metric standard in the neighborhood of 25° was investigated.

2. The melting point of purified diphenyl-methane was determined to be 25.09 ± 0.01°. Seven junction thermels were used.

3. A spontaneous decomposition occurs, which is accelerated by the presence of light, and which causes lowering of the melting point over a period of time.

[Contribution from the Chemical Laboratories of New York University]

The Reaction of Zinc with Copper Sulfate in Aqueous Solution

By F. W. van Straten[1] and W. F. Ehret

Although it has long been known[2] that the reaction of zinc with copper sulfate solution is not one of simple displacement, many authors in modern scientific literature still retain the idea that only metallic copper is produced along with zinc sulfate. At the outset of this investigation, sufficient work had been done by others to permit the generalization that in displacement reactions the deposit of the more noble metal is rich in base metal if these metals show a tendency to form compounds when cooled from the melt.[3] That the deposits formed by the action of zinc on copper sulfate were heterogeneous had been noted, particularly by Galecki and Tomaszewski,[4] who studied the variation in their coherence, color, and composition with change in concentration and acidity of the copper ion solution.

In the present work it was hoped that a systematic study of the variation in composition of such deposits with the conditions prevailing during their formation would permit postulating a mechanism for the reactions—particularly since this study involved, in addition to the determination of the over-all chemical composition, an X-ray investigation of the solid phases formed.

Experimental

Materials and Apparatus.—The copper sulfate used was Kahlbaum "pro analyse"; the zinc sulfate, Merck reagent.

The zinc was Baker zinc metal, for standardization. The zinc strips were first washed, rinsed, and then rubbed dry with towels. Next, they were annealed by placing in a glass tube which was evacuated and heated to 200°.

The cooling was fairly rapid and vacuum was maintained until the strips reached room temperature. The thickness of each strip was approximately 0.3 mm., which was sufficient to lend rigidity to the metal without introducing end effects by reaction along the sides. In order to prevent reaction on both sides of the strip, one side was covered with spar varnish. Immediately before a run was made, the four strips of zinc necessary to make the run were immersed for thirty seconds in an etching reagent made by mixing 144 ml. of hydrogen peroxide (3%), 24 ml. of concd. ammonium hydroxide, and 144 ml. of distilled water. After rinsing a few times with water, the strips were ready for the run.

A brass stirrer was constructed as shown in Fig. 1a. It was hollow and able to pump liquid from the bottom of the vessel as well as provide efficient turbulent stirring. Cavitation was prevented by insertion of two copper baffles in the solution studied. Both the stirrer and baffles were varnished to prevent reaction with the solution. The latter always had a volume of 1 liter and was contained in a 1-liter beaker immersed in a thermostat. The temperature regulation was to ±0.01° at 25° and to ±0.02° at the higher temperatures. The stirring speed was controlled to ±3 r. p. m.

The zinc strips (four) were attached to a glass cage (Fig. 1b) by cutting them slightly longer than required and folding the extra length, top and bottom, around the horizontal supports of the cage. The effective area of the exposed surface of each zinc strip was 9.6 by 1.25 cm. The long arms of the cage could be inserted in appropriate slots along the bearing of the rotor so that the cage was coaxial with the rotor and could be raised out of the solution being stirred until the latter acquired the proper temperature and until the stirrer was rotating at the required speed. At such time as everything was ready for the run, the cage with the zinc strips could be lowered rapidly into the solution. A stop at the top of one of the long arms of the cage enabled the experimenter, in one operation, to raise, swing, and lower the shaft of the rotor supporting the cage into a beaker of water, permitting the reaction to be stopped almost instantaneously and providing also for the rinsing of the deposit. The strips were placed on the cage with the varnished sides away from the rotor and so that the reacting surfaces were equidistant from the center of the shaft. The duration of all reactions, unless otherwise noted, was one minute at 25°, one-half minute at 50°, and one-fourth minute at 75°.

(1) From a thesis submitted by F. W. van Straten in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University.

(2) Wetzlar, *Schweigger's J.*, **50**, 98 (1827); Fischer, "Verhältnis der chemischen Verwandschaft zur galvanischen Elektrizität," Berlin, 1830; Odling, *J. Chem. Soc.*, **9**, 289 (1857); Raoult, *Compt. rend.*, **76**, 156 (1873); Mylius and Fromm, *Ber.*, **27**, 630 (1894); Kutzelnigg, *Z. Elektrochem.*, **38**, 154 (1932).

