

THE LAWS GOVERNING THE RATE AT WHICH METALS ARE DISSOLVED IN CONCENTRATED ACIDS. I

Ya. V. Durdin

When metals are dissolved in concentrated acids, we get two types of curves representing the variation of the rate of dissolution of the metal with the acid concentration: curves without any maximum and curves having a maximum.

Curves without any maximum have been obtained by Conroy [1], by Oranskaya and the present author [2,3], and by Krasilshchikov [4] for the dissolution of iron in hydrochloric and sulfuric acids at concentrations up to 10 N; Tsentnershver secured such curves for the dissolution of cadmium [5], tin [6], and aluminum [7] in hydrochloric acid. Similar curves have been plotted for cadmium and aluminum in our laboratory as well. On the other hand, Kayander [8] long ago pointed out that when magnesium was dissolved in concentrated acids the function $V(c)$ is represented by curves exhibiting a maximum. $V(c)$ curves with a maximum were secured by E. Müller [9]; as well as by the present author and A.M. Markevich [10] for the dissolution of chromium in hydrochloric acid, though we showed that this maximum vanished when the solution was stirred sufficiently during dissolution. In the same papers it was shown that the $V(c)$ curves exhibited a maximum for the dissolution of chromium in sulfuric acid as well (without stirring), this maximum being located at about 12 N H_2SO_4 in our tests. Ram [11] and Damon [12] secured a maximum on the $V(c)$ curves for the dissolution of iron in sulfuric acid of about 13-14 N (again in tests carried out without stirring the solution).

Several authors - Tsentnershver [13], Kayander [8], and Müller [9] - have commented that the $V(c)$ curves with maxima for the dissolution of metals resemble the specific conductance - acid concentration curves, Palmayer considering this to be a direct proof that the equation of the theory of local elements was correct. Tsentnershver, on the other hand, found that the variation of the rate of metal dissolution with the acid concentration could be expressed by the general equation:

$$V = kc^n, \quad (1)$$

where $n > 1$, for the dissolution of cadmium, tin, and aluminum he had investigated and came to the conclusion that in these instances we must reject the concept of the electrochemical mechanism of the dissolution of metals, proposing instead another mechanism, which he called "chemical" [14]. We believe that both views, that of Palmayer as well as that of Tsentnershver, are wrong, though we must admit that, independent of their views, the notion that the $V(c)$ curves with and without a maximum represent different mechanisms of interaction between metal and acid is fairly plausible at first glance. We shall, therefore, begin by endeavoring to furnish an explanation for the existence of a maximum on the $V(c)$ curves, at the same time demonstrating that both types of curves can exist for one and the same mechanism of metal-acid interaction.

The Mechanism Governing the Appearance of a Maximum on the Curves Representing the Variation of the Rate of Dissolution of Metals with Acid Concentration

Tsentnershver [13] long ago noted that the position of the maximum on the $V(c)$ curve and on the $\kappa(c)$ curve did not coincide altogether for the dissolution of magnesium in acetic acid. According to Kayander, the maximum on the $V(c)$ curve is located at approximately 6.5 N acetic acid, while the maximum conductance of acetic acid is located at about 2.5 N .

The discrepancy between the positions of the maximum on the $V(c)$ and $\kappa(c)$ is even greater in the dissolution of iron in sulfuric acid, Damon [12] finding that the maximum of the $V(c)$ curve occurs at about a 13-14 N acid, while the

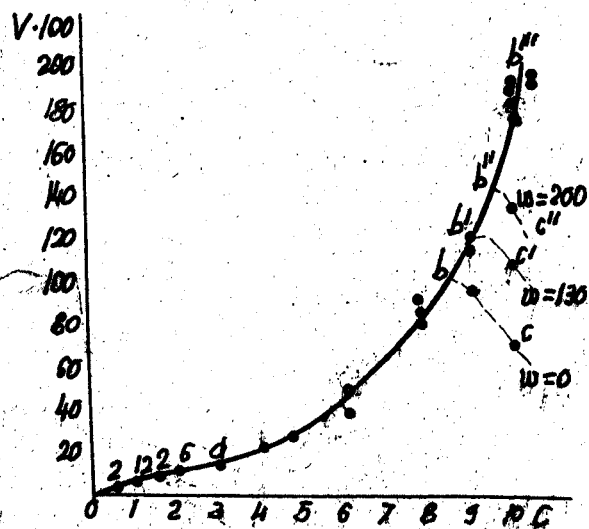


Fig. 1

We see from Fig. 1 that the position of the maximum on the $V(c)$ curve shifts as the rate of stirring rises. At $\omega = 370$ rpm the maximum vanishes altogether, the variation of the rate at which the chromium dissolves with the concentration of the hydrochloric acid being given by an exponential curve resembling the curves plotted for the dissolution of iron, cadmium, tin, and zinc.

