fully reduced with stannous chloride, and treated exactly like the samples of ferrous ammonium sulfate.

The results found for iron, as shown in Table II, average 69.10 per cent, whereas the value reported by the Bureau of Standards is 69.2 per cent. The results with bianisidine are therefore correct to within about 0.1 per cent.

TABLE III. PERMANENCE OF BIANISIDINE SOLUTION

(Titration of Mohr's salt after reduction with stannous chloride)

	1	2	3	4
Mohr's salt, grams	1.5041	1.5022	1.5021	1.5034
Potassium bichromate, cc.	37.49	37.49	37.48	37.54
Iron value	0.005694			
Iron found, %	14.20	14.21	14.21	14.22
Mean, %	14.21			
Value from previous analysis	14.21			

PERMANENCE OF INDICATOR

In order to test the effect of light on the indicator, four portions of the ferrous ammonium sulfate were titrated by the above method, using a bianisidine solution that had been exposed to light in a north window for 11 days. The results given in Table III show that this treatment did not impair the usefulness of the bianisidine solution.

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Aqua Regia and Base Metals

Rate of Corrosion of Iron and Nickel by Aqua Regia as Function of Its Composition and Time of Mixture

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SINCE the eighth century, when aqua regia was first mentioned, according to Mellor (3), much experimental work has been carried out to determine the nature of the reactions which take place when it is prepared and used, and the ratios of the constituents which give the best results in dissolving metals. Recently Priwoznik (5), and Hoke and Moore (2) determined the best compositions for dissolving gold and platinum, respectively, as approximately 4 volumes of hydrochloric acid to 1 of nitric, for the concentrated acids. Schmitz (6) studied somewhat the corrosion of nickel and chromium steels by aqua regia, but gave practically no data on this subject. Moore (4) made several suggestions as to the cause of the activity of aqua regia. Briner (1) has examined the monovariant system of phases with the two components, nitric and hydrochloric acids (pure), and has shown that the reaction $HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O$ is reversible. In all of the literature covered no work with aqua regia of low hydrochloric acid content nor a systematic study of the dissolving of base metals by this acid mixture has been mentioned.

THE BEST CONDITIONS for the rapid solution in aqua regia of base metals, as exemplified by iron and nickel, have been determined, using ordinary laboratory concentrated hydrochloric and nitric acids and controlling the temperature only roughly. For each ratio and time of mixing before introduction of the metallic sample, the time of immersion and loss in weight are recorded, the rate of corrosion being calculated and plotted. Its greatest value is obtained at a definite acid ratio and time after mixing, the former differing greatly from the 4 volumes of hydrochloric to 1 of nitric widely used for dissolving the noble metals. For nickel, 3 volumes of hydrochloric to 40 of nitric, and for iron as low-carbon steel, 7 of hydrochloric to 20 of nitric constituted the best mixtures with approximately 30 and 12 minutes' mixing, respectively. In both cases the maximum rate of corrosion obtained is about 16 times that obtained with a 4 to 1 mixture of hydrochloric and nitric acids used at the time of maximum corrosiveness.

action on nickel than had that of standard composition, 4 volumes of hydrochloric acid to 1 of nitric. It was also found that the activity of the aqua regia as measured by the rate of solution of the metal varied with the time during which the component acids had been mixed. This would be expected by one who has worked with aqua regia and observed the color changes which take place after mixing it.

Since results of practical use were desired for the chemist who must quickly dissolve samples of metals, standard pure concentrated laboratory acids were used, approximately 70 per cent nitric and 38 per cent hydrochloric acid. These acids were directly mixed from the bottle. The composition of the resulting aqua regia was expressed in terms of percentage of hydrochloric acid to total acid, the water not being considered in the calculations. It increased, of course, as the percentage of hydrochloric acid did. In practice, excess acid is invariably used, and therefore in these experiments this was done, and the rate of solution of the metal assumed approximately constant during each run. In every case the sum of the volumes of hydrochloric and nitric acids used was 50 cc. The acid to be present in larger volume was first measured into a 250-cc. beaker, and then, at a time that was recorded, the other acid was added with gentle stirring. The metal samples measured approxi-

EXPERIMENTAL PROCEDURE

From some rough preliminary experiments it was found that aqua regia low in hydrochloric acid had decidedly more
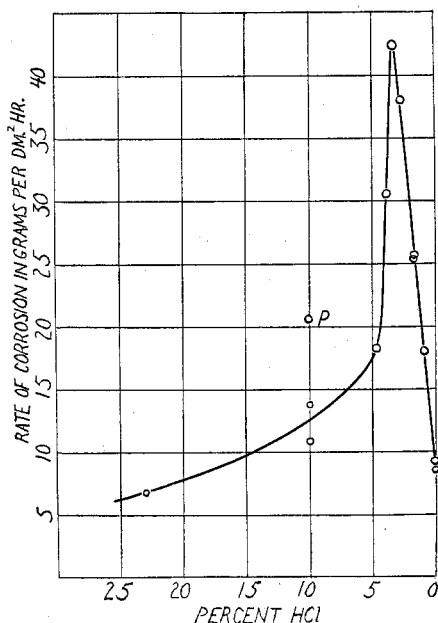
FIGURE 1. CORROSIVENESS ON NICKEL OF
AQUA REGIA PREPARED 30 MINUTES