(3) Tammann, *Nachr. Ges. Wiss. Göttingen*, 332 (1918).

(4) Galecki and Tomaszewski, *Roczniki Chem.*, **10**, 601 (1930).

X-rays were generated by means of a copper target in a Seemann-type tube, using nickel filters. Three Bohlin-type focusing cameras, made according to the specifications of Phragmén and reported by Westgren,[5] were used in connection with the usual powder technique of crystal analysis. The photograms obtained from the deposits were compared with those of known brasses prepared in the manner described elsewhere.[6]

Chemical Analysis.—The chemical analyses of the deposits were made according to a method already outlined.[6] In brief, the method consisted in the removal of the deposit from the zinc strips with a rubber brush, the strips having been rinsed previously with water for one minute, alcohol for ten seconds, and dried for one-half hour. Two samples of about 20–30 mg. were removed and weighed in a goose-neck weighing flask. The deposit was dissolved by the addition of 1.5 ml. of concd. nitric acid and 2 ml. of concd. sulfuric acid. The flasks were then transferred to a crucible furnace, heated to 400°, and kept at that temperature until all traces of sulfuric acid were removed. After cooling, the flasks were again weighed, the contents dissolved in distilled water, and analyzed for copper iodimetrically.

This procedure yields the following information directly: the weight of sample, the weight of combined zinc and copper sulfates, and the weight of copper. The weight of copper sulfate present after evaporation with sulfuric acid is calculated from the weight of copper, and the difference between this value and the weight of mixed sulfates corresponds to the weight of zinc sulfate. From this figure, the weight of zinc may be found.

Every sample of deposit included, in addition to the metals copper and zinc or their alloys, compounds of these with oxygen, hydrogen, and, or, sulfate. The non-metallic portion could not be determined directly by the method of analysis since it was destroyed by the action of the acids used in the solution of the deposits. However, the quantity of these materials could be found indirectly, since the combined weight of copper and zinc was less than that of the deposit by the amount of these radicals originally present. At 25°, this amounted to about 6% of the deposit. At higher temperatures, the value increased to about 9%.

The exact constitution of the compounds of copper and zinc present defied the authors' attempts at complete analysis. This material might consist of one or more or possibly all of the following compounds: cupric and cuprous oxides, zinc oxide, cupric hydroxide, zinc hydroxide, basic salts of copper and zinc, varying degrees of water of hydration, adsorbed water, and adsorbed hydrogen. A serious attempt was made to estimate some of these materials as present in a deposit obtained from a particular run in order to be able to interpret properly subsequent analyses.

The deposit from a representative run containing 6.2% of non-metallic constituents was heated to 230° in a nitrogen atmosphere to determine the amount of adsorbed gas, water and water of hydration (item 2 in Table I). A subsequent heating to the same temperature in a hydrogen

Fig. 1a.—Pump and   Fig. 1b.—Glass cage.
    stirrer.

atmosphere effected a reduction of the oxides of copper without reducing zinc oxide. The loss in weight due to the removal of oxygen from the oxides of copper is given by item 3. Further, the total amount of SO_4^- was determined using microanalytical technique (item 4). Items 2, 3, and 4 subtracted from item 1 gives the % oxygen combined with zinc. It was also found that the leaching of a fresh sample of deposit with ammonia water under air-free conditions in an apparatus already described[7] resulted in the solution of 3.7% copper and 15.1% zinc. The zinc was present from two sources: the solution of zinc compounds and as a result of the interaction between metallic zinc and copper compounds. In the measure in which the zinc was too high, the percentage of copper found in solution was too low.

These data were coördinated with the previous values in an attempt to ascertain the total composition of the deposits. First, the percentages of copper combining with 2.1% oxygen as cuprous and as cupric oxides were calculated (items 6 and 7). These values for copper lead to the amounts of this metal which were displaced by zinc during the leaching experiments (9 and 10), and also to the amount of zinc so dissolved (11 and 12).

(5) Westgren, *Trans. Inst. Min. Met. Eng.*, Inst. of Metals Div., p. 13 (1931).

(6) Van Straten, Master's Thesis, New York University, 1937.