We may conclude from what has been set forth above that the mechanism governing metal dissolution is apparently the same in the curves with a maximum and without one, the fundamental type being the curve without any maximum. The appearance of a maximum on these curves is due to some auxiliary controlling factor, which is not always manifested and is not the result of a decrease in the specific conductance of the acid. We believe that the appearance of this maximum is caused by the passivation of the metal surface that occurs at high acid concentrations, though this passivation may be due to different factors in different instances. Let us begin by considering the maximum on the $V(c)$ curve for the dissolution of chromium in hydrochloric acid, since we know the change in the shape of this curve that occurs when the solution is stirred. In our discussion it is convenient to have an expression for the rate of reaction at the surface of the metal as a function of the acid concentration and an expression for the rate at which the reaction products are carried away from the surface of the metal into the solution. We do not need precise expressions for these rates, however, all we require being

maximum conductance of sulfuric acid lies at a concentration of about 8 N . These facts are evidence against the theory that the maximum of the conductance curve is the underlying reason for the maximum on the curve for the rate of metal dissolution. The most convincing confirmation of this conclusion, in our opinion, is our observation that the maximum on the curve showing the variation of the dissolution of chromium with the concentration of hydrochloric acid vanishes when the solution is stirred vigorously enough. For convenience's sake, this curve is reproduced in Fig. 1. The curve abc in this figure was plotted for an unstirred solution ($\omega = 0$), the curves $ab'c'$ and $ab''c''$ representing $\omega = 130$ and 200 stirrer rpm, respectively. The curve abb''' , without a maximum, was plotted at $\omega = 370$ rpm.

equations that correctly express the general nature of the behavior patterns involved. Nor are we now interested in the mechanism of the reactions taking place at the surface of the metal.

Accordingly we represent the variation of the reaction rate at the surface of the metal with the concentration of the acid by Equation (1):

$$V_n = kc^n,$$

which agrees with the experimental data for the variation of the rate of metal dissolution with acid concentration in the region up to the maximum, provided the diffusion process does not affect it perceptibly.

We shall use the equation:

$$V_D = k(\omega^m + a) \cdot c_n \quad (2)$$

for the rate at which the dissolved metal is carried away into the solution from the surface of the metal,* where c_n is the concentration of the metal salt at the metal surface (for the sake of simplicity, we assume that the concentration of metal salt in the solution is zero); ω is the stirrer rpm; and m is an exponent whose values lie between 0.5 and 1. The variable (a) represents the intensity of the stirring due to the movement of hydrogen bubbles at the surface of the metal. In both of these equations the rates V_n and V_D are based on a unit of the geometrical surface of the metal.

Let us now consider the rate at which chromium dissolves as a function of the concentration of the hydrochloric acid. According to the data set forth in our paper written together with A.N. Markevich, the rate at which chromium dissolves in hydrochloric acid whose concentration is lower than that at the point (b) on the curve of Fig. 1 is independent of the effectiveness with which the solution is stirred. Hence, in the case of the dissolution of chromium, we may set the effect of diffusion processes as practically equal to zero in this range of hydrochloric acid concentrations,** so that Equation (1) is a valid expression of the rate at which chromium dissolves. Figure 2 is a schematic representation of the $V(c)$ curve, corresponding to this equation (the curve abb''). Furthermore, in the stationary state V_D must equal V_n , i.e.:

$$k(\omega^m + a)c_n = kc^n.$$

In the range of acid concentrations under discussion this equation may be readily imagined to occur in consequence of the fact that the concentration of the salt at the metal surface, (c_n) , automatically becomes such as to make

$$V_D = V_n.$$

Thus, the leveling out of the rates is due here to the adjustment of the rate of the diffusion process to the reaction

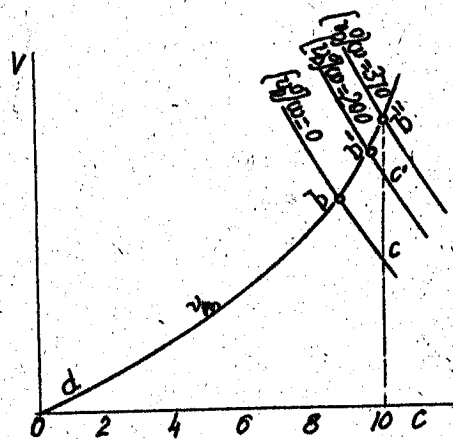


Fig. 2.

