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EFFECT OF ANIONS ON THE KINETICS OF THE DISSOLUTION OF METALS

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The dissolution of metals in electrolyte solutions is electrochemical in nature, and its velocity depends not only on the usual variables of chemical kinetics — concentration and temperature — but also on the electrochemical properties of the system, primarily on the electrode potential and the structure of the electrical double layer at the metal–solution interface. This point, obvious to electrochemists, has often been neglected, and is not always taken into account now by workers on corrosion.

From the laws of electrochemical kinetics, the dependence of rate of dissolution on potential can be represented in the simplest case by the equation

$$i_1 = k_1 \exp\left(\beta \frac{F}{RT}\varphi\right), \quad (1)$$

where i_1 is the rate of dissolution expressed as an electric current, φ the electrode potential, β the transfer coefficient, and k_1 a constant depending on the nature of the metal and the state of its surface.

Eqn. (1) is valid for a process which can be written in the general form

$$M \rightarrow M^{n+} + ne. \quad (2)$$

In the spontaneous dissolution of a metal in an acid, reaction (2) is balanced by the simultaneous cathodic discharge of hydrogen ions:

$$2H^+ + 2e \rightarrow H_2, \quad (3)$$

the kinetics of which can be expressed by the equation

$$i_2 = k_2[H^+]\exp\left(-\alpha \frac{F}{RT}\varphi\right). \quad (4)$$

On combining Eqns. (1) and (4) we find that the dependence of the rate of spontaneous dissolution of a metal on the acid concentration should be given by the equation

$$v = k_3[H^+]\frac{\beta}{\alpha+\beta}, \quad (5)$$

which in several cases shows good agreement with experiment[1-3].

In many cases, however, the rate of dissolution of metals in acid electrolyte solutions depends not only on the concentration of hydrogen ions, which are directly involved in the process, but also on the nature and the concentration of the anions, which at first sight do not appear to take part in the process. Recent investigations in this laboratory[4-9] have shown that a change in the anionic composition of the solution can lead to a change both in the cathodic process (hydrogen evolution) and in the anodic process.

The activating effect of anions on the anodic process is often associated with their influence on the state of the passivating film, *i.e.* on the magnitude of the diffusion barrier. However, recent data indicate that anions are directly involved in the discharge and the formation of metal ions[8-14].

Kolotyrkin and Medvedeva[8] have shown that the dependence of the rate of anodic dissolution of cadmium on the potential in solutions containing halides is represented by a Tafel straight line having a slope of 0.035 V, which gives a value of 1.66 for β (reckoning that $\alpha + \beta = 2$), the position of this curve depending markedly on the nature and the concentration of the added halide. The curve for the dependence of rate of dissolution on KI concentration at a given electrode potential (Fig. 1) shows that, after a certain critical concentration of the salt, in this case 0.1 N, a tenfold increase in the salt concentration is accompanied by an almost thousandfold increase in the rate of the anodic process. Bromide and chloride solutions give similar results, but with the difference that replacement of I^- by Br^- and Cl^- resulted in an increase in the critical concentration of the added salt.

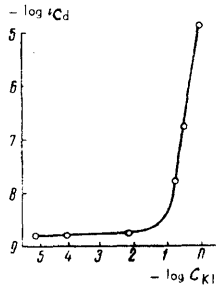


Fig. 1. Dependence of rate of dissolution of cadmium (at constant potential) in a solution of 1.0 N H_2SO_4 + x KI on the concentration of KI.

Analogous results were obtained recently by Losev and Molodov[9], who investigated the effect of the nature and the concentration of anions on the anodic dissolution of indium amalgam. They used a radioactive tracer method to determine the exchange current i_0 between the amalgam and an indium salt solution at the equilibrium potentials, and also the rate of the true anodic process of the ionisation of indium at other potentials near the equilibrium value. Combination of this method with ordinary polarisation measurements enabled the kinetics of the anodic reaction also to be investigated.

