60% of the active material was obtained in 1.5% of the barium compound. (This corresponds to 8.4 mg. of mesothorium and radium in 17 g. of barium chloride.)

3. The rich fraction from the hydroxide crystallization was fractionally crystallized as bromide and 76% of the active material obtained in 5.3% of the barium compound. (6.4 mg. of mesothorium and radium in 0.55 g. of barium bromide.)

4. The ratios of mesothorium to radium in the rich and lean fractions from the hydroxide crystallization and in the rich fraction from the bromide crystallization were practically identical with one another and also with the ratio of these elements in the starting material. The ratio of active elements to barium was over 7000 times as great in the rich fraction from the bromide process as in the lean fraction from the hydroxide process. These facts furnish further evidence for the isotopism of mesothorium and radium.

The present work was carried on under the direction of Dr. Herbert N. McCoy, to whom I wish to express my sincere thanks for inspiration and valuable instruction.

CHICAGO, ILL.

THE INFLUENCE OF COPPER ON THE RATE OF SOLUTION OF IRON IN ACIDS.

BY FREDERICK K. BELL AND WALTER A. PATRICK.

Introduction.

The effect of the presence of small amounts of copper in iron on the corrosion of the latter is a subject on which there seems to be considerable debate. Buck[1] has found that a small copper content (0.2%) materially decreases the corrosion of steel sheets under atmospheric conditions. Aitchison[2] has shown from his corrosion experiments with 10% sulfuric acid that a 0.48% copper-steel shows a greatly accelerated corrosion while 1.06%, 2.52% and 4.78% copper-steels show a marked decrease, the corrosion increasing slightly in the order given. Similar experiments carried out with the same alloys using tap water show, in general, an increased corrosion in comparison with pure carbon steel. Cushman[3] expresses the belief that "many earnest investigators have deceived themselves to the point of concluding that a little copper, say 0.25% or less, as an alloying constituent conferred resistivity on a steel." In this investigation we have restricted ourselves to the simplest case,

[1] Buck, *J. Ind. Eng. Chem.*, **5**, 452 (1913).
[2] Aitchison, *Trans. Faraday Soc.*, **11**, 212 (1916).
[3] Cushman, *ibid.*, **11**, 242 (1916).

viz., the binary system of pure iron and pure copper; by determining the rate of solution in acids of such alloys (up to 5.0% copper) as well as that of pure iron, it was hoped that the true effect of the copper could be ascertained.

It was intended to study the rate of solution in hydrochloric and sulfuric acids of various concentrations. However, it was soon found that, in general, the rate of solution was too slow for the experimental method used; consequently, our experiments have been limited to more concentrated acids, *viz.*, 28.7% hydrochloric acid and 57.0% sulfuric acid.

Preparation of Materials.

The iron was prepared according to the method of Richards and Behr,[1] which is essentially the same as that used by Richards and Baxter[2] in their atomic weight determinations.

A good grade of piano wire was cleaned, cut up into convenient sized pieces, and dissolved in dil. nitric acid. Under these conditions, according to Richards,[3] the silicon is precipitated either as silicic acid or as ferrosilicon (Fe_2Si) which is not attacked by dil. acid, and the carbon present as graphite and iron carbide is either completely oxidized or not attacked at all. By using dilute acid the possibility of oxidation of any sulfur to sulfate is diminished. The acid solution was filtered and concentrated by evaporation until crystallization took place on cooling. The ferric nitrate ($Fe(NO_3)_3$.-$9H_2O$) thus obtained was recrystallized 4 times from dil. nitric acid solution to prevent hydrolysis and then in 200-g. lots, was heated in a platinum dish to 120° from 6 to 8 hours, when the material was almost entirely dry; it was then removed and powdered, yielding a brilliant red powder. The conversion of the basic nitrate to the oxide was carried out at a red heat using a platinum resistance furnace described by Morse.[4] It was found that 30 g. basic nitrate heated in a platinum crucible for 2 hours at 900°, then repowdered and thoroughly mixed and finally heated again for one hour at 900° was completely converted to oxide. The oxide thus obtained was dark red and very finely divided.

Using a Hoskins electric furnace with a silica tube, 20 g. oxide was placed in a platinum boat and reduced in a current of commercial hydrogen at 600° for 7 hours, and during the last hour at 1000°. The iron was obtained in silver-gray lumps which could be powdered between the fingers. More than 300 g. of iron was prepared in this way the yields from the various reductions being thoroughly mixed together and stored in a glass-stoppered bottle.

The copper used was a sheet of pure copper foil which was first thoroughly cleaned with emery paper and then cut into small strips which were finally treated in the usual way, with methyl alcohol. The strips were cut into very small pieces and stored in a glass-stoppered container.