* We shall not go into the question of how the metal is diffused in the solution - as free cations, or, say, as more complicated complex ions. We believe that in every instance this rate is an increasing function of the metal salt at the metal surface; for the sake of simplicity we assume that it is proportional to that concentration.

** This applies to the diffusion of the salt from the surface of the metal into the solution as well as to the diffusion of the reagent to the metal surface.

rate at the metal surface, which conforms with the assumption that in this case it is this reaction that governs the kinetics of the metal's dissolution.*

Such a mechanism of adjusting the rates of these processes of ours is confined, however, to a limit that is represented by the condition that $c_n = C_n^0$, where C_n^0 is the concentration of the metal salt in a saturated solution of the same. Likewise, the rate V_D corresponding to the given value of ω and of the acid concentration can also rise only to a certain limiting value V_D^0 , equal to $k'c_n^0$, where

$$k' = k(\omega^m + a). \quad (3)$$

It should likewise be borne in mind that the value of C_n^0 must drop rapidly as the acid concentration rises, and that, hence, the value of the rate V_D^0 must also drop in accordance with Equation (3). The descending curves in Fig. 2 are a schematic representation of the rate V_D as a function of the acid concentration, each of the curves corresponding to a given value of ω , as noted on the curve. Let us consider the dissolution of chromium at $\omega = 0$. Since, according to Fig. 2, the curve $[V_D^0]_{\omega=0}$ lies above the V_n curve at concentrations up to 8 N, $V_n = V_D < V_D^0$ in this concentration range, and hence, $c_n < C_n^0$. Accordingly, the factor governing the kinetics of metal dissolution here will be the reaction taking place at the metal's surface, and the rate of metal dissolution will rise, in accordance with the shape of the V_n curve (the a - b section). But this increase in the rate will be paralleled by an increase in the value of c_n , while the variable C_n^0 will decrease (owing to the rise in the concentration of the acid). At the point b the rate V_D equals the rate V_D^0 , while c_n equals C_n^0 . Now any further increase in the rate of the diffusion process as the result of an increase in c_n becomes impossible. Moreover, as the acid concentration rises still further the value of C_n^0 will have to start dropping off, as a result of which the rate V_D^0 will also begin to fall (in accordance with the curve for $\omega = 0$, along the stretch from b to c). As the acid concentration is raised to 10 N, this rate must fall to the value corresponding to the point c, but since the condition $V_n = V_D$ for the stationary regime must be fulfilled, the rate V_n must also fall to the value corresponding to the point c. Therefore, the rate of dissolution of the metal actually passes through a maximum at the point b.

We still have to explain why the rate V_n drops to the value corresponding to the point c when the acid concentration is raised from 8 to 10 N, instead of rising to the value corresponding to the point b". We believe that this drop is due to the deposition on the metal surface of a precipitate of the metal salt, so that the active surface of the metal is diminished and hence the rate V_n as well.

In other words, we believe that on the descending branch of the curve $V(c)$, where the value of V_D^0 is fixed by the given values of ω and of the acid concentration, the levelling out of the rates V_n and V_D is due to a change in V_n rather than in V_D , as was the case on the ascending branch of the curve. We conceive the mechanism of this adaptation of the rate V_n to the rate V_D as follows. At $V_n > V_D$, the solution at the surface of the metal will become supersaturated with the latter's salt, which will be precipitated on the metal's surface until the diminution of the reactive metal surface causes the rate V_n to equal the rate V_D . At $V_n < V_D$, the reverse process takes place; the deposit of salt on the metal's surface will dissolve, so that the active surface will increase until the rate V_n equals the rate V_D .

It is readily seen from the family of curves reproduced in Fig. 2 that as the stirring rate is increased, the position of the maximum on the $V(c)$ curve must shift toward higher acid concentrations, which agrees with the data of Fig. 1. In general, if we imagine that the portions of the descending V_D^0 curves in Fig. 2

The rate at which the reagent diffuses toward the surface of the metal will adapt itself to the rate V_n as a result of the corresponding minute changes in the concentration of the reagent at the metal surface.

that lie above the $V(c)$ curve are discarded, we get a family of curves that are quite like the family of experimental curves reproduced in Fig. 1.

