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<u>Dissolution Rates of Zone Refined Iron
and Steel in HCl, H$_2$SO$_4$ and NaCl Aqueous
Solutions</u>

by

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Corrosion Rates of Zone Refined Iron and Steel

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Abstract

Zone refined iron is slowly attacked by acids. Rates obtained in

0.5 N H_2SO_4 and HCl are 5.6×10^{-2} and 2.3×10^{-2} mg $cm^{-2}hr^{-1}$ resp., at

25°C in the presence of air. In hydrogen the dissolution rates are

slower. In a 3% NaCl solution the rate is about one fifth of that in

0.5 N HCl. The order of reaction starting with I N H_2SO_4 is above 2,

indicating that the rate is unduly slowed down at low concentrations of

the acid and that the resistance to corrosion decreases with increasing

concentration of the acid.

The dissolution rates of two steels containing among other impuri-

ties 0.44 and 0.85% C respectively, were determined in various

concentrations (up to 7 N) of H_2SO_4 and HCl as a function of temperature

(between 15 and 25°C). It was found that the reaction order in H_2SO_4

is close to 1 and that in HCl is above 2; the reaction rate constants

were high in H_2SO_4 in comparison with those in HCl; the temperature

coefficients of the reaction rates were close to 2 and the activation

energies between 12 and 16 kcal/mole. This suggests that the dissolu-

tion rates are electrochemically controlled. The higher rate in H_2SO_4

(than in HCl of the same concentration) can be explained by the faster

disintegration of the steel (and also of pure Fe) in H_2SO_4. The rate

of dissolution increases with increasing amounts of C if its

concentration is small, but this relation may reverse at higher than 0.4% carbon in iron.

I. Zone Refined Iron

Introduction

Although there is extensive literature concerning the rates of corrosion of various kinds of iron, iron alloys and steels[1] in various liquids and aqueous solutions, very little is known about the attack of high purity iron by the same agents.[2]

The objective of the present investigation is, therefore, to narrow this gap by supplying data on rates of dissolution of zone refined iron in HCl, H_2SO_4 and NaCl aqueous solutions in the presence of air and in a hydrogen atmosphere (for H_2SO_4).

Materials

The high purity zone refined iron was obtained from the Battelle Memorial Institute in the form of a rod 32 mm in diameter and 15 cm in length, weighing about 615 g.

This sample was prepared from a special electrolytic iron which was induction melted in vacuum to partially remove the dissolved gases. It was then further refined by passing a molten zone through the bar. The operation of "floating zone-melting" was carried out in ultra-pure hydrogen. The analyses of the bar and of the special electrolytic iron were carried out by the Battelle Memorial Institute[3].

Table 1

Non metallic impurities of the zone-refined Fe-bar in parts per million
(=0.0001% by weight)

Oxygen	1.7	Hydrogen	0.2
Carbon	9 ± 4	Sulfur	5 ± 3
Nitrogen	0.2		

The concentration of the other elements present in the electrolytic iron is given in Table 2.

Table 2

Metallic impurity content in parts per million detected in the electrolytic Fe, vacuuminduction melted

Al	- 15	Cr	- 5	Mn	- 0.5
Be	- < 0.2	Co	- 5	Ni	- 20
Cd	- 5	Co	- 7	P	- 9
Ca	- <10	Mg	- >5	Si	- 10

After zone refining of the bar the concentration of the impurties as given in Table 2 did not change detectably.

All other chemicals used were of reagent grade.

Procedure

The high purity iron was attacked so slowly by strong acids that it was difficult to follow the rate of dissolution by the hydrogen volume evolved[4]. The weight loss method was, therefore, chosen.

Disks of about 3 mm thick were cut from the rod, and from these rectangular plates were prepared of approximately 10 x 20 mm. A small hole was drilled near one end of each plate in order to suspend them into the corrosive liquid. All the surfaces of the samples were smoothed with emery paper, measured with a caliper and weighed on an analytical balance.

The simple experimental arrangement is shown in Fig. 1. A are the samples on glass hangers, B is a 500 ml vessel closed with a tight rubber stopper, C is a glass tubing fitted with a stopcock to purge the reaction vessel with an inert gas and D is a glass cross arm to a water seal to take care of the increase of the gas volume in B.

The influence of the oxygen of the air on the rates of dissolution was checked by replacing the air in B with hydrogen. A volume of 150 ml of the desired electrolyte of known concentration was introduced into the vessel containing the samples suspended from glass hangers. For experiments in H_2SO_4 the vessel was flushed with H_2 and carefully sealed. The time and the temperature, $(25 \pm 2°C)$, were recorded.