Preparation of the Alloys.

Five melts of 25 g. each containing 0.1%, 0.3%, 0.5%, 1.0% and 5.0% copper, respectively, were prepared and a pure iron melt of 40 g. Through the kindness of Director Stratton the fusions were carried out at the Bureau of Standards laboratory in Washington.

[1] Richards and Behr, *Z. phys. Chem.*, **58**, 302 (1907).

[2] Richards and Baxter, *Z. anorg. Chem.*, **23**, 245 (1900).

[3] Richards, *loc. cit.*

[4] Morse, *Am. Chem. J.*, **32**, 93 (1904).

Marquardt crucibles were used for the fusion. About half of the iron, *i. e.*, 12.5 g., was weighed into the crucible and then a definite weight of copper added and finally more iron was added until the desired composition was obtained. In this way mixtures of the exact percentage composition listed above were prepared and fused in a vacuum electric furnace of the Arsem type[1]. The progress of the fusion was followed visibly through the mica window with which the furnace is equipped. After fusion the melts were retained in the molten condition until they became perfectly quiet, a period of from 10 to 15 minutes. The crucibles were removed from the furnace within an hour and a half after the heating element of the furnace had been cut off. A melt was also prepared from some of the Bureau of Standards electrolytic iron.[2] The melts thus obtained were with some difficulty due to their small size turned down on the lathe to uniform cylinders. In Table I the diameters and cross-sections of the cylinders are given.

TABLE I.

Designation. % Cu.		Diameter. Cm.	Cross section. Cm².
0	Bureau of Stand. pure elec. iron.....................	1.651	2.1408
1	0.1%...	1.664	2.1739
2	0.3%...	1.422	1.5890
3	0.5%...	1.587	1.9793
4	1.0%...	1.568	1.9320
5	5.0%...	1.385	1.5053
6	Pure iron reduced................................	1.676	2.2072

Description of Apparatus.

In devising the experimental method of measuring the rate of solution of the alloys we have frequently referred to and essentially adopted the method employed by Tzentnershver,[3] who has worked extensively on the rate of solution of zinc and its alloys in acids by measuring the rate of evolution of hydrogen and we have sought to increase the accuracy of the method. The apparatus finally adopted may be best described by referring to the diagram in Fig. 1.

The thermostat T was of the type devised by Davis[4] and under the conditions of our experiments the temperature could be held constant within 0.02°. The reaction flask R, in which the acid and the alloy were placed, was equipped with a tightly fitting rubber stopper through which was introduced a gas-tight, mercury seal stirrer, S after the design of Reid[5] with the exception that it was equipped with only one exit tube and this led directly to a gas buret. The stirrer was geared directly to the shaft of the stirrer of the thermostat.

The gas buret was of a special type compensating for both pressure and temperature. By means of the 3-way stopcock at W, the reaction flask, the manometer M and the gas buret proper could all be connected simultaneously and, of course, it was possible to connect any 2 of these units at the exclusion of the third one. The buret proper consisted of 2 arms. The right-hand arm was a 10-cc. pipet graduated

[1] THIS JOURNAL, 28, 921 (1906).

[2] Bur. Standards, *Bull.* 13, No. 1, 4 (1916).

[3] M. Tzentnershver and J. Drucker, *J. chim. phys.*, 13, 162 (1915); *J. Russ. Phys. Chem. Soc.*, 47, 1064 (1915); M. Tzentnershver and J. Sachs, *Z. physik. Chem.*, 89, 213 (1914); *ibid.*, 87, 692 (1914).

[4] P. B. Davis, *Carnegie Inst. Pub.*, 210, 121 (1915).

[5] E. E. Reid, THIS JOURNAL, 37, 2112 (1915).

in 0.05-cc. divisions and was sealed directly into the system.   The left-hand arm was a specially blown glass tube consisting of 4 bulbs, each having a capacity of approximately 10 cc. but not greater than 10 cc. with reference to scratch marks which were placed on the constricted sections of the tube.   The capacities of the bulbs were determined at 20° from the mercury capacity since the gas volumes were to be measured over mercury and were found to be (I) 9.616, (II) 9.235, (III) 8.965, and (IV) 9.627 cc. Since the accuracy of our measurements was to 0.01 cc. the capacities actually employed were 9.62, 9.24, 8.97 and 9.63 cc., respectively.

