

SOLUTION RATE AND POTENTIAL OF DISSOLVING CHROMIUM

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Notwithstanding the large number of research papers on the reaction of metals with solutions, little research has been done on the kinetics of the reactions between metals and concentrated solutions of acids. Moreover, almost all published research on the reactions of metals with acids are marked by the absence of a parallel determination of the potential of the metal in solution. And when the potential of the metal being dissolved is unknown, any effort to handle the observed behavior patterns of the metal's rate of solution becomes too arbitrary a matter.

The present paper is one of a series of research projects carried out in our laboratory on the parallel investigation of the rates of solution and the potentials of dissolving metals.*

EXPERIMENTAL METHOD

In the present research we employed, in the main, the same experimental method as in the earlier paper by the present authors on the rate of solution of magnesium [2], and we shall therefore take up in detail at this point only those factors in which our present method differs from those described in the paper mentioned.

Preparation of Sheets of Electrolytic Chromium

In the present research we investigated the rate of solution of sheets of electrolytic chromium, which were prepared in the following manner.

The electrolyte consisted of a 25% solution of chromic anhydride, slightly acidulated with sulfuric acid. Electrolysis was effected with a current density of 60 amp per sq. dm. of cathode surface, at a temperature of $25^{\circ} \pm 1^{\circ}$. We used a cathode of type metal. A cathode of this metal is convenient, for it does not deform even when a thick layer of chromium is deposited on it, and, besides, it dissolves easily in nitric acid. The back of the cathode was covered with bakelite lacquer; its front surface was divided into several parts by thin transverse strips of bakelite lacquer. The cathode was then subjected to heat treatment to polymerize the bakelite.

After electrolysis was complete, the cathode, together with the chromium deposited thereon, was cleaned of its bakelite and then subjected to the action of dilute nitric acid, the base of the cathode dissolving, and the chromium falling apart into separate sheets (according to the bakelite divisions). The edges of the chromium sheets thus obtained, 0.5 to 0.7 mm thick, were ground down on a carborundum wheel until the sheets were rectangles 1.5 x 3 cm in size. The sheets were again carefully washed in nitric acid and then in distilled water, after which they were placed in a special holder in the instrument for dissolving metals. The instrument as well as the metal holder are described in the above-mentioned paper by the present authors [2], (p. 237, Fig. 1).

* It should be stated that this research was completed before World War II, some of the experimental results having been published in Y. V. Durdin's article 'Electrochemical Mechanism of the Solution of Metals in Acids' [1].

In the present investigation the metal holder was modified so as not to end in a glass scoop for attaching a magnesium cylinder, but in a flattened glass bell, open at the bottom, within which a chromium sheet was attached with dental cement. To make the contact necessary for measuring the potential of the dissolving chromium, mercury was poured into the bell of the holder; this provided a fully dependable contact with the chromium sheet protruding beyond the edge of the cement.

On the outside, the cement, the rear surface of the sheet, and its edge were covered with bakelite lacquer, after which the whole was subjected to heat treatment to polymerize the bakelite. This operation was repeated 2-3 times. It should be mentioned that the shining side of the sheet, which faced the cathode during electrolysis, was covered with bakelite, while dissolution took place on the outer, grayish-velvety surface of the sheet.

Moreover, the chromium deposited in a freshly prepared bath may contain some impurities, and we therefore did not use the chromium obtained in the first 3 or 4 electrolyses. The chromium deposited thereafter was extremely pure. Spectral tests disclosed the presence of absolutely no impurities.

We used chemically pure hydrochloric and sulfuric acid of domestic origin in our experimental research on the solution rate of chromium. Dissolution was effected in apparatus of the type described in the above-mentioned paper by the present authors. In the present research, the volume of the apparatus was increased to 1.5 liters, and as a result the acid concentration did not vary by more than 1 or 2% even in the most prolonged tests.

Before starting a test, the solution in the apparatus was always saturated with hydrogen. The rate of solution of the metal was measured by the amount of hydrogen liberated, using a gas burette. The rate of solution of the chromium, v , was always expressed in terms of cubic centimeters of hydrogen* liberated per minute per square centimeter of chromium surface.

The potential of the dissolving chromium was measured by a compensation method with respect to a saturated calomel electrode. Henceforth, we shall call this potential, but with a plus sign, the potential of dissolving chromium.

The tests were made in a thermostat at a temperature of $40^{\circ} \pm 0.1^{\circ}$. It should also be stated that owing to the high test temperature and the rather high acid concentrations in which the chromium was dissolved, we used an electrolytic switch consisting of three glass tubes fused together to form an H. Gooch-crucible asbestos, soaked with a saturated solution of potassium chloride, was packed into the horizontal crossbar of the H. The sides of the H were filled as follows: into one there was pumped the solution in the apparatus, and into the other a saturated solution of potassium chloride; then the tops of the tubes were closed.

EXPERIMENTAL DATA

Hydrochloric Acid

1. Rate of Chromium Solution as a Function of Solution Time.

Sheets of chromium become covered with a permanent oxide film when allowed to lie about in the air. When such a sheet is placed in an acid solution, it may not dissolve for a fairly long time. This initial passivity may be manifested most readily in sulfuric acid, but it may also occur in more highly diluted solutions of hydrochloric acid. For this reason, we always activated the chromium to shorten the length of the test runs. In the experiments on the solution of

* The hydrogen volume was, of course, reduced to standard conditions.

chromium in hydrochloric acid this was done by plunging the chromium sheets into a solution of 10 N hydrochloric acid for 1 minute before they were placed in the test apparatus (the method of activating the chromium in the sulfuric-acid tests will be described under the appropriate heading).