At the end of approximately 24 hours the samples were removed, rinsed in distilled water, and then in acetone, dried under vacuum, and weighed. Then the samples were replaced into the solutions, and the time recorded again. From the weight loss w the velocity V of the reaction was calculated:

$$V = w/A\Delta t$$

where Δt is the time increment (in hours) and A - the surface area of the corroding sample in cm^2. The corrosion rate was expressed in $mg\ cm^{-2}hr^{-1}$. Only rates over a period of 0 to 150 hr were recorded. No corrections were made for the decrease in acid concentration nor for changes in the actual surface area of the samples with time. Duplicate samples were prepared to minimize the experimental error. The acid was not stirred.

Results

Sulfuric acid. The dissolution of Fe was carried out at 4 different acid concentrations at room temperature in the presence of air. As seen from Fig. 2, the rate increases sharply with acid concentration[5].

The order n of the reaction was determined from the log log plot of the rate V versus concentration N of the acid. As can be seen from Fig. 3, the order of the reaction, starting with the 1 N concentration, is about 2.53 in stagnant H_2SO_4.

It was confirmed that the rate of dissolution of Fe in oxygen containing H_2SO_4 is faster than that in a hydrogen saturated acid. The average rates obtained are summarized in Table 3.

The rates in separate experiments differed greatly as the high purity Fe samples were attacked non-uniformly. Deep pits were present on the plates after the dissolution experiments; however, they were arranged in rows corresponding to the crystallographic orientation of the grains. Some of the crystallographic planes, probably the (111), exhibited only a few etch pits and the planes were smooth and nearly parallel to the surface. Fig. 4 shows portions of 2 grains. The upper one is less strongly attacked. The black grain is corroded and is lower in height, only the nearly parallel ridges are close to the surface of the upper crystallite. There were also crystallites in the same sample which were very smooth (Fig. 5). Thus, depending upon the orientation of the crystallites in the samples, the rate of corrosion should differ considerably.

Hydrochloric acid. It was even more difficult to obtain reasonably reproductible rates in HCl. However, as can be seen from Table 3, they
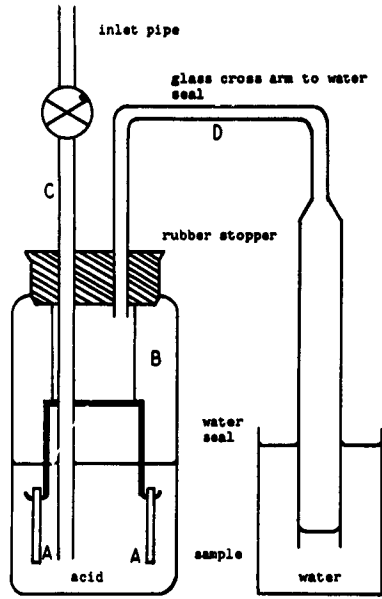
Fig. 1
Dissolution rate apparatus for
the weight loss method.
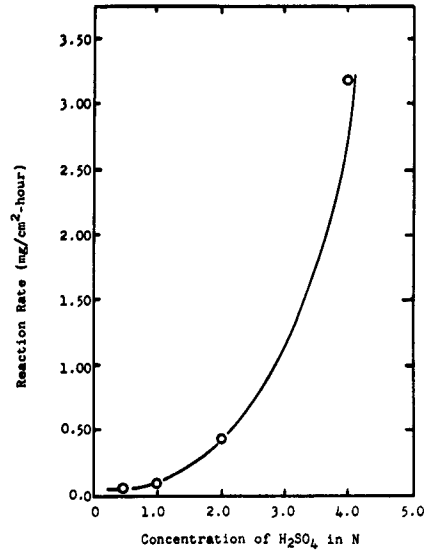

Fig. 2
Reaction rate V of high purity Fe
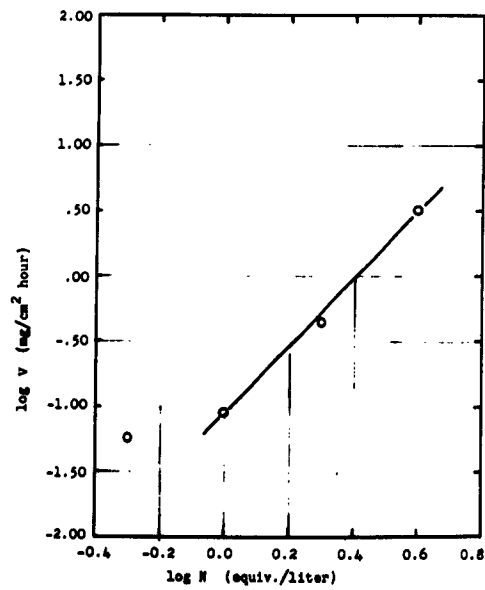versus concentration of H_2SO_4 in the
presence of air.