FIG. 1
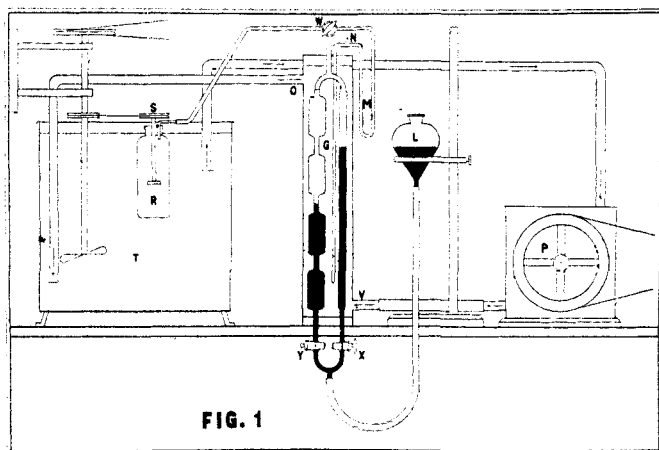
The 2 arms of the gas buret were enclosed in a water jacket consisting of a glass cylinder with an inlet tube and an outlet tube sealed into its side below and above, respectively.   The ends of the cylinder were closed by means of rubber stoppers through which the buret tubes were passed.   Water was pumped (see Fig. 1) from the thermostat into the lower part of the water jacket through Tube V and thence out of the water jacket through Tube O which emptied into the thermostat.   By regulating the velocity of the pump the temperature of the water in the water jacket never differed by more than 0.02° from that of the water in the thermostat.

Before the manometer M was sealed at N, a little water was introduced into the closed end of the manometer which was enclosed in the water jacket so that the vapor pressure of the water would partially correct for the vapor pressure of the acid used and the manometer liquid, bromoform, was introduced into the U-shaped portion of the tube which was equipped with a millimeter scale.

Procedure.

Before each experiment the bulb tube of the buret was filled with mercury up to the top-most scratch mark and the stopcock Y was turned off.   By adjusting the leveling bulb L the pipet tube was filled with mercury up to its zero reading, the stopcock X remaining open.   A reading was then made of the barometric pressure, the system being under atmospheric pressure and simultaneously a reading was made of the pressure difference as shown by the manometer M, and this reading was taken as the standard setting for a given experiment, i. e., all volume readings were made with the pressure difference in the manometer equal to the standard setting which was accomplished by adjusting the leveling bulb.

Knowing the atmospheric pressure and the corresponding manometer pressure difference, the buret is then ready to be connected with the reaction flask. As the hydrogen is evolved the mercury in the pipet tube is displaced, the stopcock X being open while the stopcock Y is closed; and a corresponding alteration in the pressure difference in the manometer results. The leveling bulb was continually lowered so that the pressure difference in the manometer was practically always equal to the standard setting. When it was desired to read the volume the stopcock W was turned so that only the gas buret and the manometer were connected. The leveling bulb was then accurately adjusted until the manometer reading was identical with the standard setting and the volume read. This operation was easily completed within one minute after which the stopcock W was immediately turned to its original position. When the pipet tube was filled with hydrogen the gas was transferred to Bulb I in the bulb tube. This was accomplished by setting the stopcock W so that only the reaction flask and the manometer were connected. The stopcock Y was opened and by means of the leveling bulb the mercury level was brought to the lower scratch mark of Bulb I when Stopcock Y is turned off. The leveling bulb was again adjusted so that the pipet is nearly filled with mercury. The stopcock W was then turned to its original position and the manometer reading was quickly adjusted to approximately the standard setting. In an exactly similar manner Bulbs II, III and IV could be filled consecutively.

We were thus able to measure gas volumes up to 50 cc. with an accuracy of 0.01 cc. at constant temperature and at constant pressure which was practically atmospheric pressure thus minimizing the possibility of leaks in the apparatus. All experiments were carried out at 20° and the usual corrections were applied to the reading of the barometer. In the reduction of gas volumes to 0° and 760 mm. therefore, a constant factor could be employed.

Experimental.

It was, of course, necessary that a known surface of the alloys be exposed to the effect of the acid and to this end the cross-section of the cylindrical melts was taken as most suitable. Before each experiment the selected cross-section was first polished down with emery cloth (No. 00) after which it was finally polished on chamois using a fine grade of alumina as an abrasive. On the surface thus obtained there were some visible scratches but the main point was to obtain identical surfaces for all experiments.