This method of activating the chromium usually eliminates or greatly shortens the time during which the chromium is entirely passive, but it does not do away with the initial change in the rate of solution of the chromium with time (in hydrochloric acid). Typical curves representing the variation of the rate of solution of chromium with the time of its dissolution in 0.5 N, 1.5 N, and 4 N hydrochloric acid are given in Fig. 1. In this figure the chromium solution time is plotted on the abscissa's axis in hours, the ordinates being the solution rate for Curves 1, 2, and 3, and the potential of the dissolving chromium for Curves 1' and 2'.

As is seen in the figure, the rate of solution of chromium in dilute hydrochloric acid involves a rather long induction period,* during which the rate of chromium solution rises gradually.

After the end of the induction period the rate of chromium solution took on a constant value in our tests, remaining constant until all the chromium sheet was used up.

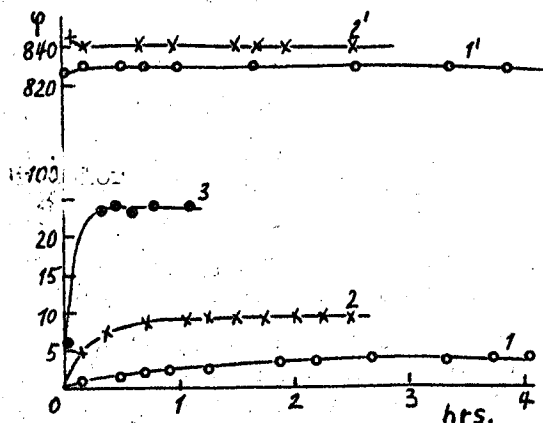


Fig. 1

It is seen at once from Fig. 1 that as the acid concentration is raised, the chromium solution rate rises and the induction period rapidly decreases. It is hard to discern the induction period in 9-10 N concentrated solutions of hydrochloric acid, it lasting usually less than one minute at these concentrations.

As Fig. 1 indicates, the potential of the chromium dissolving in hydrochloric acid grows constant somewhat earlier than the chromium solution rate, the potential of the dissolving chromium varying only very little, as a rule, during the test, less than 5 millivolts. In some tests, however, we observed variations of the potential of as much as 10 millivolts. It should also be stated that - contrary to the behavior of the potential of dissolving iron, which will be described in one of our subsequent reports - the changes in the potential of dissolving chromium follow no fixed trend with time, i.e., we found instances where the potential of the dissolving chromium rose a few millivolts toward the end of the run, as well as cases where it fell.

Several tests were made at each acid concentration. Owing to the large amount of data, we shall not reproduce the overall table covering all the tests, but merely state that the following conclusions may be drawn from a comparison of the results of repeated experiments.

Fluctuations in the value of the chromium solution rate are fairly large, the mean arithmetical experimental error $\Delta v\%$, expressed in per cent, is greatest at fairly low acid concentrations. For example $\Delta v\%$ was about 12% for 1 N hydrochloric acid, and about 3-5% for 10 N acid.

These variations in the chromium solution rate are due, apparently, to the fact that the chromium sheets are not all completely identical, despite our

*The term 'induction period' is defined as the time elapsing from the instant the chromium is plunged in the solution until its solution rate becomes constant.

maintenance of standard conditions during the deposition of the chromium sheets.

With this in mind, we always endeavored, when determining the effect of any one factor, such as temperature, intensity of stirring, etc., on the chromium solution rate, to make tests, whenever possible, in which the solution rate of a single chromium sheet was observed at various values of this factor.

As for the potential of dissolving chromium, it should be pointed out that although the average deviation of potentials corresponding to the various tests run in acid at a given concentration from their mean value was of the order of 5 millivolts, the discrepancy between the potentials found in two parallel experiments was about 10 millivolts sometimes, with discrepancies of as much as 17 millivolts observed in individual cases.

Effect of Stirring the Solution Upon the Solution

Rate of Chromium in Hydrochloric Acid

The temperature coefficient of the reaction rate and the effect of stirring the solution upon this rate are the principal criteria for evaluating the magnitude of the kinetic weight of the diffusion process in the given reaction.

The effect of stirring upon the chromium solution rate in hydrochloric acid is illustrated by the curves plotted in Figs. 2 and 3.

Figure 2 is like Fig. 1, with the sole difference that the curve plotted in Fig. 2 expresses the variation of the chromium solution rate in hydrochloric acid (1 N) with time for different stirring rates: 370, 630, 0 and 370 rpm of the stirrer. Figure 2 shows at once that the solution rate of chromium in 1 N hydrochloric acid is completely independent of the stirring rate.

Nor does a change in the stirring rate from 370 to 630 stirrer rpm have any effect upon the potential of the dissolving chromium, as is also seen in Fig. 2. When the stirrer was stopped completely, the potential was observed to rise slightly, by 9 millivolts, in this test run.

Fig. 3 illustrates the effect of stirring upon the rate of chromium dissolution in solutions of hydrochloric acid of varying concentrations. The ordinates in this graph represent the chromium solution rate, while the rpm of the stirrer, w , are plotted as abscissas.

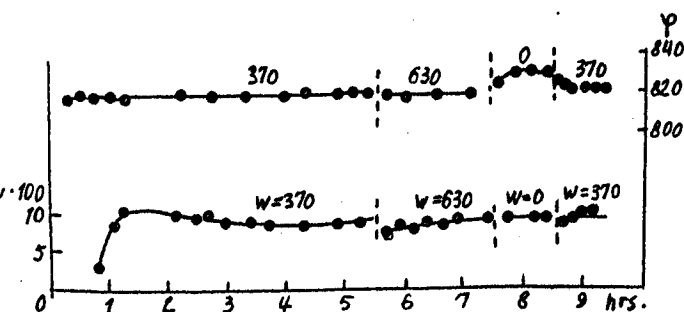


Fig. 2.