Fig. 3
logV versus logN for high purity Fe
dissolving in H_2SO_4 in presence of air

Fig. 4
High purity Fe surface
after corrosion in 1 N H_2SO_4
for about 180 hours 145x

Fig. 5
Another grain of the same
sample (Fig. 4) shows a
much lesser attack. 145x

are all significantly lower in (oxygen containing) HCl than in H_2SO_4.
As to the effect of increasing the concentration of HCl, it seems that
at lower concentrations (0.5 to 2N) the rate even decreases slightly and
then increases strongly with concentration. Because of all the irregu-
lar rate fluctuations, the measurements in HCl were discontinued. The
surface of the samples exhibited, after the experiments, a pronounced
preferred orientation of attack.

Sodium chloride solution. Table 3 also lists the corrosion rate of high
purity iron in an aqueous 3% NaCl solution. The rate turned out to be
about one fifth as fast as the rates in 0.5 N acid solutions.

In the NaCl solution a brown film formed on the iron surface. This
film fell periodically from the surface to the bottom of the reactor
vessel.

Discussion and Conclusions

The results of the present investigation are all listed in Table 3.

Table 3

Corrosion or dissolution rates* of high purity zone refined iron in
NaCl, H_2SO_4 and HCl solutions at 25 $\pm$ 2°C.

Concent.	3%	0.5 N	1.0 N	2.0 N	4.0 N	5.0 N
Solutions			Rates in mg cm^{-2} hr^{-1}			
NaCl	7.4×10^{-3}	—	—	—	—	—
H_2SO_4 open to air	—	5.6×10^{-2}	9.6×10^{-2}	43.9×10^{-2}	321×10^{-2}	—
H_2SO_4 hydrogen saturated	—	4.6×10^{-2}	—	—	—	—
HCl open to air	—	2.3×10^{-2}	2.1×10^{-2}	2.0×10^{-2}	—	333×10^{-2}

*These are rates over a period of 150 hrs in test.

A comparison of these results with a previous investigation made with carbonyl iron (obtained by thermal decomposition of Fe-carbonyl), reveals the rates to be higher than those previously obtained[2]. For instance, the final rates obtained for carbonyl iron in 6 and 10 N H_2SO_4 were 3.0 and 3.59 mg $cm^{-2}hr^{-1}$ respectively, as compared with 3.2 (Table 3) in the 4 N acid. In highly concentrated HCl (10 to 11.45N) the final rates for carbonyl iron fluctuated between 2.0 to 2.5 while for zone refined iron they were 3.3 mg $cm^{-2}hr^{-1}$ in a 5 N HCl. In part, the lower rates obtained with carbonyl Fe may be explained by its smaller C content: 7 ± 2 p.p.m. (see table 1).

These results seem to indicate that the carbon content at very low concentrations is still responsible for the increased rate of corrosion of very pure iron.[6, 7, 8]

In both investigations it was found that the rate of corrosion in H_2SO_4 is faster than in HCl of the same normality (see Table 3), although the hydrogen ion concentration is larger in the latter. The reasons for this behavior could not be determined with the high purity material because of its very slow reaction with acids and the strong fluctuations in rates. Therefore, a less pure Fe was chosen in order to determine the activation energies of dissolution, the reaction rate constants, the reaction order, the average temperature coefficients and the possibility of disintegration of the metal, since it seemed reasonable that the knowledge of these qualities would contribute to explanation of the higher corrosive activity of Fe in H_2SO_4.

II. Carbon Steel

Introduction

The activation energies obtained for the dissolution reaction of carbon steels in acids ranged from 4.5 to 32.9 Kcal/mole, depending upon conditions of dissolution. Abramson and King[9] found activation energies of 4.5 to 5.1 Kcal/mole at stirring speeds of 2000-8000 rpm for iron dissolving in HCl in presence of sufficient amounts of a depolarizer. At higher stirring speeds (above 10,000 rpm) and lower acid concentrations they calculated activation energies between 12.2 and 14.4 Kcal/mole. Akulov and Khimchenko[7] obtained activation energies which varied from 30.9 to 32.9 Kcal/mole.