The mechanism involved in the formation of a maximum on the $V(c)$ curve proposed by us also provides a good explanation of the peculiarities we have observed in the effect of stirring upon the rate of solution of chromium in hydrochloric acid. These peculiarities are as follows: up to a certain acid concentration, about 8 N, the rate at which the chromium dissolves is independent of any stirring of the solution, while at higher acid concentrations a pronounced stirring effect is manifested; this effect, however, is characterized by the existence of a limiting stirring rate, above which the rate of solution again becomes independent of the rate of stirring. For the sake of convenience, we reproduce in Fig. 3 the curve plotted by A.M. Markevich and the present author [10]

that illustrates the variation of the rate at which chromium is dissolved in 10 N hydrochloric acid with the stirrer rpm ω . This phenomenon may be readily explained as follows with the aid of Fig. 2. Let us assume that we are observing the dissolution of chromium in 10 N hydrochloric acid at $\omega = 0$; then the rate of solution of chromium must be that given by point C in Fig. 2. As the stirring rate is raised to $\omega = 200$ rpm, the rate of solution of the chromium rises to the value given by the point c', the rate of the diffusion process rising as the direct result of the increase in the stirring rate, while the reaction rate at the surface of the metal rises as the result of the dissolution of part of the salt deposited on the metal surface and

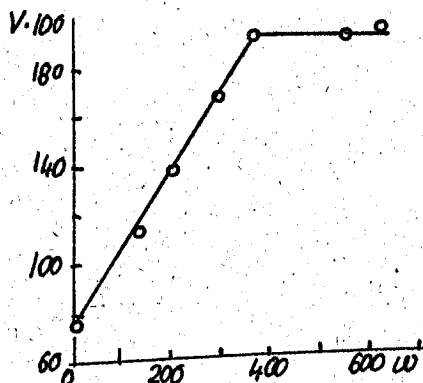


Fig. 3.

the salt deposited on the metal surface and the corresponding increase in the active area of the surface. When the ω is increased to 370 rpm, the rate of solution rises to the value given by the point b", the metal surface being completely freed of the precipitate. Any further increase in ω can then have no effect on the rate at which the chromium dissolves, since it leads merely to the condition $c_n < c_n^0$, at which the factor controlling the kinetics of the process is the reaction at the metal's surface, the rate of which does not depend upon ω when there is no deposit of salt upon the surface. It is obvious that the variation of V with ω will then be expressed by the curve shown in Fig. 3. Thus, the mechanism we have suggested provides a satisfactory explanation of the fairly complicated system of behavior patterns involved in the manifestation of a maximum on the $V(c)$ curve for the dissolution of chromium in hydrochloric acid. We might also mention that this explanation of the maximum is also of fundamental significance, since it illustrates the possibility of abrupt changes in the relationship between the effects of two consecutive processes. Actually, in the case in question the factor controlling the kinetics of dissolution of the metal to the left of the maximum was the reaction at the metal's surface, whereas to the right of the maximum the appearance of a new phase in the system (the salt deposit) made the process of the diffusion of the reaction products the factor that governed the kinetics of the metal's dissolution. The controlling factor likewise changes - the area of the active surface begins to act as this factor instead of the concentration c_n .

It may be thought that the explanation of the maximum on the $V(c)$ curve we have suggested for the dissolution of chromium also applies to the dissolution

other metals in other acids. In support of this we have the following considerations. According to this explanation, curves exhibiting a maximum will be secured whenever the concentration of the metal salt at the metal surface reaches saturation; the higher the rate of dissolution of the metal, the weaker the stirring of the solution, the lower the solubility of the metal salt, and the higher the acid concentration, the faster will saturation set in. These assertions are buttressed by the following facts. We got a maximum on the $V(c)$ curve for the dissolution of chromium in hydrochloric acid at 8-9 N hydrochloric acid (at $\omega = 0$), and at 12 N sulfuric acid for dissolution in that acid, which may be explained as due to the fact that chromium dissolves in sulfuric acid at a much lower rate than in hydrochloric acid. In Damon's experiments mentioned above, the maximum on the $V(c)$ curve was also shifted toward somewhat lower concentrations of sulfuric acid for the grades of steel that dissolved most rapidly. Whenever curves without any maximum are secured for the dissolution of a metal, even when there is no stirring of the solution, as in the dissolution of iron, cadmium, or zinc in hydrochloric acid, we believe that the auto-stirring of the solution due to the hydrogen evolved at the metal surface is enough to prevent the formation of a saturated solution of the metal salt at the surface of the dissolving metal. Regarded in this light, the absence of a maximum in the dissolution of cadmium and tin could have been predicted from the following facts: 1) the comparatively low rate at which they dissolve, even in hydrochloric acid; 2) the tendency of these metals to form complex ions in hydrochloric acid. It might be thought at first glance that our explanation of the curve's maximum does not hold for the case of the maximum on the curve representing the rate at which magnesium dissolves in acetic acid, inasmuch as the rate of solution of magnesium in moderate concentrations of acetic acid is governed by the rate at which the molecules of the acid diffuse toward the surface of the magnesium rather than by the rate of the chemical reaction at the latter's surface. This is not the case, however; in this instance, the variation of the rate of diffusion of the acid molecules toward the surface of the magnesium (and, hence, the variation of the rate of solution of the magnesium) with the concentration of this acid may be expressed by Equation (1), with $n = 1$. Thus, all our arguments apply here as well, the sole difference being that when magnesium is dissolved in acetic acid, the appearance of a maximum will be governed by the abrupt change in the relative weight of the two diffusion processes, since the factor controlling the kinetics of magnesium dissolution will be the diffusion of the acid toward its surface on the ascending branch of the $V(c)$ curve, and the diffusion of the magnesium salt into the solution on the descending branch.

