 minutes' contact with the acid and the $KMnO_4$ allowed to absorb the SO_2 during a further 60 minutes at the same temperature .... 11·05 „

Experiment 2. *At* 85°. Same piece of copper used with fresh acid.

1. Removed after the acid had been heated for 30 minutes before the addition of the copper .... 5·0 c.c.
2. Removed 12 minutes after the addition of the copper .... 4·8 „
3. „ 20 „ „ „ „ „ .... 4·8 „

First indication of film formation.

4. Copper removed after 45 minutes' immersion, the $KMnO_4$ being allowed to absorb the total SO_2 during a period of 2 days (30 c.c. of $KMnO_4$ and 20 c.c. of oxalic acid being used in this case) .... 7·2 „

These experiments again show that no sulphur dioxide is derived from the action before the film of sulphide has been formed, that no sulphur dioxide is derived from the acid itself at this temperature, and that the production of sulphur dioxide commences after the sulphide has formed.

There is, therefore, no justification for asserting that two primary reactions occur. For, if the first primary reaction of Pickering and Baskerville predominated at all temperatures, sulphur dioxide would be expected before the formation of the film, and if the second primary reaction took precedence, as asserted by Baskerville at the particular temperature of these experiments, no change should be observable in the sulphide film, and the gas evolved should first appear on the surface of the metal.

There is only one primary reaction, that one producing cuprous sulphide and cupric sulphate irrespective of the temperature at which the experiment is carried out, the sulphide then decomposing in the usual manner. The formation of the sulphur dioxide is thus dependent on the secondary reactions between the acid, the sulphides and the sulphur, the quantity actually formed being governed by the extent of occlusion of the sulphides by the sulphate, and the volatility of the sulphur in addition to the time and concentration factors.

The following experiments were made with the object of ascertaining the total production of sulphur dioxide at different temperatures, its amount being also expressed as a percentage of that theoretically obtainable from the simple equation

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O.$$

The experiments were prolonged until all the sulphides had disappeared, and the sulphur had either reacted, volatilised, or remained practically inactive, and all the sulphur dioxide had been collected :

Temp.	Cu used.	SO_2 found.	Per cent.	Temp.	Cu used.	SO_2 found.	Per cent.
50°	0·0013	0·0009	69	140°	0·2146	0·1853	86
50	0·0011	0·0006	55	180	0·3621	0·3317	91
85	0·0052	0·0025	50	200	0·3165	0·2849	90
100	0·0131	0·0075	57	270	0·4920	0·4841	98
110	0·0163	0·0124	76	270	0·4450	0·4208	95
120	0·0251	0·0213	85				

It is clear that the percentage of sulphur dioxide increases with increase of temperature. So also does the rate of reaction between the sulphides, the sulphur, and the acid, so that these substances have less chance of being occluded or volatilised. As the temperature increases, they are acted upon more and more rapidly until, in the region of 270°, they are removed practically as fast as they are formed. It is also evident that below 100° the sulphur must react with the acid very slowly, in fact it is sometimes possible to find quite large particles present in the liquid after several days. If the quantity of acid employed be sufficiently large to dissolve the whole of the sulphate produced, thus preventing occlusion, and the time of the experiment be prolonged, there seems no reason, other than the volatility of the sulphur, why results closely agreeing with the simple equation should not be obtained at any temperature at which appreciable action between the substances concerned takes place. In particular, over the range 130—200°, the sulphur is volatilised to an extent sufficient to allow its weight to be determined. The continuous removal of the sulphide makes impossible the direct determination of the quantitative relationships of the first reaction, but if an experiment be stopped at any point, and the cuprous sulphide and the sulphur dioxide be estimated, it is possible to obtain approximate values. From the consideration of the secondary reactions, it is known that 40% of the sulphur dioxide evolved in the completed reactions is due to the decomposition of the sulphides. If the corresponding amount of cuprous sulphide be calculated and this result be added to the sulphide actually found, the total must represent that portion of the copper which has either passed, or is passing through, the sulphide stage. The difference between this figure and the total copper used gives the amount of metal which would have been found as sulphate had no sulphide been decomposed. The ratio of copper as cuprous sulphide to copper as cupric sulphate then determines the action.