Therefore, it was of interest to know the activation energies of two steel samples containing various concentrations of impurities, dissolving at a slow stirring speed in aqueous solutions of H_2SO_4 and HCl.

The activation energies were calculated from the Arrhenius equation, which in turn, requests the knowledge of the reaction constants k at various temperatures. These values were obtained from

$$k = c^n/V \qquad (1)$$

where n represents the reaction order, c - the concentration of the acid (in N) and V - the velocity (or rate) of the dissolution reaction expressed in mm^3 of hydrogen per min and each cm^2 of the surface area A of the dissolving steel. The reaction rates were determined from

$$V = \Delta v/\Delta tA \qquad (2)$$

where Δv is the amount of H_2 (in mm^3) developed during the time Δt(min).

Since the dissolution reaction has the stoichiometry[4)]

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (3)$$
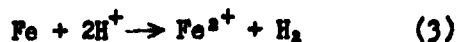
and the rate of increase of H_2 corresponds to the rate loss of Fe, the velocity of reaction V can easily be converted from $mm^3 cm^{-2} min^{-1}$ into $mg cm^{-2} min^{-1}$, simply by multiplying the number of mm^3 by 2.4916×10^{-3}. The hydrogen volume, in all cases, was reduced to standard conditions (STP).

Materials and the Dissolution Apparatus

The steel samples were prepared by the U.S. Steel Corporation, E.C. Bain Laboratory for Fundamental Research, Monroeville, Pennsylvania. From the five kinds of steel samples (about one foot long, one inch wide, hot rolled to a thickness of 1/8 inch) two were chosen containing all impurities of the same order of magnitude, except for C, which differed by a factor of about two. The analyses supplied with the steel samples No 1 and 4 (USS 1045 and 1085) are given in Table 4. The difference in C content would also reveal the

Table 4

Analyses (in % by weight) of the 2 steel samples (balance-Fe).

Admixture	Samples No. 1	No. 4
C	0.44	0.85
Mn	0.86	0.70
P	0.027	0.023
S	0.035	0.030
Si	0.20	0.25

influence of this element (present in considerable amounts) on the dissolution rate of this steel.

The acids used were of reagent grade and conformed to ACS specifications.

The dissolution of Fe and steel in nonoxidizing acids proceeds according to reaction (3) and the rate can be followed by collecting the hydrogen volume evolved. The equipment used for the determination of dissolution rates was similar to that described previously[10]. The reaction flask (for the acids) had a capacity of 500 ml. A polyvinyl chloride foot was attached to the mercury seal stirring mechanism to hold the steel sample. The entire assembly was immersed in a water bath, the temperature of which could be controlled within $\pm$ 0.1°C. The hydrogen was collected over distilled water in a 100 ml gas burette by means of a leveling bulb.

The samples were prepared by cutting the steel strips into squares of 1 cm² area exposed to the acid. All the other sides were insulated. To prevent extensive edge attack by the acids the sides (except 1 cm²) were covered with epoxy cement. After hardening of the cement the samples were mounted in lucite. The excess lucite was trimmed and the exposed metal surface ground with 3/0 grit metallographic paper. Then the samples were attached to the foot of the stirrer, which in all experiments had a rate of about 200 r.p.m. In order to prevent the oxidation of Fe^{2+} to Fe^{3+} by the oxygen in the flask, the air was replaced by H_2 prior to the experiment. Each of the dissolution rate measurements were performed at least twice in order to minimize the experimental error.

Results

Plots of the volume of H_2 reduced to STP, against time were prepared. These plots turned out to be mostly linear, indicating that there is only a short induction period in the dissolution reaction.

Therefore, there was no need to continue the dissolution experiments for longer periods of time, since a duration of 1 to 2 hours was sufficient. An example of the accumulation rate of H_2 is given in Fig. 6.

All other experiments gave plots more or less similar to Fig. 6. The rate of dissolution was then simply calculated from the inclination of the straight part of the curve. As the dissolution has to start with a zero rate, the time up to the straight line represents the duration of the induction period (about 10 min in Fig. 6).

After the dissolution experiments the surface of the steel samples was not evenly attacked but pitted. No corrections could be made for the increase of the actual reaction surface. The change in concentration of the acids, as the reactions proceeded, was small and was disregarded.