mately 50 by 20 by 4 mm. in size, and weighed about 30
grams each. Before each run the samples to be used were
treated with a standard acid mixture for the same length
of time, assumed long enough to give them similar surface
structures. The samples were washed with water, then
alcohol, and dried and weighed. At the proper time after
mixing the acids, the metal sample was placed in the beaker
with one end supported off the bottom by means of a short
section of glass rod. This gave approximately equal convec-
tion conditions in the different runs. The action was allowed
to continue long enough to dissolve about 20 to 50 mg.,
usually 30 to 300 seconds. Then the beaker was flooded
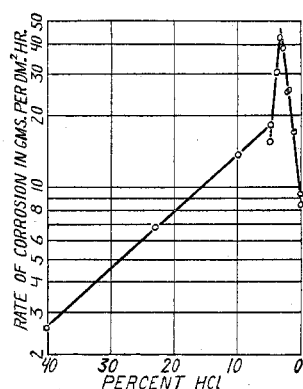with water, any surface powder washed off, and the sample

FIGURE 2. CORROSIVENESS ON
LOG SCALE OF AQUA REGIA
ON NICKEL

dried and weighed. The loss in weight was calculated to
grams per square decimeter of apparent surface per hour.
No attempt was made to determine the actual surface.
The time of mixture of the acids was computed to the middle
of the corrosion period, which was relatively much smaller
and would permit this.

RESULTS FOR NICKEL

The nickel used was in the form of annealed sheets, and
had the following analysis:

	%
Nickel	99.0
Copper	0.15
Iron	0.20
Cobalt	0.60

It was decided that 30 minutes would be a fair average
for the time required by a chemist to prepare and weigh a
sample to be dissolved, and therefore the aqua regia was
used 30 minutes after being prepared, the immersion of the
sample lasting 4 minutes more. From preliminary work
it seemed probable that this time interval of 30 minutes
would also correspond to near the time of maximum corro-
siveness of the aqua regia for nickel. The temperature was
kept between 15° and 20° C. by immersion of the beaker
when necessary in colder water. Not much heat was gen-
erated. The data are plotted in Figure 1.

There is a very definite and sharp peak of high corrosion
rate corresponding to about 3.3 per cent of hydrochloric
acid, or 1 cc. of hydrochloric to 13 cc. of nitric acid. It
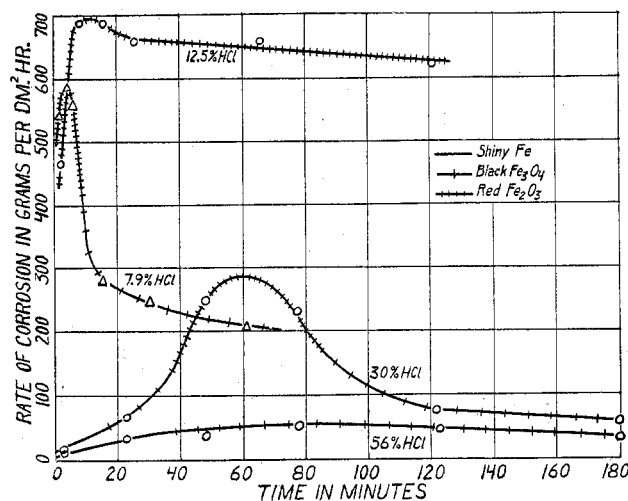was noticed that while the acid mixture was standing, streams

FIGURE 3. CORROSIVENESS OF AQUA REGIA ON LOW-CARBON
STEEL

of small bubbles were liberated at a few points of the wetted
surfaces, mainly the sharp edges of the section of glass rod
supporting the end of the metal sample. This was ascribed
to a catalytic action of a sharp edge, well known in hetero-
geneous reactions. The point corresponding to 10 per cent
of hydrochloric acid was re-run with a newly cut section of
glass rod instead of the former one, and a higher rate of
corrosion was obtained, 13.7 grams per sq. dm. per hour
instead of 10.7. Then the point was again determined,
using eight of the glass sections of the same size, about 2
cm. long and 6 mm. in diameter. The rate of corrosion was
found to have been raised further to 20.5, which is point P
in Figure 1. Thus, sharp edges either increase the speed
of only a heterogeneous reaction between the hydrochloric
and nitric acids and possibly water, giving a mixture with
the corrosiveness of one otherwise left standing longer, or
else they increase the rate of some heterogeneous reaction
over that of another, probably homogeneous. At the point
for pure nitric acid (0.0 per cent hydrochloric) the action
was not allowed to continue long enough to cause passivity
of the nickel.

An interesting result was obtained by plotting the data
on semi-log paper, as shown in Figure 2. It was seen that
three practically straight lines constitute the graph. For
each straight portion the relationship $dC/d(\%\mathrm{HCl}) = kC$
holds, where C is the rate of corrosion and k a constant for

the line. Possibly over each of these straight sections a different reaction occurs between the aqua regia and the nickel, owing to changes in the reactions that occur between the hydrochloric and nitric acids.