The following table shows the results of a number of experiments calculated in this manner :

Temp.	Cu used.	Cu as Cu_2S.	SO_2.	Cu as Cu_2S =40% of SO_2.	Total Cu as Cu_2S =*A*.	Residual Cu as $CuSO_4$ =*B*.	Ratio *A*/*B*.
16°	0·1176	0·0113	0·0513	0·0205	0·0318	0·0858	2/5·4
80	0·0280	0·0013	0·0215	0·0086	0·0099	0·0181	2/3·7
80—90	0·0235	0·0005	0·0216	0·0086	0·0091	0·0144	2/3·2
100	0·0135	0·0016	0·0092	0·0037	0·0053	0·0082	2/3·1
100	0·0417	0·0120	0·0084	0·0034	0·0154	0·0263	2/3·4
120	0·0431	0·0085	0·0200	0·0080	0·0165	0·0266	2/3·2
140	0·0526	0·0079	0·0288	0·0115	0·0194	0·0332	2/3·4
160	0·2167	0·0217	0·1473	0·0589	0·0806	0·1361	2/3·4
170	0·2483	0·0198	0·1926	0·0771	0·0969	0·1514	2/3·1
190	0·2936	0·0176	0·2387	0·0995	0·1131	0·1805	2/3·2
200	0·3137	0·0157	0·2585	0·1034	0·1191	0·1946	2/3·3
240	0·4361	0·0087	0·3972	0·1589	0·1676	0·2685	2/3·2

Making allowance for the comparative inactivity of the sulphur at 16° and for the volatilisation of the sulphur at the higher temperatures, both of which tend to lower the ratio, it is clear that the value of Cu as Cuprous Sulphide/Cu as Cupric Sulphate approximates to 2/3. This is satisfied by the following equation :

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O,$$

which is the second primary reaction of Pickering and Baskerville. If this equation be added to those given for the secondary reactions, the simple equation—the first primary of Pickering and Baskerville —is obtained.

It will now be evident why it was considered that one of the primary reactions proceeded alone at 270°. The various actions succeed one another so rapidly that there is little chance of any sulphide or sulphur escaping. Hence the quantity of sulphur dioxide evolved agrees closely with that required theoretically. Pickering's failure to determine the temperature at which his second primary reaction took place exclusively is also explained. It proceeds alone momentarily only, for as soon as a film of cuprous sulphide is formed it begins to react with the acid. The obstructive properties attributed to the compact deposit of sulphide on the surface of the metal are due not so much to the sulphide itself as to the layer of inert sulphate with which it soon becomes covered when the acid is saturated; for, if a further quantity of acid be added so as to reduce the concentration of the sulphate, and thereby allow some of that on the metal to dissolve, the action at once becomes vigorous again.

Summary.

It is shown by these experiments that :

1. There is only one primary reaction.

2. The sulphur produced exercises a considerable influence on the final results of the reaction, very much more than has been ascribed to it hitherto.

3. The white crystalline deposit is undoubtedly anhydrous cupric sulphate, and this substance is at least dimorphous.

4. At any temperature the completed reaction may be represented by the simple equation

$$Cu + 2H_2SO_4 = SO_2 + CuSO_4 + 2H_2O,$$

which is the sum of the equations

$$\begin{aligned} 5Cu + 4H_2SO_4 &= Cu_2S + 3CuSO_4 + 4H_2O, \\ Cu_2S + 2H_2SO_4 &= CuS + CuSO_4 + 2H_2O + SO_2, \\ CuS + 2H_2SO_4 &= CuSO_4 + 2H_2O + SO_2 + S, \\ S + 2H_2SO_4 &= 2H_2O + 3SO_2, \end{aligned}$$

these representing the actual sequence of events, and which, in suitable combination, will yield an equation expressing the stage attained by the reactants at any particular moment during an interaction.

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