Sulfuric acid. The dissolution rates of samples 1 and 4 turned out to be proportional, within the limits of experimental errors, to the concentration of the acid even at various temperatures used (15, 25, 35, 45, and 55°C). A plot is given in Fig. 7.

In Table 5 all the dissolution rates obtained with the two samples are summarized and the rates can be compared.

Table 5

Dissolution rates of samples 1 and 4 in H_2SO_4; 200 r.p.m.
Composition of the samples see Table 4.
Rates in $mm^3cm^{-2}min^{-1}$

N \ Temp. °C Sample	15 1	4	25 1	4	35 1	4	45 1	4	55 1	4
0.5	-	-	-	-	-	-	-	-	70.2	-
1.0	-	-	-	-	-	-	59.8	-	122.0	59.7
1.5	-	-	-	-	-	-	-	-	133.0	65.5
2.0	-	-	-	-	54.3	-	122.5	-	203.0	108.6
2.5	-	-	-	-	-	-	-	-	-	-
3.0	17.3	11.9	39.5	21.0	63.3	30.7	157.0	73.6	-	-
4.0	25.5	13.8	57.0	25.1	108.2	46.3	228.0	98.9	-	-
5.0	34.0	21.8	76.0	34.0	119.7	50.9		110.9	-	-
6.0	43.2	22.4	96.0	43.0	-	67.8		134.4	-	-

By multiplying these rates with 2.4916×10^{-3}, rates in $mgcm^{-2}min^{-1}$ are obtained.

Contrary to expectations the increased amount of C (sample 4) caused not an increase, but a decrease in rate.

To obtain the reaction order, the log of rate was plotted versus the log of concentration (Fig. 8). From the inclination of the straight line the order n (eq. 1) was calculated. A reaction order of 0.97 ± 0.20 was obtained for sample 1, and 1.02 ± 0.05 for sample 4. It seemed advantageous to plot the log V not against log N (equat. 1) but against the experimentally determined pH. The n from this plot 0.98 ± 0.2 compares favorably with 0.97 ± 0.2 calculated from the plot against normality (see Table 7.)

The reaction rate constants k (eq. 1) were calculated knowing the order n and are listed in Table 8.

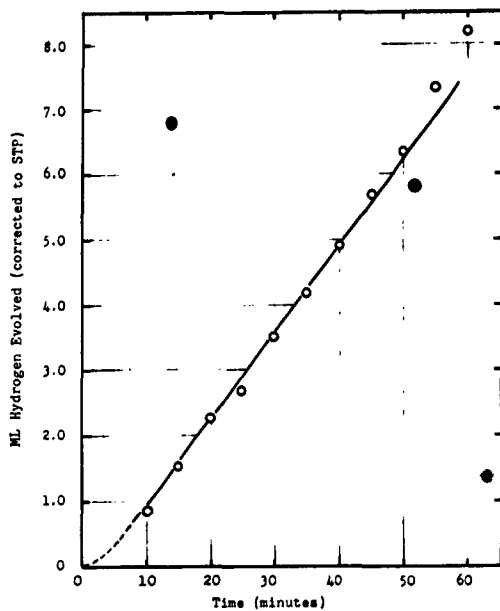The temperature coefficients for both samples using 4 temperature intervals of 10° are summarized in Table 9.

Fig. 6
H₂ evolution from steel sample No. 1
in 3.0 N H₂SO₄ at 45°C. Rate calculated:
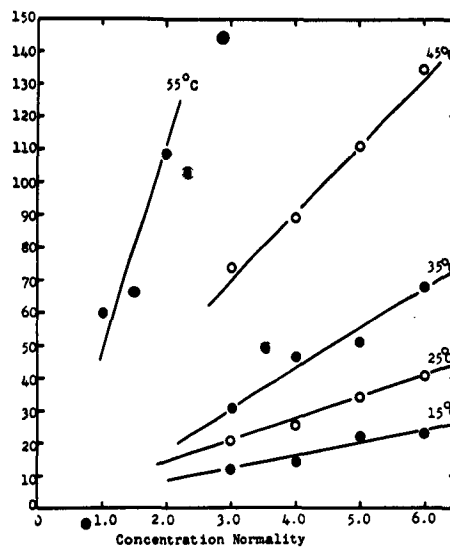135 mm³ min⁻¹ cm⁻² or 0.336 mg min⁻¹ cm⁻².