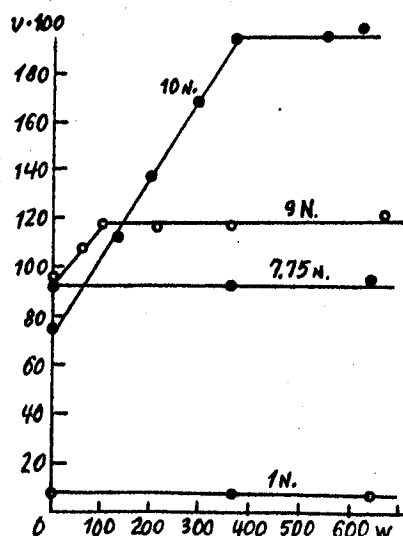


Fig. 3.

We see from Fig. 3 that the chromium solution rate is unaffected by the intensity of stirring; this is so not only for 1 N hydrochloric acid, but for hydrochloric acid that is about 8 N (7.75 N). On the other hand, stirring exerts a quite special effect upon the chromium solution rate at higher concentrations of hydrochloric acid. This peculiarity consists of the following: when the stirrer is started, the chromium solution rate first rises rapidly with increasing stirrer rpm. But when the rotational speed of stirrer reaches a certain rpm, the chromium solution rate becomes independent of the rate at which the solution is stirred.

In 9 N hydrochloric acid, this critical speed of the stirrer was about 100 rpm in our apparatus, as is seen in Fig. 3.

As is seen in Fig. 3, this critical speed rises quickly as the acid concentration is increased. At 10 N HCl it is about 300-400 rpm.

Thus, we can say that when chromium is dissolved in hydrochloric acid, the solution rate is a function of the rate at which the solution is stirred only at high acid concentrations and is of the specific nature described above.

The effect of stirring upon the potential of dissolving chromium was not investigated by us in all our experiments. Nevertheless, it may be said that at hydrochloric-acid concentrations below 10 N the potential of dissolving chromium was practically independent of the rate at which the solution was stirred. (In 1 N hydrochloric acid, the potential rose slightly, by a few millivolts,* in some cases when the stirrer was stopped).

In 10 N hydrochloric acid, on the other hand, we observed a marked rise in the potential of dissolving chromium when the rate at which the solution was stirred was raised; this rise was as much as ~20 millivolts when the stirrer speed was raised from zero to 550 rpm. As will be shown in one of our subsequent papers, however, this change in the potential is not the cause of the variation of the chromium solution rate with the rate of stirring observed in 10 N HCl.

3. Temperature Coefficient of the Chromium Solution Rate in Hydrochloric Acid

To determine the temperature coefficient of the chromium solution rate we ran special experiments in which a given sheet of chromium was first dissolved at a certain temperature. When the chromium solution rate had grown constant at this temperature, the temperature was changed, and the constant solution rate of the same chromium sheet was determined at the new temperature, etc., etc.

Figure 4 serves as an illustration of one of these tests. In this figure time in hours is plotted as the abscissa, and the chromium solution rate as the ordinate. The curves shown in this graph express the chromium solution rate as a function of time for the temperatures marked on the curves. The test was made in 1 N HCl with $w = 370$ rpm.

The results of some of these tests for 1 N and 10 N hydrochloric acid are listed in Table 1.

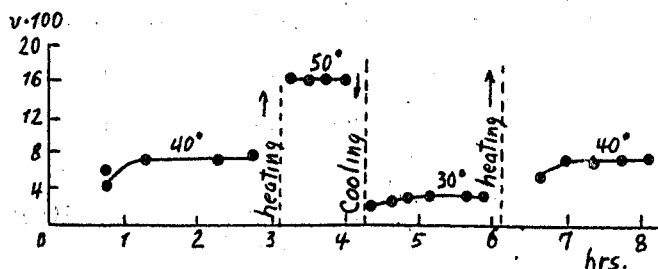


Fig. 4

* It should be remembered that we refer to a chromium potential as measured against a calomel electrode, but with a plus sign, so that an increase in potential signifies a transition to a poorer value.

TABLE 1

Temperature Coefficient of the Chromium Solution Rate in Hydrochloric Acid

Solution	N _{Cr}	t°C	w	v x 100	A	α%	$\frac{v_{t+10}}{v_t}$	φ
1 N HCl	9	20	370	1.08	14.400	8.7	2.4	797
	9	30	370	2.60	15.900	8.4	2.3	815
	9	40	370	6.03	17.000	8.5	2.3	832
	9	50	370	14.1				843
	10	30	370	3.4	14.800	7.8	2.2	807
	10	40	370	7.45	15.600	7.9	2.2	821
	10	50	370	16.00				833
4 N HCl + 0.5 N KCl	3	30	370	2.7	16.000	8.4	2.3	821
	3	40	370	6.3	17.300	8.5	2.4	839
	3	50	370	14.9				
10 N HCl	29	30	370	85.5	13.700	7.2	2.06	854
	29	40	370	176				846
	29	30	0	38.5	13.300	7.0	2.02	843
	29	40	0	78.0				827
	30	30	0	35.5	13.800	7.3	2.08	837
	30	40	0	74.0				828
	30	30	550	91.0	13.300	7.0	2.02	848
	30	40	550	183				846
	15	30	370	85	15.300	8.0	2.25	-
	15	40	370	191				-
	15	30	0	40.5	15.300	8.0	2.25	-
	15	40	0	91				-
1 N HCl	Mean values:							
	A = 16000 ± 700							
10 N HCl	α% = 8.3%							
	$\frac{v_{t+10}}{v_t} = 2.3$							
10 N HCl	A = 14500 ± 1000							
	α% = 7.4%							
	$\frac{v_{t+10}}{v_t} = 2.1$							

In this table NCr denotes the number of sheets of chromium used in the given test; w = stirrer rpm; A = critical increment of the chromium solution rate, computed from the Arrhenius equation $\lg v = \frac{A}{RT} + B$; $\alpha\%$ = temperature coefficient of the chromium solution rate, expressed as per cent per degree; and ϕ = the potential of dissolving chromium. The significance of the other notation is self-evident.