Nor does the high temperature coefficient we measured for the rate at which chromium is dissolved in 10 N HCl at $\omega = 0$ disprove this explanation, since the increase in the rate at which the chromium salt is diffused from the chromium's surface into the solution must be governed not only by the increase in the diffusion coefficient, but also by the increase in the solubility of the salt (i.e., the increase in C_n^0), the temperature coefficient of which may be high.

Lastly, we must also point out that Evans put forward the concept of a protective film of ferric sulfate as the reason for the passivation of iron in sulfuric acid. In Damon's paper [12] this hypothesis was confirmed by the following: iron plates passivated in sulfuric acid were first quickly washed with cold water and then placed in a beaker with warm water, where the whitish film on the surface of the plates disappeared within a few minutes, after which the plates became active again, ions of iron and of SO_4 being detected in the water.

It may therefore be concluded that the explanation we have advanced for the mechanism and the laws governing the appearance of a maximum on the $V(c)$ curve observed during the dissolution of metals is applicable fairly generally.

Moreover, it must be borne in mind that the phenomenon of passivation in the dissolution of such metals as chromium, and probably iron as well, in concentrated sulfuric acid, especially at high temperatures, may be due to the oxidizing effect of the sulfuric acid as well as to the deposition of the metal's salt upon its surface.

SUMMARY

1. The problem of the cause that produces a maximum on the $V(c)$ curves representing the variation of dissolution of metals with acid concentration has been examined.

2. It has been shown that this maximum is not related to the maximum conductance of the acid.

3. The occurrence of a maximum on the $V(c)$ curve representing the dissolution of chromium in hydrochloric acid has been used to demonstrate that this maximum may be explained by assuming that the rate at which the chromium dissolves is governed by the rate of the reaction occurring at the surface of the metal at the acid concentrations lying along the ascending branch of the $V(c)$ curve, while it is governed by the diffusion of the metal's salt or its ions from the surface of the metal into the solution of the acid at the latter's concentrations on the descending branch of the same curve, the concentration of the metal's salt at the latter's surface attaining concentration at the point where the maximum occurs on the $V(c)$ curve.

LITERATURE CITED

- [1] J. Conroy, J. Soc. Chem. Ind., 20, 316 (1901).
- [2] M. Oranskaya, Sci. Notes. Leningrad State University, Chem. Series, 2, 54, 235 (1940).
- [3] Ya. Durdin and M. Oranskaya, J. Gen. Chem. 21, No. 4, (1951).
- [4] A. Krasilshchikov, J. Gen. Chem. 14, 261 (1944).
- [5] M. Tsentnershver, Z. phys. Chem., 137, 352 (1928).
- [6] M. Tsentnershver, Z. phys. Chem., 141, 167 (1929).
- [7] M. Tsentnershver, Z. phys. Chem. 122, 455 (1926).
- [8] N. Kayander, J. Russ. Phys. Chem. Soc., 13, 457 (1881); 12, 61 (1880).
- [9] E. Müller, Z. phys. Chem., 159, 68 (1932).
- [10] Ya. Durdin and A. Markevich, J. Gen. Chem. 19, 2131 (1949).
- [11] S. Ram, J. Soc. Chem. Ind., 54, 107 (1935).
- [12] G. Damon, Ind. Eng. Chem. 33, 67 (1941).
- [13] M. Tsentnershver, J. Russ. Phys. Chem. Soc., 47, 1064 (1915).
- [14] M. Tsentnershver, Trans. Mendeleev Jubilee Congress II, 254 (1937).

Laboratory of Inorganic Chemistry,
A.A. Zhdanov State University, Leningrad

Received July 12, 1949.

See CB translation p. a-605 ff.