The remaining surface of each cylinder, after cleaning in acid, was coated with a high-melting paraffin. Bakelite was tried for this purpose but was found to chip off readily. Experiments were first tried placing the alloy on the bottom of the reaction flask in a vertical position just

beneath the stirrer, but the rate of evolution was not, in general, as uniform as when the alloy was fastened to the stirrer. This was accomplished by means of insulated copper wire which was wrapped around the alloys already protected with paraffin, and then around the stirrer, after which the wire was thoroughly coated with paraffin. Even under these conditions there was a strong tendency for the evolved hydrogen to form in bubbles on the paraffin to which they adhered tenaciously, and doubtless affected the observed uniformity of the hydrogen evolution, especially when the evolution was rapid. All experiments were carried out at a constant rate of stirring, and in all cases 200 cc. of acid was used.

The stopper of the reaction flask through which the stirrer was introduced and the melt attached to the stirrer could be handled as a single piece of apparatus. In starting an experiment the acid which had previously been suspended in a bottle in the thermostat was poured into the reaction flask and the stopper (with stirrer and melt attached thereto) was tightly inserted into the mouth of the reaction flask and the flask then clamped in its proper place in the thermostat. The exit tube of the reaction flask was connected then by means of rubber tubing with the glass tube leading to the gas buret. Finally the pulley of the stirrer was connected with a corresponding pulley on the shaft of the thermostat stirrer. Not more than one minute elapsed between the time the alloy first touched the acid and the time the flask was connected with the gas buret. The volume of the gas evolved was measured at definite time intervals which, depending upon the magnitude of the volume change, varied from 5 minutes to one hour.

At the end of each experiment the metal cylinder was removed from the stirrer, thoroughly washed in water and dried. The surface which was exposed to the effect of the acid was examined under the microscope and micro-photographs and photographic enlargements of the total surface were made in order that any plating of copper might be detected.

Tabulation of the Experimental Data.

The data obtained from each experiment were tabulated under 2 columns. In the first column, under t, the time is given in minutes which has elapsed since the beginning of the experiment and the time the volume reading was made. The figures in the second column under $\dfrac{\Delta V_0}{\Delta t}/cm^2$. are obtained by reducing to $0°$ and 760 mm. pressure the volume of hydrogen evolved between 2 consecutive volume readings divided by the time in minutes which has elapsed between the 2 readings and finally divided by the area of the surface of the metal in sq. cm. exposed to the action of the acid (see Table I), $i.$ $e.$, the number of cc. of hydrogen at $0°$ and 760 mm. pressure evolved per minute per sq. cm. of surface.

The results of each experiment may be represented graphically by

plotting the figures in Col. 1 against the corresponding values in Col. 2, i. e., velocity-time curves.

Since the rates of solution are comparatively so small it should be noted that it has been necessary to exaggerate greatly the units of the vertical axis, i. e., velocity, for purposes of reproduction in publication. When the various curves are plotted on a more appropriate scale such as unit velocity equivalent to 50 min., as employed by Tzentnershver,[1] the locus of the points is very closely represented by a smooth curve. This is especially true with the copper alloys, but in other experiments where the velocities are comparatively much higher the uniformity is less marked.

Experiments with Hydrochloric Acid.

For the experiments in hydrochloric acid a 28.0% acid was used, and was prepared by diluting conc. c. p. acid with distilled water, the strength of the acid being determined by specific gravity measurements. Just before each experiment the metal cylinder to be used, already well protected with paraffin as has been previously described, was treated in a beaker with the 28% hydrochloric acid for 15 minutes, after which it was removed and placed in the reaction vessel containing the acid and the experiment was started. In this manner it was expected that all induction phenomena could be eliminated. This expectation was fulfilled.

TABLE II.

28% HCl at 20°.

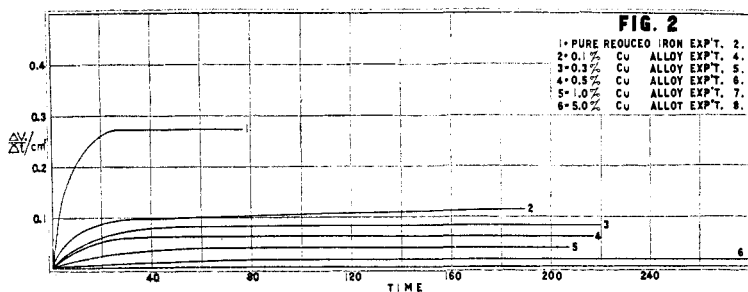| Expt. 1. Melt No. 6. 0.0% Cu.		Expt. 8. Melt No. 5. 5.0% Cu.	
t.	$\frac{\Delta V_0}{\Delta t}$/cm².	t.	$\frac{\Delta V_0}{\Delta t}$/cm².
0	...	0	...
4	0.141	53	0.004
9	0.205	73	0.016
14	0.247	93	0.005
19	0.243	113	0.010
24	0.226	133	0.016
29	0.240	153	0.016
34	0.237	213	0.018
39	0.249	233	0.007
44	0.253	253	0.019
49	0.259	273	0.012
54	0.276	293	0.013
59	0.246	313	0.013
64	0.220	333	0.021
69	0.245	353	0.010
74	0.243	373	0.015
79	0.254	403	0.012
84	0.252	423	0.012
		443	0.015
	Mean, 0.246	463	0.012
	±0.009		
		Mean, 0.013	
		±0.003	