The results show that the dependence of the velocity of the anodic process on potential is also characterised by a Tafel straight line, with a slope of 0.025 V. This value of the slope, and hence the transfer coefficient $\beta = 2.3RT/b_a F = 2.32$ (on the condition that $\alpha + \beta = 3$), remained unchanged with change in the nature and the concentration of the halide in the solution. Variation in the anionic composition of the solution did, however, lead to a change in the overpotential of the process, as shown in Fig. 2, which gives curves for the dependence on the halide concentration of the rate of the anodic reaction at constant potential (-0.330 V for Cl^- and -0.276 V for Br^- and I^-). After a certain concentration, further increase in the halide concentration leads to a systematic increase in the rate of dissolution.

This critical concentration increases appreciably in the series $I^- \rightarrow Br^- \rightarrow Cl^-$, having values of 2×10^{-3}, 5×10^{-2}, and 5×10^{-1} N respectively, the corresponding increases in the rate of dissolution of the amalgam for a subsequent tenfold increase in concentration of the added salt being almost $\times$ 10, $\times$ 10^2, and $\times$ 10^3, respectively.

It can be concluded from these data that the dissolution of metals involves the direct participation of halide ions, and consequently that the kinetics of these reactions can be written in the following form (at constant pH):

$$i_a = kC^{\delta} \exp\left(\beta \frac{F}{RT} \varphi\right), \qquad (6)$$

where C is the concentration of the halide salt and δ is a constant having a value of 3 for the dissolution of cadmium in the presence of I^- ions, and 1, 2, and 3 for the dissolution of indium amalgam in iodide, bromide, and chlorine solutions respectively.

Interesting results on the mechanism of the activating effect of halide ions on the anodic dissolution of certain metals have recently been obtained by Medvedeva for the silver electrode (compare references cited elsewhere[7]) with which an appreciable decrease in overpotential for the anodic process also occurs on passing from a solution of pure sulphuric acid to one containing KI. The adsorption of iodide ions on the electrode surface at different potentials was investigated by a radioactive tracer method using ^{131}I. Preliminary experiments showed that iodide ions are very strongly adsorbed on the silver surface, which enabled adsorption measurements to be made on smooth electrodes with low initial concentrations in the solution (10^{-9}–10^{-7} N).

The results showed primarily that adsorptive and chemical interaction between iodide ions and the surface silver atoms occurs at potentials which are appreciably more negative than those for the dissolution of this metal, the degree of coverage of the metal surface with adsorbed ions and the strength of bonding of these ions with the surface metal atoms increasing appreciably with potential. Fig. 3 shows that, for the range of polarisation investigated, the amount (A) of I^- ions adsorbed varies linearly with the potential of the silver. If it is assumed that such a relation is maintained even at very low degrees of coverage, it follows from the above data that at a KI concentration of 2.6×10^{-9} N this interaction begins at -1.15 V, which is almost 1.5 V more negative than the potential at which silver is observed to dissolve in the corresponding solution.

It is noteworthy that this adsorption is reversible in the sense that, with a given KI concentration in the solution, the quantity of I^- ions adsorbed is determined unambiguously by the potential: change to a more negative potential always leads to the desorption of a definite quantity of ions.

A study of the rate of desorption of I^- as a function of the potential to which the electrode has first been polarised indicates that the strength of the adsorption increases with potential. Since these experiments were carried out in solutions having a very low KI concentration, it was easy to reach a potential at which iodide ions were completely adsorbed from the solution. The same degree of coverage of the surface corresponded to different potentials more positive than this value.

Fig. 4 shows the results of one such experiment, curves *1* and *2* representing the rate of desorption of ions at -0.335 V after preliminary polarisation of the silver at -0.174 and -0.124 V respectively, corresponding to the same coverage of the surface, 16.9×10^{11} ions cm^{-2}. A shift in the preliminary polarisation potential towards more positive values is seen to lead to a considerable slowing

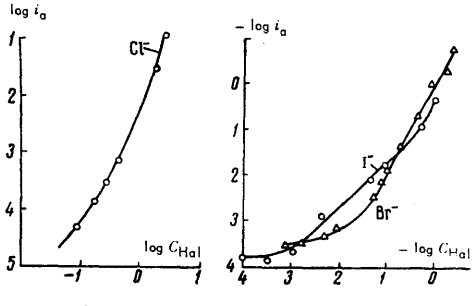


Fig. 2. Dependence of rate of dissolution of indium amalgam (at constant potential) in a solution of 0.01 N $In(ClO_4)_3$ + + 0.01 N $HClO_4$ + x NaHal on the concentration of NaCl, NaBr, and NaI.