The straight line in Fig. 5 represents the variation of $\lg v$ with $\frac{1}{T}$ in one of our tests. Figure 5 and Table 1 enable us to say that the temperature variation of the chromium solution rate is in good agreement with Arrhenius' equation, the magnitude of the temperature coefficient of the chromium solution rate in 1 N as well as in 10 N HCl corresponding to the normal value of the temperature coefficient for the velocity of chemical reactions.

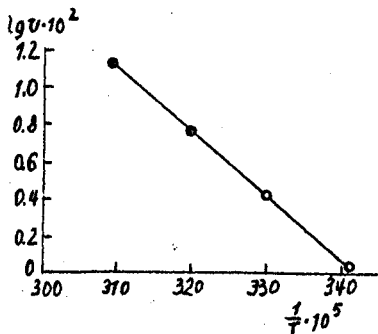


Fig. 5

4. Chromium Solution Rate as a Function of the Concentration of Hydrochloric Acid

The chromium solution rate was investigated by us in hydrochloric acid solutions whose concentrations ranged from 0.5 N to 10.5 N.

Figure 6 shows the curves that express the variation of the chromium solution rate with hydrochloric-acid concentration as found by us. In this figure the hydrochloric-acid concentration is plotted in normalities along the axis of abscissas, the mean value of the chromium solution rate being plotted along the axis of ordinates. The numbers above the points denote the number of determinations on which the mean value of the given rate is based. Where no number is given, the point in question was plotted on the basis of a single experiment.

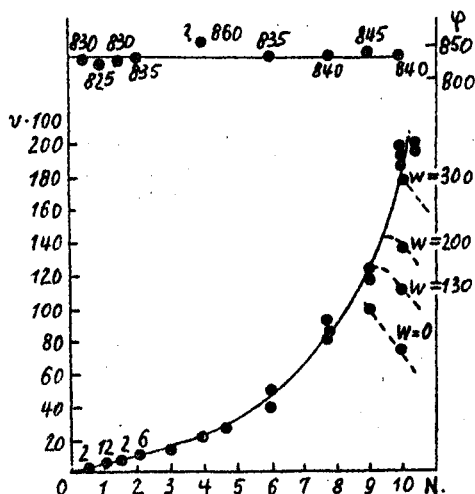


Fig. 6.

At the top of the axis of ordinates there are also plotted the potential values.

The straight line across the top of the figure represents the variation of this potential with the hydrochloric-acid concentration. The figures near the several points on this line denote the respective values of the potential for the points in question.

The solid curve in Fig. 6 expresses the variation of the chromium solution rate with the hydrochloric-acid concentration for values of w that exceed the critical value; *i.e.*, this curve corresponds to chromium solution rates obtained at stirring speeds at which the chromium solution rate is no longer a function of increases in the stirrer speed.

The points on the dotted sections of the curve were obtained for values of

w below the critical value of this variable in hydrochloric acid at the given concentration.

The corresponding values of w are given in the graph.

According to Fig. 6, there is only one curve of $v(c_{\text{HCl}})$ in the range of hydrochloric-acid concentrations from 0.5 N to about 8 N that expresses the chromium solution rate as a function of the hydrochloric-acid concentration for all rates at which the solution is stirred.

At high HCl concentrations two different kinds of curves can be plotted. When the solution is not stirred ($\underline{w} = 0$), we get a curve with a maximum at an acid concentration of about 8 N. As the rpm of the stirrer is raised, this maximum shifts toward the region of higher acid concentrations and higher chromium solution rates of the curves in Fig. 6 that correspond to $\underline{w} = 0$, $\underline{w} = 133$, $\underline{w} = 200$, and $\underline{w} = 300$ rpm).

At values of w that exceed 300 rpm there is a single curve of the exponential type without a maximum for the entire range of hydrochloric-acid concentrations investigated by us.

This duality in the variation of the chromium solution rate with acid concentration evidently is a direct consequence of the peculiar effect of stirring upon the chromium solution rate described in section 2.

Still another fundamental fact follows from Fig. 6, namely, that the potential of chromium dissolving in hydrochloric acid may be taken as constant in the first approximation and equal to 0.83 ± 0.01 volt.

It should be noted, however, that a more detailed study of all the data on the potential of dissolving chromium leads to the conclusion that the potential of dissolving chromium has an evident tendency to rise slightly as the acid concentration is increased; it is probable that this rise is of the order of 10-15 millivolts and thus is canceled out by the experimental error.

This conclusion is reinforced by the data of Fig. 6 if the point denoted by a question mark is discarded.

Lastly, it should also be noted that unsystematic fluctuations of the chromium dissolution potential of the order of ± 0.01 volt from the mean value are also present; these fluctuations find no noticeable reflection in the curve representing the variation of chromium solution rate with acid concentration.