[1] Loc. cit.

in general, and in most cases, due to the fact that the large excess of acid (200 cc.) remained practically constant in concentration during the comparatively short period of each experiment, the velocity of solution reached a constant maximum value shortly after the experiment was started.   In such cases a mean of these maximum values has been taken and this value was considered as the rate of solution of metal under the experimental conditions.

The results of these experiments are given in Table II in full for Expts. 1 and 2, which are typical.   In each case, with the exception of the Bureau of Standards' electrolytic iron (Expt. 9) the velocity reaches a maximum constant value, the mean value of which has been taken, omitting in most cases the first value or two of the velocity.   These means, with their average variations, are given in Table III.   Experiments 1, 4, 5, 6, 7 and

TABLE III.

| Expt.	% Cu.	$\frac{\Delta v_0}{\Delta t}$/cm².		
1, 2	0.0	0.257	±	0.010
4	0.1	0.110	±	0.008
5	0.3	0.079	±	0.006
6	0.5	0.058	±	0.003
7	1.0	0.037	±	0.004
8	5.0	0.013	±	0.003

8 are shown graphically in Fig. 2, where the velocity has been plotted against the time.   The Bureau of Standards' electrolytic iron shows a

FIG. 2

1 • PURE REDUCED IRON EXP'T. 2.
2 • 0.1 % Cu   ALLOY EXP'T. 4.
3 • 0.3 % Cu   ALLOY EXP'T. 5.
4 • 0.5 % Cu   ALLOY EXP'T. 6.
5 • 1.0 % Cu   ALLOY EXP'T. 7.
6 • 5.0 % Cu   ALLOY EXP'T. 8.

gradual increase in velocity and its relation to the behavior of the reduced iron is shown in Fig. 4, where the velocity-time curves of Expts. 2 and 9 have been plotted.   In Fig. 3 the mean velocity of solution taken from Expts. 1, 2, 4, 5, 6, 7 and 8 has been plotted against the percentage of copper giving the relation between the copper content and the rate of solution in 28% hydrochloric acid.   For the value of the pure reduced iron we have taken 0.257, the average of the mean values of Expts. 1 and 2.

FIG. 3
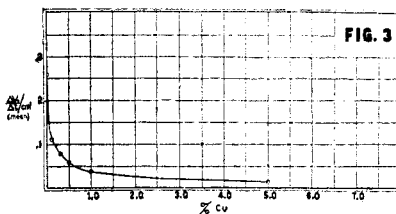
Several experiments were carried out in hydrochloric acid with the pure reduced iron (Melt 6) in contact with copper, silver and platinum. This was accomplished in the following manner. A piece of wire of the de-sired metal, thoroughly cleaned, was tightly wrapped once around the metal cylinder which had not yet been coated with paraffin so that the top-most portions of the wire were flush with the surface, already pol-


FIG. 4

1 = PURE REDUCED IRON EXP'T. 2.
2 = PURE ELECT. IRON EXP'T. 9.
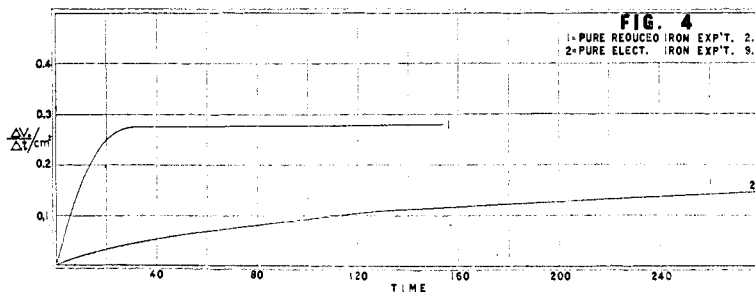
ished, which was to be subjected to the action of the acid. The bottom and the sides of the metal cylinder were then covered with paraffin as far as the under side of the wire so that the greater portion of the surface of the wire would be in contact with the acid as well as that of the iron. The rest of the procedure was identical with that of the previous experi-ments. The results of these experiments are tabulated in Table IV.

TABLE IV.

Pure Reduced Iron (Melt 6) in Contact with Various Metals.