Fig. 7
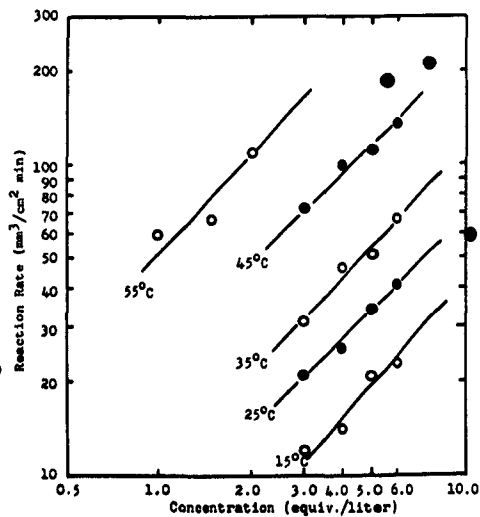Reaction rates of sample 4 versus concentration
of H₂SO₄ at various temperatures.

Fig. 8
Reaction order n for the dissolution
of sample 4 in H₂SO₄ log-log plot.

Finally the activation energy was calculated from the Arrhenius equation of the form

$$\ln k = \ln A + (-E*/RT) \qquad (4)$$

where k is the reaction constant (eq. 1, Table 8), A - a frequency factor, E* - the activation energy (in Kcal/mole), R - the gas constant (cal/mole deg) and T the absolute temperature (°K). If now lnk is plotted versus 1/T, assuming that A is a constant, a straight line, the slope of which is -E*/R should be obtained. Fig. 9 shows how well the straight lines pass through the experimental points. 13.4 and 12.7 Kcal/mole were obtained for samples 1 and 4 respectively.

Hydrochloric acid. The rates of dissolution of samples 1 and 4 in this acid were lower and were subjected to greater fluctuations than in H_2SO_4. The rate-concentration curves were not linear throughout. However, an approximate straight line could be drawn through the experimental points. These curves were used to obtain the reaction order, rate constants, temperature coefficients and finally the activation energies. In table 6 the rates of the dissolution reaction (3) in HCl are listed. Again, the rate of dissolution of the sample 4, richer in carbon, is lower.
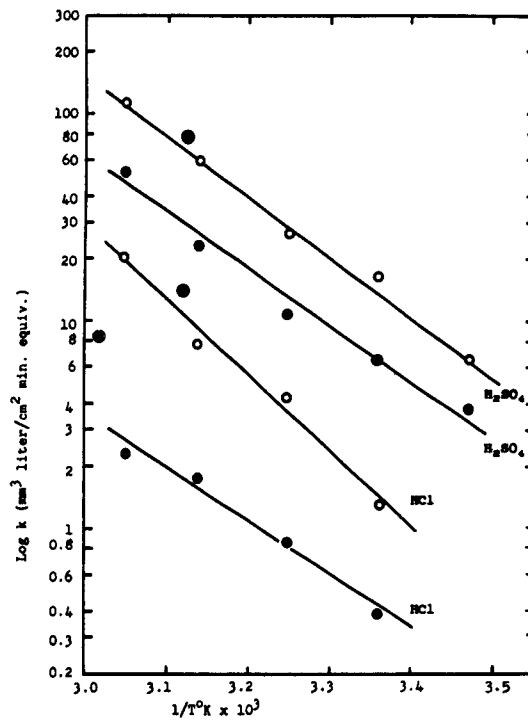
Fig. 9
Logk versus 1/T°K for the samples1(circles) and 4
(full circles) dissolving in H_2SO_4 and HCl.

Table 6

Dissolution reaction rates of samples 1 and 4 in HCl; 200 r.p.m.
Composition of the samples see Table 4.

N \ Temp.°C	25° Sample 1	25° 4	35° 1	35° 4	45° 1	45° 4	55° 1	55° 4
1.0	-	-	-	-	30.3	-	48.5	-
2.0	-	-	27.3	-	34.6	17.6	98.1	-
2.5	-	-	-	-	-	-	121.5	18.0
3.0	15.3	-	45.9	25.0	67.9	31.9	205.0	44.3
3.5	-	-	-	-	-	-	-	65.7
4.0	19.6	18.8	84.3	32.8	142.9	61.9	-	98.1
5.0	38.9	34.8	137.0	62.1	-	129.7	-	-
6.0	68.6	52.4	-	116.1	-	-	-	-
7.0	-	77.2	-	-	-	-	-	-

By multiplying these rates with 2.4916×10^{-3} rates in $mg\,cm^{-2}min^{-1}$ are

obtained.