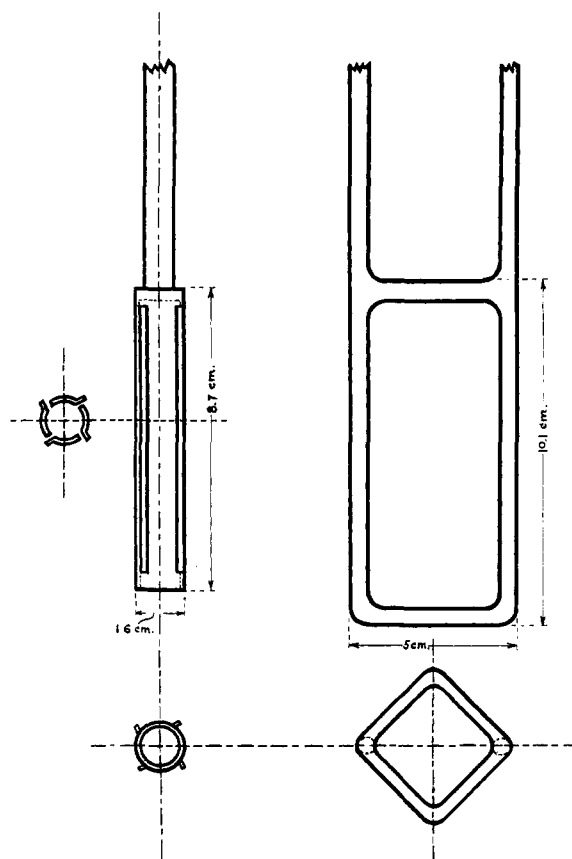(7) Van Straten and Ehret, *Mikrochemie*, **26**, 56 (1939).

Items 13 and 14 then show how much zinc had been present as oxide in the original deposit and 15 and 16 the percentage of oxygen combined with the zinc. In this dual set of data, one item represents the assumption that the cupric was the only oxide of copper present and the other that only cuprous oxide was present. Items 15 and 16 must be compared to item 5. Since there is a closer approximation between item 15 and item 5, it is deduced that cuprous oxide is present predominantly. The presence of cuprous oxide may be accounted for by the interaction of copper with cupric ions or by the incomplete reduction of cupric ions by zinc.

Table I

1	% non-metallic constituents (100 minus total % Cu minus total % Zn)	6.2
2	% adsorbed gases, water, etc.	1.6
3	% oxygen combined with Cu as cupric or cuprous oxide	2.1
4	% sulfate combined with Zn[a]	1.1
5	% oxygen combined with Zn as zinc oxide	1.4

[a] Sulfate is considered to be combined only with zinc since copper sulfate if present during washing and drying operations would have been given ample opportunity to react with metallic zinc or alloy.

Calculations

6	% Cu which was combined with oxygen (item 3) if only cuprous and no cupric oxide were present	16.8
7	% Cu which was combined with oxygen (item 3) if cupric oxide were the only oxide of Cu present	8.4
8	% Zn combined with sulfate (item 4)	0.7
9	Item 6 minus 3.7% (leaching data) equals the % Cu which was displaced by Zn	13.1
10	Item 7 minus 3.7% equals the % of Cu which was displaced by Zn	4.7
11	On basis $[Cu(NH_3)_4]^{++} + Zn \longrightarrow Cu + [Zn(NH_3)_4]^{++}$, % Zn equivalent to item 10	4.7
12	On basis $2[Cu(NH_3)_2]^+ + Zn \longrightarrow 2Cu + [Zn(NH_3)_4]^{++}$, % Zn equivalent to item 9	6.6
13	15.1 (leaching data) minus item 12 minus item 8 equals the % Zn present which was combined with oxygen as zinc oxide	7.7
14	15.1 minus item 11 minus item 8 equals the % Zn present which was combined with oxygen as zinc oxide	9.7
15	% oxygen which was combined with Zn as per item 13	1.9
16	% oxygen which was combined with Zn as per item 14	2.4

These determinations made it possible to offer a complete analysis for a representative sample of deposit formed at 25° (Table II). The authors believe that this is as close an approximation to the true composition as can be made with present methods.