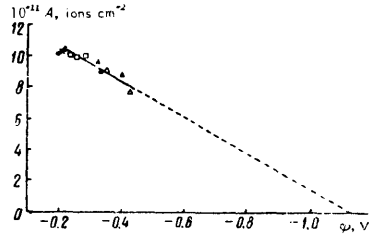


Fig. 3. Dependence of quantity of iodide ions adsorbed per cm^2 of a silver electrode on its potential in a solution of 1.0 N H_2SO_4 + 2.6×10^{-9} N KI.

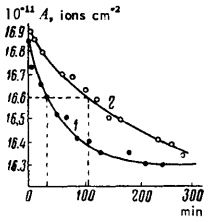


Fig. 4. Dependence of rate of desorption of iodide ions at -0.335 V on potential of preliminary polarisation of silver electrode: 1) -0.174 V; 2) -0.124 V.

down of desorption. Thus, for example, the time required for the desorption of the same amount of KI, 3×10^{10} ions cm^{-2}, was 27 min in the first case and 110 min in the second.

On the basis of these results the specific adsorption of anions, beginning at considerably more negative potentials than the solution potential of the electrode metal, must be regarded as the start of the formation of the corresponding salt (by means of covalent bonds). In the initial stages of adsorption, however, the strength of this bond differs appreciably from that in the corresponding free compound. As the potential shifts towards more positive values, this difference decreases, and finally disappears altogether. Starting from this potential, the metal ions begin to pass into solution in the form of complexes with the adsorbed anions. In this case the mechanism of metal dissolution can obviously be represented by two consecutive reactions[8]:

$$M + \partial Hal^- \rightarrow MHal_{\partial}^{\partial-}, \quad (7)$$

$$MHal_{\partial}^{\partial-} \rightarrow MHal_{\partial}^{(n-\partial)+} + ne, \quad (8)$$

the first of which corresponds to the specific adsorption of an anion on the surface of the metal with the formation of a surface complex, and the second to the ionisation of the metal atom in this complex.

In explaining the mechanism of the effect of anions on the kinetics of electrode processes, we must take into account the change in structure of the electrical double layer caused by their adsorption and the appearance of a negative ψ_1 potential at the metal–solution interface. However, allowance for these effects alone is insufficient for a satisfactory interpretation of many of the existing experimental results. In particular, it is obvious that a change in the ψ_1 potential should lead to identical changes in the rates of the forward (anodic) and the reverse (cathodic) reactions, and consequently to a change in the exchange current i_0. However, such a parallelism is not generally observed[9]. It has been established, for example, that an increase in chloride concentration to 0.5 N, while accompanied by an appreciable increase in the rate of the anodic dissolution of indium amalgam, does not lead to an increase in the exchange current, which remains the same as in the original $NaClO_4$ solution (without added NaCl)†.

† To explain this effect by the ψ_1 potential alone, it would be necessary to assume that only In^{3+} ions take part in the electrode process, and that the retardation of the cathodic reaction with increase in the KCl concentration, resulting from the decrease in concentration of the In^{3+} ions due to complex formation, is exactly double the accelerating influence of the ψ_1 potential on the anodic process.

It can be concluded from present results that direct participation of the components of a solution in the elementary act of ionisation of metal atoms is evidently a necessary stage in these processes. Of course, it is mainly those components that possess the greatest chemical affinity for the electrode metal under the given conditions which are involved in this way. Recent experiments by Losev have shown, for example, that not only specifically adsorbed anions but even water molecules can act in this way. These experiments established that the rate of the anodic dissolution of indium amalgam in acidified concentrated perchlorate solutions, which are known to exhibit no tendency to specific adsorption, is appreciably retarded with decrease in the concentration of free water in the solution. These results evidently indicate that hydration (at least partial) of the metal ion occurs before the latter passes from the metal lattice into the solution.