The reaction order was determined and the data obtained for both

acids are summarized in Table 7. From this table the fact follows

Table 7

Reaction order n (equat. 1) for samples 1 and 4
dissolving in HCl and H_2SO_4

Reaction Order n

°C \ Acid Sample	H_2SO_4 1	H_2SO_4 4	HCl 1	HCl 4
15	0.99	0.99	-	-
25	1.15	1.04	2.67	2.63
35	1.08	1.07	2.00	3.02
45	0.85	0.99	1.88	2.72
55	0.76	0.99	2.03	2.71
Average	$0.97^{\pm}0.2$	$1.02^{\pm}0.05$	$2.15^{\pm}0.5$	$2.77^{\pm}0.3$

that the reaction order in HCl is above 2, while the reaction in H_2SO_4

is first order.

The reaction rate constants obtained in both acids are given in

Table 8. In both acids a lower rate constant is obtained with the sample 4, having a higher C-content. Comparing Tables 7 and 8 it appears

Table 8

Reaction rate constants k (equat. 1)
at different temperatures for samples 1 and 4 in H_2SO_4 and HCl.

Acid	H_2SO_4		HCl	
Sample Temp. °C	1	4	1	4
15	6.59	3.79	-	-
25	16.5	6.55	1.24	0.38
35	25.9	10.6	4.22	0.85
45	59.2	22.9	7.43	1.73
55	113.0	52.3	20.3	2.23

that a high rate constant goes with a low reaction order (in H_2SO_4) and vice versa (in HCl).

The following relation was used for the calculation of the temperature coefficient per 10°C:

$$\text{Temp. coeff. per } 10°C = V_{(t + 10°)} / V_t \qquad (5)$$

According to Abramson and King such a temperature coefficient, if less than 1.5, indicates that the reaction is diffusion controlled, but if between 2.0 and 2.2, the reaction is electrochemically controlled. The temperature coefficients obtained are listed in Table 9. Each of the coefficients is larger than 1.5

Table 9

Temperature coefficients of reaction (3) in H_2SO_4 and HCl

Average temperature coefficients (of 4 concentrations)

Acid	H_2SO_4		HCl	
Sample Temp. °C	1	4	1	4
15-25	2.25	1.74	———	———
25-35	1.69	1.62	3.68	1.91
35-45	2.28	2.24	1.48	1.75
45-55	1.85	———	2.48	1.48
Average	2.02	1.87	2.55	1.71

and the average of all is above 2.0. So it appears that electro-chemical control is predominant.

The activation energy E* was calculated from Eq. (4), and the log k versus 1/T°K slopes (Fig. 9): 16.5 and 11.7 Kcal was obtained in HCl for the samples 1 and 4 respectively. These values as well as those in H_2SO_4 (13.4 and 12.7 Kcal) suggest that the slow step is electrochemically controlled[9].

Disintegration of the Fe-Samples

Zone refined Fe. So far, the results did not explain why samples of iron dissolved faster in H_2SO_4 than in HCl. The suspicion arose that metallic disintegration might have proceeded at a faster rate in H_2SO_4 than in HCl. Disintegration of metals was observed previously during anodic and self dissolution.[11, 12, 13]

Therefore, zone refined iron was introduced, as an anode into solutions of H_2SO_4 and HCl. At current densities up to 1 amp/cm² in less than 1 N H_2SO_4 the solutions remained clear. However, when the current density in 1 N H_2SO_4 was increased to 2.4 and more (amp/cm²),

a black dispersion in the form of very fine particles was observed at
the anodic surface. Unfortunately the dispersion (by dissolution in
the acid) disappeared before it could be washed free of acid. It is
very probable that the dark dispersion consisted of metallic Fe
particles.[14] Large black particles were also observed in the solution,
which quickly dissolved.

In HCl a fluffy brown precipitate was observed to fall from the
anode. However, there was no microscopic evidence for the presence of
metallic particles in this substance.

Disintegration of sample 1. A black deposit was noticed to have
formed on the surface of the steel samples in both H_2SO_4 and HCl acids
after a short period of exposure. This deposit formed more readily in
H_2SO_4 than in HCl. After a period of about one hour the H_2SO_4 itself
started to discolor and then the solution became dull gray. In HCl, even
after 6 hours, the solution remained clear.