Table II

	%
Water and adsorbed gases	1.6
Cuprous oxide	18.9
Zinc oxide	7.0
Zinc sulfate	1.8
Zinc and copper as metal or alloy	70.7
	100.0

Experimental Results.—In Fig. 2 are given the results of the experiments designed to show the variation in the composition of the deposits with change in stirring speed. The X-ray photogram of all the deposits shown by points on the graph, except for those on curve 5, indicated the presence of copper as principal phase and α-solid solution as secondary. The deposits shown on curve 5 consisted of a mixture of α- and β-brasses.

The variations in composition of the deposits with increase in reaction time and increase in the length of time that the deposits, already formed, were in contact with copper sulfate solution are shown in Figs. 3 and 4. In the former, curve 1 represents runs made at 25° and the additional time is given in fractions of a minute beyond the first minute; curve 2 gives results obtained at 50° and the additional time represents fractions of a half-minute beyond the first half-minute. The deposits used for the runs of Fig. 4 were obtained by one-minute immersion of zinc in 0.0484 M copper sulfate solution at 25° and 1000 r. p. m.

X-ray analyses of the deposits from the runs shown in Fig. 5 indicated copper as the principal phase with α-brass of variable concentration secondary at 25°. At the higher temperatures and for low concentrations of copper sulfate there were increasing amounts of α as well as some β-brass.

Figure 6 and Table III show the influence of the addition of zinc sulfate to the bulk solution. The results of the X-ray examination here were particularly interesting and will be referred to later. The symbols used under the column headed *phases* have the usual significance, i. e., Cu > α means there was more of the copper phase than of α; $\alpha \gg \beta$ means there was mostly α and very little β, etc.

The change in pH during representative runs is given in Table IV and when these figures are compared with those of Table V in which changes in
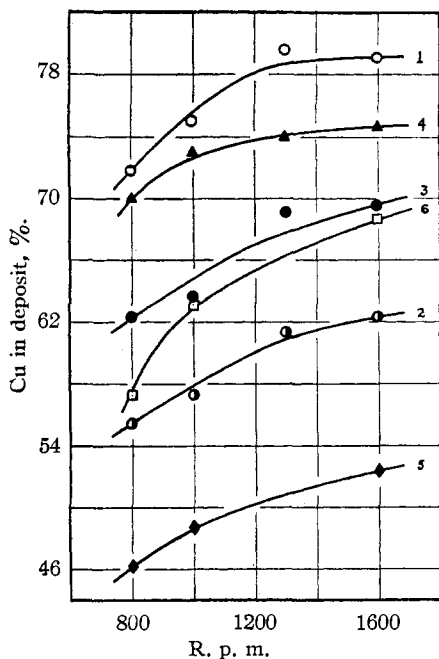
Fig. 2.—Variation in composition of deposit with change in stirring speed in CuSO₄: 1, 0.0847 M, 25°; 2, 0.0121 M, 50°; 3, 0.0484 M, 50°; 4, 0.0847 M, 50°; 5, 0.0121 M, 75°; 6, 0.0484 M, 75°.

TABLE III

VARIATION IN COMPOSITION OF DEPOSITS FORMED WITH ADDITION OF VARYING AMOUNTS OF ZINC SULFATE, SOLUTIONS STIRRED AT 1000 R. P. M.

M CuSO₄	M ZnSO₄	Temp., °C.	% Cu in deposit	Phases
0.0242	0.0000	25	65.1	Cu $\gg \alpha$
	.0254		64.1	
	.0381		60.7	
	.0508		60.3	α
.0484	.0000		68.1	Cu $> \alpha$
	.0508		63.5	α
	.0762		62.9	Cu, satd. α
	.1016		61.4	Cu $\gg \alpha$
.0242	.0000	50	61.7	$\alpha > \beta$
	.0254		55.6	$\alpha > \beta$
	.0381		55.2	$\beta > \alpha$
	.0508		52.0	$\alpha (\gg \beta?)$
.0484	.0000		63.7	Cu $> \alpha$
	.0508		59.3	α
	.0762		58.6	$\alpha > \beta$
	.1016		58.3	$\alpha \gg \beta$

composition with deliberate changes in acidity are recorded, it is seen that hydrolytic influences play a negligible part in the displacement experiments here reported.