5. Effect of Increasing the Concentration of Cr^{++} Ions Upon the Chromium Solution Rate and the Potential of the Dissolving Chromium

In our experiments, the dissolution of the Chromium began in pure acid; but toward the end of the experiment the concentration of chromium ions usually was of the order of 0.01 N, in some experiments going as high as ~ 0.02 N when the chromium was completely dissolved. This accumulation of chromium ions in the solution had no noticeable effect upon the potential of the dissolving chromium or upon its solution rate. We could explain this fact by the circumstance that as soon as the metal begins to dissolve, a certain concentration of its ions is immediately formed at its surface, it being quite conceivable that this concentration attains a level of hundredths of normal at extremely low metal solution rates, such as the rate of dissolution of chromium in hydrochloric acid that is $\sim 1 - 2$ N.

This is why we set up a special experiment in which the concentration of chromium ions in the solution was artificially raised to a concentration of 1 N.

When chromium dissolves in hydrochloric acid, it enters solution as bivalent ions. Solutions of bivalent chromium oxidize very easily, which is why setting up experiments to determine the effect of the concentration of Cr^{++} ions upon its solution rate encounters several difficulties.

This experiment was set up by dissolving a weighed quantity of electrolytic chromium in 3 N hydrochloric acid so as to yield a solution of 2 N HCl + 1 N CrCl_2 .

The values of the chromium solution rate and the potential of dissolving chromium were measured at $\underline{w} = 370$ rpm, $\underline{w} = 0$ rpm, and again at $\underline{w} = 370$ rpm.

Table 2

	$\underline{w} = 370$	$\underline{w} = 0$	$\underline{w} = 370$
$\underline{v} \times 100$	12.5	13.1	13.2
ϕ mV	827	833	824

The data in the table indicate that even when a high concentration of Cr^{++} ions is present, the chromium solution rate is unaffected by stirring the solution, as was the case in pure 2 N HCl.

According to Table 2, the mean value of the chromium solution rate, $\underline{v} \times 100$, is 12.9 ml/min, the potential ranging from 824 to 833 millivolts. When the chromium was dissolved in pure 2 N hydrochloric acid, the values of the chromium solution rate and of the potential ϕ were $\underline{v} \times 100 = 11.5$ ml/min and $\phi = 830$ -835 millivolts, respectively, according to the data in Fig. 6.

We may conclude from these data that increasing the concentration of Cr^{++} ions to one-normal exerts no appreciable effect (i.e., going beyond the limits of experimental error) on either the chromium solution rate or on its potential.

Sulfuric Acid

1. Induction Period

The laws governing the determination of the chromium solution rate in sulfuric acid differ fundamentally from the corresponding laws for dissolution in hydrochloric acid. This difference is chiefly manifested in the fact that the chromium's change from a passive to an active state takes place with much more difficulty in sulfuric acid than in hydrochloric acid. The rate of solution of electrolytic chromium immersed in a sulfuric-acid solution ordinarily remains zero for several hours; we therefore had to activate the chromium before using it in our sulfuric-acid experiments.

At first, we activated the chromium by immersing it in a solution of concentrated hydrochloric acid for one or two minutes. We later employed an electrochemical method of activating the chromium. This method consisted of immersing the chromium sheet, still in its holder, in a solution of sulfuric acid as one element of a couple with a sheet of platinum, the acid being of the same concentration as that used in the experiment proper. Current was passed through this circuit for a minute or two, the chromium sheet acting as the cathode. The metal holder was then quickly transferred to the reaction apparatus. Both methods yielded the same results, in respect of shortening the induction period as well as of establishing a constant chromium solution rate.

By way of example, curves representing the chromium solution rate and the potential of dissolving chromium as functions of time are shown in Fig. 7, Curves 1, 2 and 3 showing the chromium solution rate, and Curves 1', 2', and 3' the

potential. The beginnings of Curves 1, 2, and 3 are somewhat to the left of the origin, since the first reading of hydrogen volume usually is made a few minutes after the chromium has been immersed in the sulfuric acid. Curves 1 and 2 represent experiments with 1 N acid; Curve 3 is for an experiment with 3 N acid.

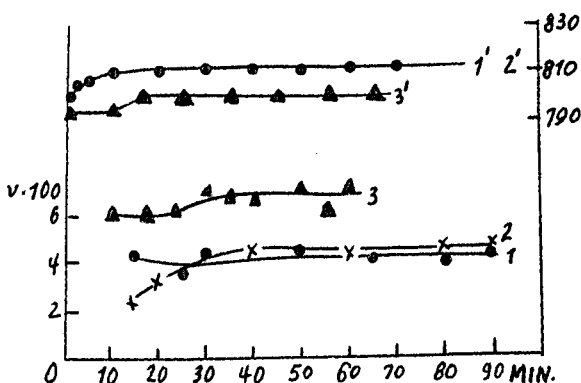


Fig. 7.

Curve 1 reflects the variation of the chromium solution rate with time for a chromium sheet that had been activated in concentrated hydrochloric acid. Curve 2 corresponds to another experiment with another sheet of chromium, which was activated with hydrochloric acid and then placed in a vessel containing 12 N sulfuric acid, where it was washed and allowed to dissolve for 5 minutes, after which it was placed in the reaction apparatus. As may be seen in Fig. 7, the chromium solution rate was the same in both cases, within the limits of experimental accuracy, after the steady state had been reached.

Curve 2' expresses the potential of dissolving chromium as a function of time during the second test.

No corresponding curve was plotted for the first test, since it practically coincided with the one shown. This seems to indicate that the small quantity of chromium ions that enters the solution when the chromium is activated in hydrochloric acid evidently does not effect the experimental results. As we shall see later on, this fact is corroborated by the experiments on the effect of adding KCl upon the chromium solution rate in H_2SO_4 .

Curves 3 and 3' indicate the chromium solution rate and the potential of dissolving chromium, respectively, in 3 N sulfuric acid, in these tests the chromium being activated electrolytically.