Expt.	Metal.	$\dfrac{\Delta T_0}{\Delta t}$ /cm².
10	Copper	0.020 ± 0.002
11	Platinum	0.278 ± 0.012
12	Platinum	0.283 ± 0.010
13	Silver	0.280 ± 0.013
14	Silver	0.287 ± 0.016

The corresponding velocity-time curves are given in Figs. 5 to 9. The average velocity of solution in the experiment with the copper wire (Expt. 10) corresponds to an approximately 2.0% copper alloy according to Fig. 3. A qualitative experiment was also carried out with the iron in contact

FIG. 5

1 = PURE REDUCED IRON   EXP'T. 1.
2 = PURE REDUCED IRON IN CONTACT WITH COPPER   EXP'T. 10.
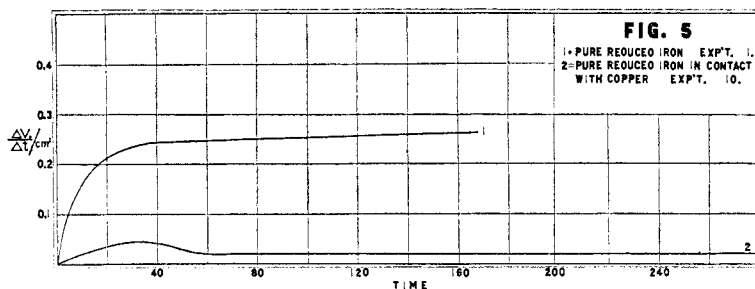
with copper.   The 2 metals in contact were placed in an open beaker containing 28% hydrochloric acid.   No evolution of hydrogen from the copper could be detected.

The average velocities obtained in the platinum and silver experiments are slightly higher than those of the pure iron; however, there is a small but significant increase in surface, consisting of a narrow band around the side of the cylinder extending, in width, from the top surface of the melt to the point where the wire is in contact with the iron.   If correction could
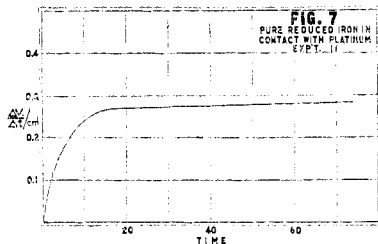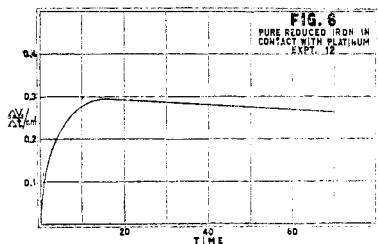
be accurately made for this surface the velocities would probably check closely with those of pure iron.

Microscopic examination of the surface exposed to the action of the acid showed in no case the presence of copper plating.   The surfaces when thoroughly cleaned retained their brilliant metallic luster for some time. Microphotographs and enlarged (app. 8 times) photographs showing the total surface exposed to the action of the acid, offered visible evidence of the fact that copper decreases the rate of solution of iron in conc. hydro-chloric acid.   In the absence of copper or in the presence of platinum
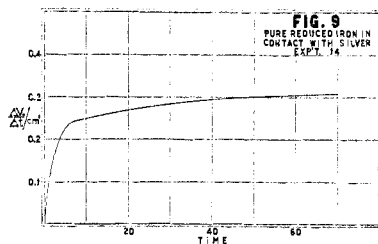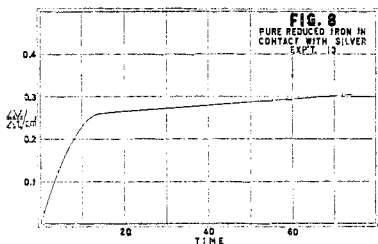
the iron is eroded between the crystals.   On the other hand, in the case of the copper alloy or in the case of the copper band around the pure iron, very little erosion was indicated by the photographs.
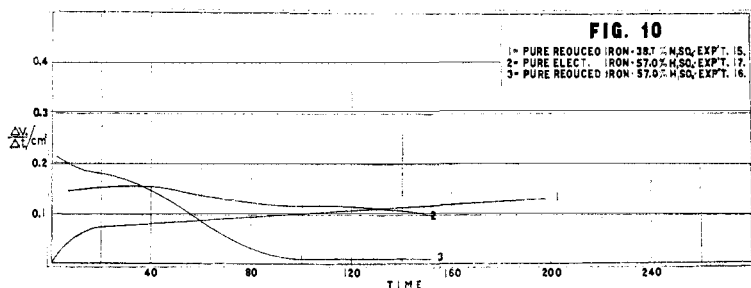
It was thought advisable to determine the agreement between the total hydrogen evolved and the iron content in the acid solution at the end of an experiment.   For this purpose the solutions from Expts. 11, 12, 13 and 14 were analyzed.   The following method of analysis was used.   The solution strong in hydrochloric acid was evaporated with sulfuric acid until fumes of sulfur trioxide were evolved.   The residue was diluted with