Discussion

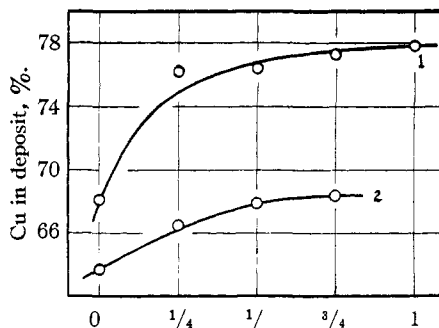Preliminary to the interpretation of the experimental results it will be well to discuss the

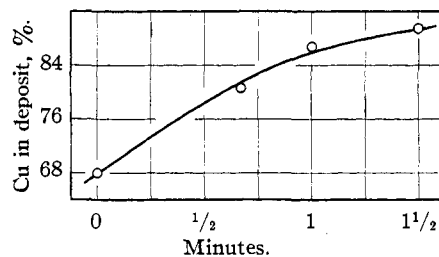Fig. 3.—Additional time deposit on strip was in contact with CuSO₄ solution: 1, 0.0484 M, 25°; 2, 0.0242 M, 50°.

Fig. 4.—Additional time deposit removed from strip was in contact with 0.0484 M CuSO₄ soln. at room temperature.

TABLE IV

COMPARISON OF THE pH OF SOLUTIONS MOST FREQUENTLY USED

Values reported for solutions at 25°. pH of same solutions at other temperatures comparable.

M CuSO₄	M ZnSO₄	pH before run	pH after run
0.0242	....	4.61	4.61
.0484	....	4.42	4.39
.0847	....	4.25	4.27
.0242	0.0508	4.62	4.55
.0484	0.1016	4.40	4.36

TABLE V

VARIATION IN COMPOSITION OF DEPOSIT FORMED WITH CHANGE IN ACIDITY OF SOLUTION

Deposited in 0.0484 M CuSO₄ at 1000 r. p. m., H₂SO₄ added.

Temp., °C.	pH	% Cu in deposit	Phases
25	4.42	68.1	Cu $> \alpha$
	3.86	69.0	Cu $\gg \alpha$
	3.48	72.3	Cu $\gg$ satd. α
	3.35	72.3	Cu $\gg$ satd. α
50	4.00	63.7	Cu $> \alpha$
	3.80	67.6	Cu
	3.59	69.1	Cu $\gg \alpha$
	3.50	68.7	Cu $\gg \alpha$

chemistry of the reaction and the mechanism which will account for the results obtained.

A displacement of this sort is obviously an electrochemical reaction in which the anodic and
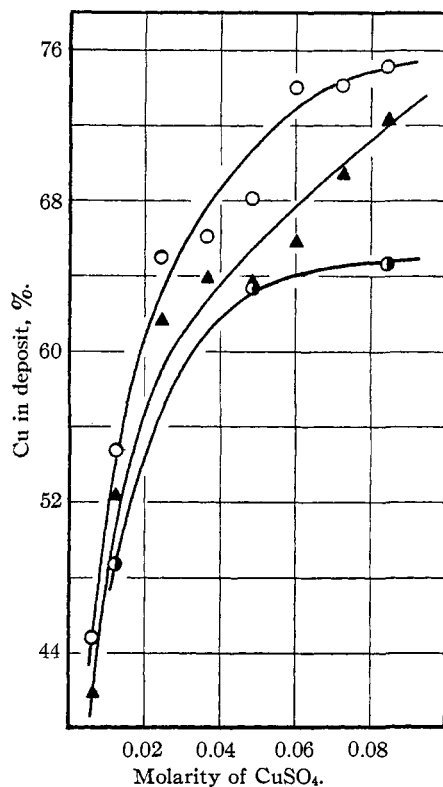
Fig. 5.—Influence of change in concentration of the solution upon the composition of the deposit, at 1000 r. p. m.: ○, 25°; ▲, 50°; ◑, 75°.
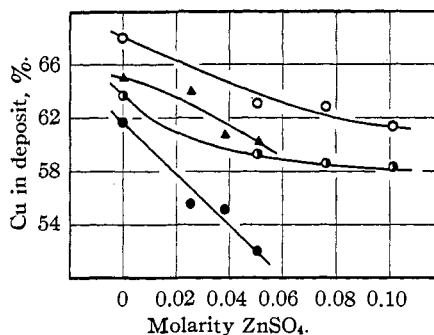

Fig. 6.—Composition of deposits as affected by zinc sulfate addition, in $CuSO_4$ at 1000 r. p. m.: ▲, 0.0242, 25°; ○, 0.0484, 25°; ●, 0.0242, 50°; ◑, 0.0484, 50°.

cathodic areas are in close contact with each other, forming local elements. The initial reaction is the simple one in which zinc goes into solution and copper plates out at the less active points. According to Erbacher[8] this process is initiated by surface inequalities forming "solubility" local elements whereby one portion of the more active element passes into solution more readily than another, thus resulting in an exchange of surface atoms, less noble for more noble.