We see that curves of the same type are obtained with all the methods outlined above, the induction period being sufficiently brief in all instances - some 10 to 30 minutes.

2. Effect of Stirring Upon the Chromium Solution Rate in Sulfuric Acid and the Temperature Coefficient of this Solution Rate

In 1 N to 10 N sulfuric acid, the chromium solution rate positively does not rise as the stirring rate is increased. In fact, we observed the contrary phenomenon: the chromium solution rate rose slightly in fairly dilute solutions, from 1 N to 7 N, when the stirrer was stopped. The stirring rate has practically no effect upon the chromium solution rate in sulfuric acid whose concentration is 8 N to 10.5 N. Lastly, in 15 N sulfuric acid, the chromium solution rate rises sharply as the rate at which the solution is stirred is increased.

To illustrate this, we give in Table 3 the values of $\frac{v}{v^0}$, the ratio of the chromium solution rate at $w = 600$ rpm to the rate at $w = 0$ rpm for various concentrations of sulfuric acid.

The figures in Table 3 were obtained from data on the chromium solution rate derived by interpolation from the curves shown in Figs. 8 and 9.

As seen in Table 3, the drop in the chromium solution rate due to stirring

is extremely slight, actually lying within the limits of experimental error; we shall, therefore, confine ourselves to the statement that there is absolutely no increase in the chromium solution rate due to stirring in solutions of sulfuric acid at concentrations up to 10 N.

In 15 N sulfuric acid we see that the chromium solution rate rises markedly as a result of stirring the solution, like the rise in the chromium solution rate due to stirring described above for 10 N hydrochloric acid.

The slight observed drop in the chromium solution rate due to stirring will be noted for the present as possibly of some interest, but we shall stipulate that this fact still requires checking, since its magnitude is so close to the experimental error.

Table 3

$C_{H_2SO_4}$	2	4	6	8	10	15
$\underline{v}/\underline{v}^0$	0.85	0.90	0.90	1	1	2.8

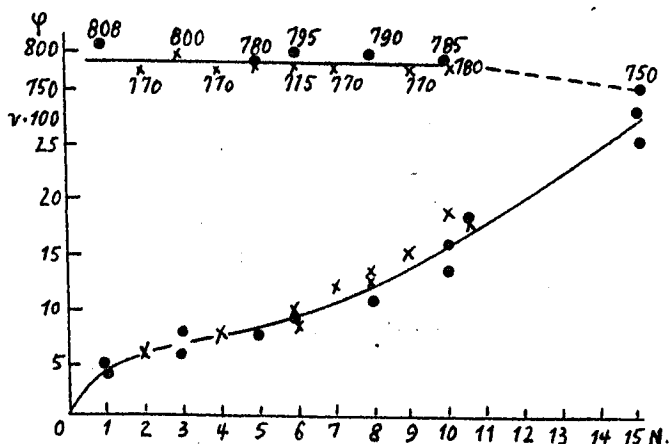


Fig. 8.

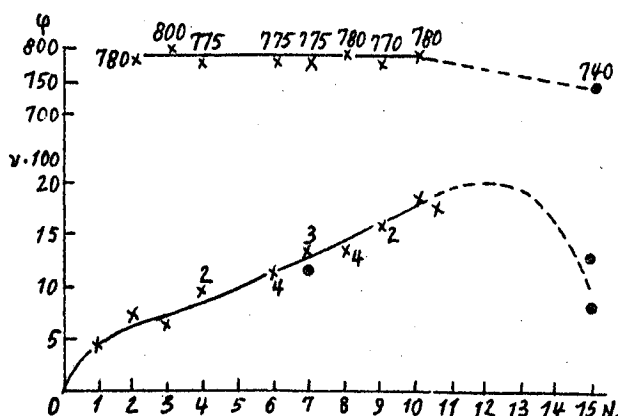


Fig. 9.

The very absence of any increase in the chromium solution rate in sulfuric acid as the result of stirring enables us to state that the kinetic weight of the diffusion process in this process is zero (with the exception of 15 N H_2SO_4).

This assertion is supported by the relatively low chromium solution rate in sulfuric acid; this is why the temperature coefficient of the chromium solution rate in sulfuric acid was determined only in two control experiments, one in 1 N sulfuric acid, and the other in 15 N sulfuric acid; in both tests $\underline{w}$ was 600 rpm.

These experiments yielded the following values for $\underline{A}$, $\alpha\%$, and $\frac{\underline{v}_{t+10}}{\underline{v}_t}$.

Table 4

$C_{H_2SO_4}$	$\underline{A}$	$\alpha\%$	$\frac{\underline{v}_{t+10}}{\underline{v}_t}$	
1 N	14.900	7.5	2.1	For the temperature range 40 - 50°
15 N	14.400	7.5	2.1	For the temperature range 30 - 40°

These figures show that the temperature coefficient of the chromium solution rate is high in sulfuric acid, both in 15 N acid and in 1 N acid.

3. The Chromium Solution Rate and the Potential of Dissolving Chromium as Functions of the Concentration of Sulfuric Acid.

The curves expressing these functions are shown in Figs. 8 and 9. The notation in these figures is the same as in Fig. 6. The data of Fig. 8 cover tests at $w = 370$ rpm; those in Fig. 9 are for tests in which there was no stirring.

The dots represent the initial test series, made by Y. Durdin with A.M. Markevich; the crosses represent a supplementary series of tests made by Y. Durdin and M.A. Oranskaya to clear up the problem of the effect of stirring on the chromium solution rate in sulfuric acid. As we see in Fig. 8, both test series yielded results that agreed fairly well with one another.