RESULTS FOR IRON

It was decided that the effect of varying the time of mixture of the acids on the corrosiveness of the resulting aqua regia should be more carefully investigated. The iron samples were cut from a light structural steel member which had
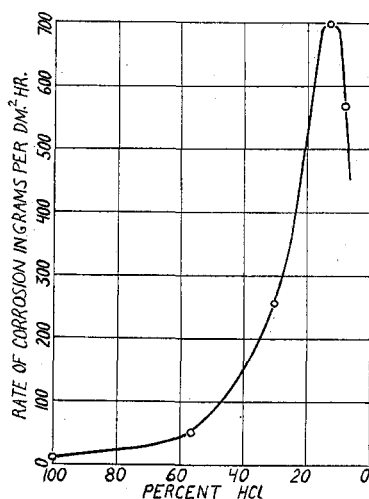

FIGURE 4. MAXIMUM CORROSIVENESS ON IRON *vs.* PER CENT HCl IN AQUA REGIA

been hot-rolled and contained 0.2 to 0.3 per cent of carbon. It was decided that actual conditions would be more closely approached if the temperature were not controlled. It also developed that owing to the more rapid action, it would have been much more difficult to control the temperature. The acids were mixed at room temperature and allowed to stand the required length of time, and the sample was inserted as before. The temperature then increased because of the action, and in several instances at points of high corrosion it reached the boiling point. Thus, if the temperature had been maintained low, the peaks of the rate of corrosion curves would have been lowered considerably, and the rest of the curves lowered somewhat also.
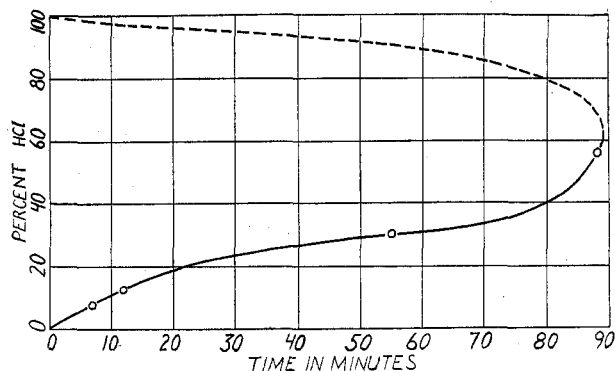

FIGURE 5. TIME OF MIXING FOR MAXIMUM CORROSIVENESS ON IRON *vs.* PER CENT HCl IN AQUA REGIA

Rates of corrosion were determined after varying times of mixing for aqua regia containing 56, 30, 12.5, and 7.9 per cent of hydrochloric acid. The results are plotted in Figure 3. It is seen that clearly defined peaks are obtained with the maximum rate of corrosion corresponding to a definite time of mixing the acids for a given aqua regia composition.

From these curves the maxima were taken and plotted against the corresponding percentages of hydrochloric acid in Figure 4, from which the maximum rate of corrosion for any given aqua regia composition can be obtained. From Figure 5 the requisite time of mixing the acids to give the maximum rate of corrosion can be obtained for a given aqua regia composition. It is seen that the highest rate of corrosion, 700 grams per sq. dm. per hour, corresponds to about 12 to 14 per cent of hydrochloric acid, and that it is obtained after 10 minutes' standing, although after about 5 minutes the corrosiveness has reached 600 and does not drop below this value for about 3 hours. This aqua regia is made from 7 cc. of hydrochloric acid and 20 cc. of nitric. If the samples had been left in long after boiling started, the rates of corrosion would be considerably increased.

These experiments took on added interest when it was observed that different products were formed by the action when differently constituted aqua regias were used. When the rate of corrosion was low, all of the iron dissolved passed to the form of ferric ions. However, at higher rates of solution, Fe_2O_3 or Fe_3O_4 was formed, either simultaneously with the ferric ions or as an intermediate step. At the highest rates only Fe_2O_3 was formed, besides ferric ion. These results are shown in Figure 3; no smaller ones have been seen mentioned anywhere in the literature.[1] These oxides were obtained on the surface of the samples after flooding at the end of the run. They were fine adherent powders, but easily wiped off, and usually did not cover the surface uniformly or entirely. The two oxides were never found together on the same sample. Their mass was always only a small fraction of the mass of the metal dissolved. Thus, an appreciable part of the action of aqua regia, if not a large part, at high rates of corrosion, forms oxides as an end product, probably owing to the nitric acid. The acids and ions present would cause some dissolving of the oxides, which must take place more slowly than their formation at these high corrosion rates.

Iron as a silicon iron was also studied for corrosion by aqua regia. The samples had the following composition:

	%
Silicon	14.5
Manganese	2.2
Carbon	1.0
Sulfur	0.1
Phosphorus, about	0.5
Iron, balance	81.7

The action on this metal was so slow as to be almost within the experimental error of the weighing for the time intervals of immersion that could be used. No water was added to the aqua regia; it is probable that more dilute acid would have more rapidly corroded the alloy.

ACKNOWLEDGMENT

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