This process causes a building up in zinc sulfate concentration due to the solution of metallic zinc. The local elements, Zn/Cu, are bathed, therefore, in a solution of both copper and zinc sulfates. From such a solution brass is deposited rather than pure copper. From this point on, local cells of the type $Zn/ZnSO_4$, $CuSO_4/brass$ play an important part in the formation of the deposit. Variation in the composition of the brass makes it possible for one crystal, poor in copper, to act as anode while another, rich in copper, is cathodic. Also both can act as cathode with respect to the

original zinc. However, as the deposit grows out from the zinc strip, this last reaction becomes less prominent due to the distance between the outermost deposit and the zinc. The main reaction is then the one caused by having brasses of different phase and composition act as cathode and anode. The potential developed by such cells is considerably less than that of the original cell, Zn/Cu, and the proportion of zinc which is plated out on the fringes of the deposit must be reduced greatly since a fairly high potential would be required to deposit zinc-rich alloys. This reduction in zinc is enhanced further by the fact that any zinc and all the copper that plate out, do so at the expense of zinc already laid down in the deposit.

In our work, this effect was somewhat counterbalanced by another. Turbulent stirring and the increased bulk of the loosely adherent deposit caused the ripping off of some of the outer layers. This was only prominent when the run was long or when the reaction was rapid as at the higher temperatures and concentrations of copper sulfate. Since the outer layers were richer in copper than the inner ones and since it was the outer layers which ripped off when droppage occurred, more copper than zinc was lost, and the remaining adherent deposit was thus made relatively zinc rich. Since the deposit lost from the strip was not recovered, the net result was the increase in zinc concentration in the deposit analyzed.

The mechanism postulated above will probably hold for all cases of displacement in which the more noble and the baser metal show a tendency to form compounds or solid solutions. It seems quite capable of explaining the results of Natta[9] who, using the electron diffraction method,

(8) Erbacher, Z. physik. Chem., A163, 196 (1933).

(9) Natta, Gazz. chim. ital., 67, 10 (1937).

identified the solid solutions formed when palladium, silver or gold was displaced by copper. A similar mechanism with but minor modification was used by Hoar and Price[10] to explain the atmospheric corrosion of base metals.

Although the mechanism given above is capable of explaining the nature of our deposits, it should be noted that the *rates* of displacement were governed by a physical process, diffusion. This was demonstrated both by experiments in which the viscosity of the reacting solution was increased by means of sugar, thus decreasing the diffusion rate and the proportion of copper in the deposit, and by the experiments (Fig. 2) involving the simultaneous increase in stirring speed, diffusion rate, and proportion of copper in the deposit.

The diminishing slope of the curves representing the experiments in Fig. 2 may be accounted for as follows. The higher the stirring speed, the greater was the droppage of deposit, and since, as mentioned earlier, increased droppage corresponds to a decrease in the amount of copper found, the rate of increase in copper due to an increase in stirring speed would be counteracted by the decrease due to droppage.

Statements concerning the effect of droppage on the composition of the deposit are justified by the data shown in Figs. 3 and 4. As the deposit grows out from the zinc strip, beyond a certain point, it becomes progressively richer in copper, due to the decrease in the amount of zinc present in the solution with increasing distance from the zinc strip and also due to the secondary reaction by which zinc is dissolved out of already deposited brass and is replaced by more copper. This process is indicated by the data in Fig. 4, which may be considered a study of secondary reactions. In getting the information for this figure, deposit from a regular run was removed from the zinc strip and then placed in contact with further amounts of solution for varying lengths of time. All the deposit was then analyzed. It was immediately apparent that the rise in copper concentration in the deposit for this material is much greater than that for the deposit formed when the zinc strip with the adherent deposit remains in contact with copper sulfate solution for longer periods of time (Fig. 3). In this latter case, the huge increase noticed in the former is counterbalanced by droppage.