We see in Figs. 8 and 9 that the chromium solution rate increases much more slowly as the sulfuric-acid concentration is raised than was the case in hydrochloric acid.

We once [1] supposed that the chromium solution rate in sulfuric acid might be considered to be a linear function of the acid concentration. The supplementary data on the chromium solution rate in 15 N sulfuric acid and, especially, the data obtained in our work with M. A. Oranskaya indicated that even in sulfuric acid we also find a curve that is convex upward, though much less so than in hydrochloric acid.

As we see in Fig. 8, when the solution is stirred rapidly enough, this curve has no maximum, as was the case with the corresponding chromium solution-rate curve in hydrochloric acid, though the curve has a maximum in the concentration region between 10 N and 15 N sulfuric acid when the solution is not stirred. In hydrochloric acid, this maximum lay between the 8 N and 10 N acid.

As for the potential of dissolving chromium in sulfuric acid, Figs. 8 and 9 enable us to reach the following conclusions.

a) In the range from 1 N to 10 N sulfuric acid the change in the potential of dissolving chromium as the sulfuric-acid concentration is increased is very slight. The mean value of the potential of dissolving chromium in this concentration region may be taken as 0.78 ± 0.015 volt.

b) The indicated error of 15 millivolts is determined by the random fluctuations of the potential of dissolving chromium, which are somewhat higher in sulfuric acid than in hydrochloric acid. As is seen in Fig. 8, these fluctuations are as high as 20-30 millivolts in some instances, these potential fluctuations not affecting the curve of chromium solution rates appreciably, as was also true when chromium was dissolved in hydrochloric acid.

c) The potential of chromium dissolving in sulfuric acid is somewhat lower than the potential of chromium dissolving in hydrochloric acid: 0.78 volt as against 0.83 volt.

d) When the concentration of sulfuric acid is changed from 10 N to 15 N, an appreciable drop in the potential of dissolving chromium, of about 30 millivolts, is observed. In the sulfuric-acid concentration range from 1 N to 10 N we find that the potential remains constant, within the limits of experimental error. It may be thought, however, that even in this region of sulfuric-acid concentrations we have a slight drop of the potential, of the order of 5 to 10 millivolts, contrary to what occurs in hydrochloric acid.

Comparisons of the data in Figs. 6, 8, and 9 indicates that the differences

in the dissolution of chromium in hydrochloric and sulfuric acids are as follows: that the curve of $\underline{v(c)}$ rises much more steeply in hydrochloric acid than in sulfuric acid, as a result of which the chromium solution rate in concentrated solutions of hydrochloric acid is many times as high as it is in sulfuric acid of the same normality.

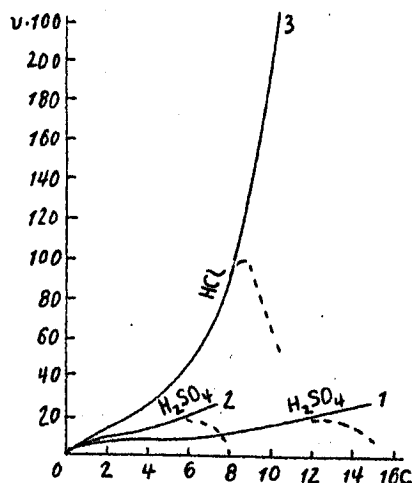


Fig. 10.

4. Effect of Adding KCl to Solutions of HCl and H₂SO₄

Upon the Chromium Solution Rate in These Acids

According to the foregoing, the chromium solution rate is greatly affected by the nature of the Cl⁻ or SO₄⁻ anion. To ascertain the basic nature of this effect we ran several auxiliary experiments. In these experiments (which were of a preliminary nature), we first determined the solution rate of a given sheet of chromium in a solution of 1 N hydrochloric or sulfuric acid, after which enough potassium chloride was added to the acid solution to produce a solution of 1 N acid plus 0.5 N KCl; the solution rate of the same chromium sheet then being measured in the latter solution. These tests showed that in 1 N acids, whether hydrochloric or sulfuric, such an addition of potassium chloride and, hence, a corresponding increase in the concentration of Cl⁻ ions, exerts but a very slight influence upon the chromium solution rate, raising it by some 5 to 10%, so that this effect is close to the limits of experimental error.

The results are quite different when potassium chloride is added to concentrated solutions of sulfuric acid. The data for two such experiments are listed in Table 5.

Table 5

Composition of solution	$\underline{v} \times 100$	ϕ
7.5 mol. H ₂ SO ₄	28	750
7.5 mol. H ₂ SO ₄ + 0.1 mol. KCl.	41	768
7.0 mol. H ₂ SO ₄ + 0.5 mol. KCl.	50	790
7.0 mol. HCl	65	835
5 mol H ₂ SO ₄	16	790
5 mol H ₂ SO ₄ + 1.8 mol. KCl ...	29	840
5 mol HCl	33	833

We may see by Table 5 that the addition of potassium chloride in decimolar concentration to 7-7.5 mol (14-15 N) sulfuric acid increases both the chromium

solution rate and the potential of the dissolving chromium. Raising the concentration of the potassium chloride to 0.5 mole doubles the chromium solution rate and increases the potential by about 40 millivolts.

Moreover, as we see from the same table, it may be considered that as the concentration of potassium chloride is further increased, the chromium solution rate as well as the potential of the dissolving chromium would rise to values corresponding to the chromium solution rate in 7 mol. of hydrochloric acid. The possibility of such an equalization of the chromium solution rate and the potential of dissolving chromium in hydrochloric and sulfuric acids of the same molarity by adding enough potassium chloride to the acid is likewise in agreement with the data obtained in the experiment in which potassium chloride was added to 5 mol. sulfuric acid until its own concentration reaches 1.8 normal, as seen in Table 5.