It was suspected that the discoloration of H_2SO_4 arose from the
carbon of the metal (see Table 4). To collect larger amounts of the
dispersion, (which slowly settled) 2 x 3 cm pieces of sample 1 were
placed in 5.0 N H_2SO_4. After one half hour the solution became gray and
a black deposit was observed on the bottom of the reaction vessel. The
acid was decanted from the deposit, rinsed with distilled water and
finally washed with acetone. Then the dry deposit was examined in the
reflecting light of an optical microscope at high magnification
(1430x oil immersion). A number of specks exhibited a metallic luster
(see Fig. 10, a and b). Some of them were dispersed in a brown-pink

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Fig. 10
Bright particles (iron chunks) of metallic luster
formed as a result of attack of steel,(sample 1),
by 5.0 N H_2SO_4; above - larger chunks;
below - smaller particles. 1430x.

substance. In transmitted light the shiny particles appeared as opague
spots, characteristic of particles of higher density. X-ray powder
pictures of the black deposit showed the definite presence of lines of
free iron. The black particles consisted, therefore, of iron and were
observed in all instances to come from the surface of the steel samples.

Formation of black particles during dissolution of sample 1 in HCl
was not observed. In order to check the surface of the dissolving metal
for the presence of Fe chunks, the surface was washed using a soft rub-
ber policeman. Some single particles were collected in this way and
the microscope revealed that they had the same general appearance as
those formed in H_2SO_4.

Discussion and Conclusions

The data of the second part of this investigation are summarized
in Table 10. According to Abramson and King[9] there is a general

Table 10

Summary of the activation energies E*. The reaction rate constants k,
the reaction orders n, and the average temperature coefficients c_t.

	H_2SO_4		HCl	
	Sm I	Sm. IV	I	IV
E* cal/mole	13.4×10^3	12.7×10^3	16.5×10^3	11.7×10^3
k at 35°	25.9	10.6	4.22	0.85
n	$0.97 \pm .2$	1.02 ± 0.5	2.15 ± 0.4	2.77 ± 0.2
C_t(per 10°C)	2.02	1.87	2.55	1.71

relation between the activation energy, the temperature coefficient,
and the controlling mechanism of a dissolution reaction. For electro-
chemically controlled reactions they found temperature coefficients
from 2.0 to 2.2/10°C and activation energies in the range of

11 to 14 kcal/mole. For diffusion controlled dissolution mechanisms these figures are substantially lower. Table 10 shows a temperature coefficient between 1.71 to 2.55 and an activation energy in the range of 11.7 to 165 Kcal/mole, which strongly suggests that the dissolution of both steels in H_2SO_4 and HCl is electrochemical in nature. There are large fluctuations in the same values obtained in HCl (Table 10), which indicates that the formation of some protective layers alters the dissolution rates in an uncontrollable manner. Activation energies up to 16 Kcal could also be obtained for sample 4, if the curves were drawn differently (but still permissibly) through the experimental points. In such a case the activation energies for steels dissolving in HCl would be significantly larger than those in H_2SO_4, indicating that the resistance to dissolution is larger in HCl. As a result iron dissolves faster in H_2SO_4 than in HCl. This accelerated rate is explained by the more rapid disintegration of Fe and steel in H_2SO_4 than in HCl. In the former acid the separation of the Fe particles was very rapid as evidenced by the fast discoloration of the acid, which did not occur in HCl. Therefore, during the dissolution of Fe and steel in H_2SO_4, particles of the metal constantly separated from the surface exposing fresh metal to the action of the acid. This phenomenon as well as the rapid dissolution of the separated particles in the acid increase substantially the rate of dissolution, lowering the activation energy and increasing the reaction constant k.

The reaction order n is very close to 1 for the steel dissolving in H_2SO_4 suggesting that the total rate of dissolution (including the disintegration) is directly proportional to the concentration of the acid. However in HCl the reaction order is larger than 2, and the reaction constant k is low. This can only be explained by the assumption that in HCl of low concentration some protective films (in the form of basic salts) are present on the surface of the metal and decrease the active surface exposed to the acid. Evidently, these salts are more soluble in HCl of increased concentrations, a larger extent of the metallic surface area becomes exposed to the action of the acid and the rate of disintegration may also increase. As a overall result the rate of dissolution increases faster than expected with increasing concentration of the acid.

The fact that the steel of lower C content dissolves faster than that of higher (see Tables 5 and 6) is not expected and is difficult to explain. Usually rate increases with augmentation of the C content[7]. However, there is the possibility that the presence of Mn somehow balanced the increase in rate which should be expected due to the presence of larger amounts of C.

The low corrosion rates obtained with zone refined Fe are, however, in agreement with the theoretical expectations that the decrease of the concentration of impurities decreases the rate of corrosion.

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