(10) Hoar and Price, *Trans. Faraday Soc.*, **34**, 867 (1938).

Examination of Fig. 5 makes it immediately apparent that although increase in concentration of the copper sulfate increases the concentration of copper in the deposit, the effect is more pronounced when the solution is dilute than when it is concentrated. This phenomenon, the authors believe, can be explained by the fact that in the dilute solutions, little deposit is formed during the specified time of reaction. In this way, even the outermost part of the deposit, at the end of the reaction, is not far removed from the zinc strip, accounting both for the high percentage of zinc in the deposit and the large decrease in this percentage with slight increase in concentration of the copper sulfate. The former is explained by the fact that with such intimate contact between the bulk of the deposit and the zinc strip, this continues to furnish the bulk of the anodic areas for the electrochemical reaction so that there is little solution of the zinc which has already plated out with the copper, and the total zinc concentration in the deposit remains high. The latter effect, the rapid increase with increased concentration, is probably due to the absence of droppage. The outermost layers which are relatively rich in copper are not ripped off so that the full effect of these last layers of copper-rich brass is felt in the analyses. The change in slope as the solution becomes more concentrated, as well as the slight irregularities of the points with respect to the curve, may be explained by the appearance of droppage at these concentrations.

The data of Table III and the corresponding Fig. 6 show the effect produced on the composition of the deposit by the addition of zinc sulfate to the copper sulfate solution. Although the effect is not particularly marked in three of the four cases, it is nevertheless true that increase in the amount of zinc ions in the solution decreases the copper in the deposit. The X-ray data for the lowest of the four curves show that these deposits contain a much greater proportion of β-brass than do the others, which in turn indicates that the conditions in the solution were made progressively more favorable for the deposition of β-brass as the concentration of copper sulfate was lowered and the temperature and zinc sulfate concentration increased. The more rapid descent of the curve in this case is probably due to this preferential β-brass formation. The gradual descent of the other curves may be explained by the nature of the diffusion gradient of the zinc sulfate

solution. In the case of deposition from pure copper sulfate solution, the concentration of zinc sulfate drops from a relatively high value immediately adjacent to the zinc strip to a very low value at the edge of the deposit where this is in contact with the bulk solution. This corresponds to a progressive diminution in zinc ion concentration in contact with the deposit as the deposit is further removed from the zinc strip. When the bulk solution already contains zinc ions, the rate of diminution in zinc ion concentration with distance is not as rapid. However, even fairly large additions of zinc sulfate cause but small alteration in the composition of the deposit, since the over-all increase in zinc ion concentration throughout the deposit is small.

The X-ray part of this investigation was undertaken primarily to prove irrefutably that various kinds of brass are formed by displacement reactions and that change in concentration of the solution from which the deposit is formed may change the phases plated out. However, due to the limitations of the X-ray method of analysis, the data obtained were not very useful in the interpretation of the results. The production of satisfactory X-ray photograms depends to a large extent upon having present a sufficient number of diffracting crystals of dimensions greater than 1×10^{-6} cm. Judging from the line-breadths and general scattering produced, our deposits often contained particles of about this magnitude or smaller. It is not possible to determine the lattice parameters of such crystals and sometimes impossible to detect the phases themselves. The absence of any X-ray indication of the gamma phase (or any other zinc-rich phase) which must be present according to the corresponding chemical analysis, is probably due to this limitation of the X-ray method.

Summary

1. A study was made of the displacement reactions involving the formation of brasses by reaction of zinc with copper sulfate solution at 25, 50, and 75°.

2. The compositions of the deposits obtained by displacement were determined by chemical and X-ray diffraction methods.

3. An increase in concentration of copper sulfate was found to increase the copper content of the deposits, whereas zinc sulfate, added to the copper sulfate solutions, decreased the copper content. These results are in general agreement with work reported by Galecki and Tomaszewski although in their experiments the conditions were less carefully controlled.

4. The amount of copper in the deposit increased with increased stirring of the solution, an indication that the reaction was diffusion controlled.

5. The influence of the changing acidity of the solutions on the nature of the deposits was found to be negligible in the course of the time allotted to a run.

6. An investigation was made of the secondary reactions resulting from prolonged exposure of deposits, in and out of contact with zinc, to copper sulfate solution.

7. An electrochemical mechanism is offered to explain the formation of brasses by displacement.

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