EVALUATION OF RESULTS

The problem of the laws governing the solution rates of metals in concentrated acids, and more particularly the underlying reasons therefor, are rather complicated. That is why we propose to make this problem the subject of a special research project, in which we shall examine not only the dissolution of chromium, but also that of other metals. In the present paper we shall confine ourselves, in the main, to a formal discussion of the foregoing experimental data.

1) In accordance with what has been stated above, the chromium solution rate is independent of the rate at which the solution is stirred in hydrochloric acid up to concentrations of 8 normal and in sulfuric acid in concentrations up to 10 normal, and we may therefore consider that in these concentration regions the chromium solution rate is unaffected by the process of diffusion, which likewise agrees with the high value of the temperature coefficient of the chromium solution rate.

In regions of higher acid concentrations - 9-10 N hydrochloric acid and 10-15 N sulfuric acid - the stirring rate exerts a marked effect upon the chromium solution rate, but with the specific peculiarities mentioned above.

It is significant, however, that the temperature coefficient of the chromium solution rate remains practically as high as in more dilute solutions. We shall endeavor to furnish an explanation of this phenomenon in one of our future papers.

2) This phenomenon of the effect of stirring upon the chromium solution rate is directly related to the general nature of the $\bar{v}(c)$ curves, expressing the chromium solution rate as a function of the acid concentration.

According to our data, these curves have a maximum when no stirring takes place, but this maximum vanishes when the chromium solution rate is measured at a high enough stirring rate.

The maximum on the $\bar{v}(c)$ curves in concentrated acid solutions was found long ago by Kayander during his research on the solution rate of magnesium [3].

In the case of chromium, curves exhibiting a maximum were recorded by E. Muller in his investigation of the solution rate of chromium in hydrochloric and sulfuric acids without stirring the solution [4].

This maximum was usually considered to correspond to the maximum on the curve of the acid's specific conductivity.

Our data indicate, however, that the reason for a maximum on the $\bar{v}(c)$ curve (at any rate, in the case of chromium) cannot be a change in the acid's conductivity, inasmuch as this maximum vanishes when the rate at which the solution is stirred is increased.

When the rate at which the solution is stirred is high enough, the $\bar{v}$:

variation of the chromium solution rate with the hydrochloric-acid concentration is expressed by an exponential curve of a type corresponding to those plotted by Tsentnershver for the solution rates of cadmium [5], tin [8], and aluminum [7]. At the time Tsentnershver held that explanation of these curves required abandoning the electrochemical mechanism of the solution of metals in acids and adopting a mechanism that he called a chemical one, according to which the solution of the metal takes place by its reacting with an acid molecule or with Cl^- ions [8]. As Y. V. Durdin [1] and A.I. Shultin [9] demonstrated, however, this type of curve can also be brought into agreement with the electrochemical mechanism of metal dissolution by assuming that the factors governing the kinetics of this reaction are electrode processes. This possibility will be examined in detail in the special research referred to above.

3) According to our data, the potential of dissolving chromium in 1 N to 10 N hydrochloric and sulfuric acids is nearly constant: 0.83 ± 0.01 volt in hydrochloric acid and 0.78 ± 0.15 volt in sulfuric acid.

If we take the potential of the saturated calomel electrode with respect to the normal hydrogen electrode at 40° as 0.236 volt, we get the potential of dissolving chromium with respect to the normal hydrogen electrode, taken with a positive sign, as $\phi = 0.59$ volt for hydrochloric acid, and $\phi = 0.54$ volt for sulfuric acid. This value of the potential of dissolving chromium is close to the value of the normal potential of chromium usually cited: 0.56 volt.

Correspondingly, we previously [1] expressed the hypothesis that when chromium is dissolved, its potential is close to equilibrium. According to Latimer's data, however, the $\text{Cr} = \text{Cr}^{+++} + 3e^-$ reaction corresponds to a potential of 0.71 volt; whereas the $\text{Cr}^{++} = \text{Cr}^{+++} + e^-$ reaction corresponds to a potential of 0.41 volt. It follows that for the $\text{Cr} = \text{Cr}^{++} + 2e^-$ reaction we get $\phi^\circ = 0.86$ volt as the equilibrium potential, taken (as we have done) with a plus sign, i.e., a value that is higher than what we have found as the potential of dissolving chromium. Bearing this in mind, we now believe it possible to assume that the anodic process of supplying metal ions to the solution is accompanied by an essential anodic polarization in the dissolution of chromium, of the order of ~ 0.25 to 0.30 volt.

SUMMARY

1. The chromium solution rate and the potential of dissolving chromium has been measured in hydrochloric and sulfuric acids.

2. It has been found that the chromium solution rate in hydrochloric acid at concentrations up to 8 normal and in sulfuric acid at concentrations up to 10 normal is independent of the rate at which the solution is stirred. This provides a basis for the conclusion that the chromium solution rate in these acids is unaffected by the diffusion process, at these concentrations, which agrees with the high temperature coefficient of this rate.

In solutions of higher concentrations, stirring has a marked effect upon the chromium solution rate.

3. The variations of the chromium solution rate with the acid concentration when the solution is not stirred is expressed by a curve exhibiting a maximum, the curve having no maximum when the stirring is vigorous enough.

4. The potential of dissolving chromium varies but little with concentration in the range from 1 N to 10 N hydrochloric and sulfuric acids; it may be taken as -0.59 ± 0.01 volt in hydrochloric acid and -0.54 ± 0.015 volt in sulfuric acid (with respect to the normal hydrogen electrode).

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