water and then titrated with permanganate. The ferric iron thus obtained was titrated with titanium trichloride, using ammonium thiocyanate as an indicator. All of the results thus obtained were consistently higher than the corresponding hydrogen volume values. An explanation of this difference may be based on the following considerations. (1) The solubility of hydrogen in the acid solution; (2) the occlusion of hydrogen by the metal; and (3) the adherence of gas (hydrogen) bubbles to the walls of the reaction chamber and to the paraffin coating of the metal, which was always apparent and perhaps the most significant factor.

Experiments with Sulfuric Acid.

The acids used in these experiments were prepared by diluting conc. c. p. acid with distilled water. The composition was determined from the specific gravity.

Using the pure reduced iron (Melt 6) an experiment was made in 38.7% acid after a preliminary treatment of 15 minutes in acid of the same strength. The results of this experiment are shown graphically in Fig. 10, tabulated under Expt. 15. The rate of solution showed a steady increase with the time. In the hope of obtaining a rate of solution comparable to the corresponding experiment in hydrochloric acid the concentration of the acid was increased to 57% and the preliminary treatment consisted of 5 minutes in contact with conc. hydrochloric acid and then, after thorough washing, 10 minutes in 57% sulfuric acid. Electrolytic iron was treated in the same way. The results of these experiments, 16 and 17, are shown graphically in Fig. 10.

FIG. 10

1 = PURE REDUCED IRON - 38.7 % H₂SO₄ EXP'T. 15.
2 = PURE ELECT. IRON - 57.0 % H₂SO₄ EXP'T. 17.
3 = PURE REDUCED IRON - 57.0 % H₂SO₄ EXP'T. 16.

The results obtained with the 57% acid were very unsatisfactory. In the case of Melts 1, 2 and 3 the solution was extremely slow, and after a period of about 2 hours a decrease in volume was observed. Expt. 18 is given as representative of several experiments in which the decrease in volume was noted. In these experiments the surface of the melt became covered with a dark smudge which, when analyzed on removal, gave a negative test for copper. At the end of one experiment it was thought that the odor of hydrogen sulfide was detected on emptying the gas buret. Several attempts to confirm this observation gave negative results.

With Melts 5 and 6 (Expts. 19 and 20, respectively) the rate of solution was very slow but no volume decrease was observed.   In Expt. 20 (5.0% copper) there was a visible plating of copper on the metallic surface within 5 minutes after the experiment was started.

On removal from the acid after an experiment all the melts showed a strong tendency to oxidize even after thorough cleaning and drying.   The surfaces were immediately examined under the microscope.   Microphotographs and enlarged photographs of the total surface exposed to the acid were prepared.   In the entire investigation a copper plating was detected only after Expt. 20 and in this case the plating was plainly visible to the naked eye.

Discussion of Results.

It cannot be too strongly emphasized that the acids employed in the present investigation were concentrated.   The reasons for confining ourselves to such strength of acids was found in the fact that our method of following the rate required the use of strong acids in order to obtain an appreciable gas evolution.   This fact is mentioned in order that our results will not be extrapolated to include weak acids and conclusions drawn as to the ordinary corrosion of copper-iron alloys.   We do not know what would take place in weak acids.

Theories have been advanced to explain the retarding action of copper upon the rate of solution of iron in acids.   In the present discussion no serious attempt will be made to explain the phenomenon, inasmuch as at the present time we have not collected our complete experimental data. Nevertheless, our experiments are sufficient to disprove several of the explanations which have been advanced.

We can dismiss at once the question of the influence of the copper upon the usual impurities occurring in ordinary iron or steel, inasmuch as our iron was pure.   Similarly, the influence of copper upon the grain size is clearly without effect.

Likewise, the question of the electrode potential of iron-copper alloy is of no weight because we observe the same retarding effect with metallic copper in contact with pure iron (see Expt. 10).   In this connection it should be mentioned that up to 8.0% copper, iron-copper alloys have been found to exist as solid solutions,[1] and recent work by Tammann[2] indicates that the electrode potential of most alloys which exist as solid solutions does not vary continuously with the composition.

Another explanation that has been offered is that the decreased rate of solution is due to a deposit of metallic copper over the surface of the iron.   Our microscopic sections do not reveal any trace of copper.   The

[1] Stead, *J. Iron Steel Inst.*, **11**, 112 (1901).
[2] Tammann. *Z. anorg. Chem.*, **107**, 136 (1919); **109**, 80 (1919).