It follows from these ideas that the activating effect of a given anion on anodic dissolution can be exerted only when a definite critical potential is reached, at which the strength of the bond between a surface metal atom and the adsorbed ion is equal to that of the covalent bond in the corresponding free compound. Different anions should obviously correspond to different critical potentials. When, therefore, the electrode potential of the metal is maintained at values at which only one of the components of the solution can exert an activating influence on the anodic process, the adsorption on the surface of other components, active at more positive potentials, must be expected to lead to a retardation of dissolution. In other words, if several components of a solution are adsorbed simultaneously on the surface of a metal at a given potential, not all of the surface complexes formed can pass into solution, but only those for which the strength of the chemical bond has reached the necessary value. This can evidently explain the passivating influence of iodide and chloride ions on the spontaneous dissolution of iron and its alloys in sulphuric acid[15-23], in spite of the fact that at more positive potentials these ions are extremely corrosive reagents.

The Passivation of Metals

We can evidently explain not only the activation of the anodic dissolution of an electrode metal by adsorbed components of the solution but also the passivation of the metal surface.

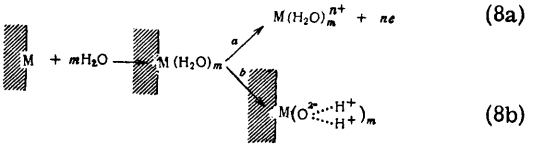
Recent results show more and more convincingly that many features of the electrochemical behaviour of passivated metals cannot be explained on the phase theory of passivity without resorting to additional and frequently improbable hypotheses. A fundamental principle of this theory is the irreversibility of anodic passivation in the sense that, when a definite potential has been reached, at which film formation takes place, the metal becomes inert, and that this inertness will be maintained subsequently at all more positive potentials; any breakdown of the passivating film, leading to an increase in the rate of dissolution of the metal, should also result in a shift in the electrode potential towards more negative values.

Recently it has been clearly established, however, that this view of the effect of passivity is incorrect. Detailed investigations on chromium, nickel, stainless steels, and other metals and alloys have shown that in many cases the passive state remains stable only within a comparatively narrow potential range dependent on the nature of the metal

and the pH of the solution, and that on the more positive side of this range the metal again begins to dissolve readily. The most surprising fact is that the rate of such dissolution varies with potential in conformity with the usual Tafel straight line, *i.e.* in conformity with the ordinary laws of electrochemical kinetics[24-35]. Such a dependence under conditions far removed from equilibrium obviously indicates the absence of diffusion hindrances to the process, which is incompatible with the presence of a continuous film on the surface of the metal.

Such a discrepancy is avoided by the adsorption theory of passivity. However, the further hypothesis is then necessary that the usual adsorption of water, which accelerates the anodic dissolution of the metal as ions of a lower degree of oxidation, is accompanied by chemisorptive interaction of the surface metal atoms with the oxygen of the water, resulting in passivation, the link between the passivating oxygen and the surface atoms being similar in nature to that in oxygen complexes of metal ions of a higher degree of oxidation, such as $Cr_2O_7^{2-}$. This means that such adsorption is to be regarded as the start of the formation of a metal salt of a higher degree of oxidation.

This hypothesis is quite reasonable in view of the above statement that halide ions start to interact with the metal surface also at appreciably more negative potentials than those at which the metal dissolves in the presence of these ions. The interaction of water molecules (or OH^- ions) with the surface metal atoms can then be represented by the following scheme



(8a)

(8b)

which is similar to that which was once suggested by Kabanov *et al.*[36] for the passivation of iron in alkalis. However, their work contains no hypotheses as to the nature of the bond between the passivating oxygen and the surface metal atoms.

It is natural to suppose that the link between oxygen and the metal atom will change and become stronger the longer the adsorbed H_2O (or OH^-) remains on the metal surface. This should evidently be favoured by an increase in the pH of the solution and a shift in the electrode potential to more positive values. It is now known that passivating reactions begin to take place at an appreciable rate only when a definite potential (the passivation potential) is reached, the value of which for a given metal increases as the pH of the solution falls. It is extremely likely that passivating adsorption first begins on the most active portions (centres) of the surface, and only afterwards, as the potential becomes more positive, does it extend to other sites.