5.0% copper alloy in sulfuric acid showed a marked deposit of copper, but in no case did this occur in the experiments with hydrochloric acid.

It has been suggested by Tzentnershver[1] that passivity of the metal is produced by the alloyed metal and that this is the explanation of the retarded solution rate. At first sight this idea appears rather attractive but is not able to stand against the experimental facts. In sulfuric acid we found that our 5.0% copper alloy became coated with copper (Expt. 20), notwithstanding the fact that passive iron does not precipitate copper from solution. Furthermore, it is well known that the chloride ion is most effective in preventing iron from becoming passive, nevertheless our experiments in hydrochloric acid showed a marked retardation in the rate of solution of the alloys.

The question of overvoltage has been mentioned in connection with the phenomenon. If it is more difficult for hydrogen to be evolved from the copper than it is from the iron, then copper in contact with the pure iron should not interfere with rate of solution and this is contrary to the results obtained in Expt. 10. Furthermore, the experiments with platinum in contact with iron are most conclusive on this point. It is to be remembered that platinum exerted practically no effect on the rate of solution of the iron. This is clearly a point against the overvoltage theory, inasmuch as platinum possesses such a low overvoltage. If the curve in Fig. 3 is examined it will be seen that the rate of solution decreases with increase in copper content and then gradually reaches a practically constant value. The form of the curve also shows that the rate of solution is not inversely proportional to the copper content. In fact, it appears that a considerable area of iron is affected by the presence of copper. One might say that the copper is surrounded by a sphere of influence within which hydrogen ions are discharged with difficulty. This idea is suggested by an examination of the action of acid upon iron in contact with a piece of copper. It is noticed that there is a visible diminution of the evolution of hydrogen throughout a zone in the vicinity of the copper.

The explanation of the retardation observed in hydrochloric acid that suggests itself after a study of the experimental evidence unfortunately is not proved and we therefore only offer it tentatively. It is this.

Copper is dissolved in strong acids to a limited extent. This solution of copper is possible because of the formation of complexes[2] with the acid thereby reducing the copper ion concentration to such an extent that hydrogen ions may be electrically discharged. This dissolved copper, however, in the presence of iron does not remain in solution but is precipitated out in a finely divided state. This latter state of the copper

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[1] *Loc. cit.*

[2] Odling, *J. Chem. Soc.*, **9**, 291 (1857); Berthelot. "Mecanique chemique," Vol. II. 524; Engel. *Compt. rend.*, **121**, 528 (1895).

renders it more readily attacked by the acid and it redissolves and we have the copper oscillating back and forth between the solution and the surface of the iron.   The changes may be written thus:

$$Cu + 2H^+ \longrightarrow Cu^{++} + H_2 \qquad (I)$$

$$Cu^{++} + Fe \longrightarrow Fe^{++} + Cu \qquad (II)$$
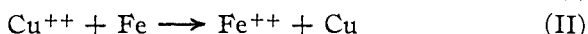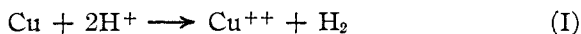
Reaction II undoubtedly occurs very rapidly and the occurrence of Reaction I is responsible for the retardation of the rate of solution of the iron, i. e.,

$$Fe + 2H^+ \longrightarrow Fe^{++} + H_2. \qquad (III)$$
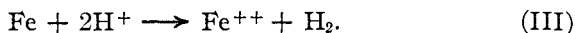
The initial amount of the copper dissolved which depends upon the copper content of the alloy for a given acid concentration is considered then as being intermittently precipitated in a finely divided state and, therefore, more soluble than the copper of the alloy and redissolved and this layer of precipitated copper which is intermittently present on the surface of the iron retards the solution of the latter, i. e., Reaction III.

Summary.

1. The rate of solution of pure electrolytic iron and pure reduced iron and 0.1%, 0.3%, 0.5%, 1.0% and 5.0% copper alloys of the latter have been determined in 28.7% hydrochloric acid at 20°.

2. The rate of solution of the alloys shows a definite decrease in comparison with pure reduced iron as the copper content increases.

3. The rate of solution of pure reduced iron in contact with platinum, silver, and copper in 28.0% hydrochloric acid at 20° has been measured. Platinum and silver show apparently no effect while copper greatly lowers the velocity.

4. Experiments in 57.0% sulfuric were unsatisfactory lacking in uniformity and suggesting that experimental conditions were not under control.

5. An explanation of the retarding effect of copper in hydrochloric acid has been offered.

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