In conformity with this, a passivating oxide of this type may remain on the surface and inhibit the anodic reaction up to a certain potential, at which it is able to pass into solution in the form of a complex with a metal ion of higher oxidation state. At such positive potentials the surface complex will obviously be readily regenerated, which will lead to a continuous dissolution of the metal by this mechanism.

Electrochemical Basis of the Pitting of Metals

It is now known that the passive state of a metal or an alloy can in many cases be broken down (either partly or completely) by introducing certain anions, expecially Cl^-, Br^-, and I^-, into the solution.

Numerous experimental observations have shown that the presence of these ions in solution is frequently a cause of irregular corrosion, leading to the formation of deep pits in the metal surface. This type of corrosion is, of course, most dangerous, since with relatively small overall corrosion losses it can put metal structures or individual parts completely out of action.

Many investigators have studied pitting corrosion, without, however, being able to elucidate the mechanism of this process. In spite of this, several workers[37] are inclined to regard it as a purely chemical process, not an electrochemical one. To the writer, however, such a conclusion appears to be completely unjustified. Analysis of available data shows that, with certain, quite plausible assumptions, the occurrence and development of pitting can be satisfactorily explained on the basis of an electrochemical mechanism for the dissolution of metals.

Available data indicate that the presence of Cl^-, Br^-, or I^- ions in the solution is a necessary but not a sufficient condition for the acceleration of corrosion and the formation of pits. Often the corrosive action of these ions is observed only at potentials which are more positive than a certain critical value[38,39], which depends on the nature and the concentration of the halide ion in the solution and also on the nature of the metal itself and several other factors. Data recently obtained by Gil'man[40] show conclusively that, under conditions of spontaneous dissolution of metallic zirconium in pure 1.0 N H_2SO_4, the passive state remains stable and the rate of corrosion of the zirconium (with hydrogen depolarisation) does not exceed 5×10^{-7} A cm^{-2}. A very important fact is that this rate does not change appreciably as the potential becomes more positive right up to 2.0 V (see Fig. 5, curve *1*). Addition to the acid solution of chloride, bromide, or iodide also produces no appreciable change in the rate of spontaneous dissolution or the steady-state potential of the zirconium. These ions do, however, exert a corrosive action when anodic polarisation is applied and the electrode potential is shifted to a certain value which increases regularly in the series Cl^-, Br^-, I^-.

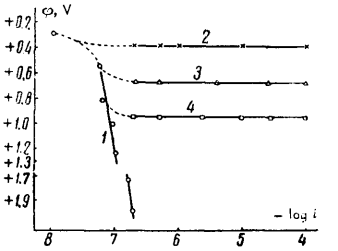


Fig. 5. Dependence of rate of dissolution of zirconium on potential in solutions of: 1) 1.0 N H_2SO_4; 2) 1.0 N HCl; 3) 1.0 N H_2SO_4 + + 1.0 N KBr; 4) 1.0 N H_2SO_4 + 1.0 N KI.

As Fig. 5 (curves *2–4*) shows, the value of this critical potential under stationary conditions is practically independent of the anodic polarising current density, and hence of the rate of dissolution of the zirconium, although immediately after the current has been stepped up (or down) a momentary shift of the potential in the positive (or negative) direction is observed followed by its quite rapid return to the original value (see Fig. 6). Visual observation showed that under these conditions the zirconium does not dissolve uniformly over its whole surface, the dissolution being distinctly local in character and leading to the formation of pits.

The critical potential can be reached not only by polarising the electrode but also by introducing an oxidant into the solution. The oxidant employed by Gil'man[40] was a ferric salt, sufficiently high concentrations of which in chloride solutions shifted the potential of zirconium to the critical value and resulted in pitting of the metal surface.

The behaviour of zirconium in solutions containing chlorides, bromides, or iodides does not differ fundamentally from that of several other metals (iron, magnesium, aluminium, chromium, etc.) and alloys.

Since the solution potential of zirconium in acid chloride solutions is definitely irreversible, its independence of the current can be satisfactorily explained on the assumption that under these conditions the effective surface S increases in proportion to the growth in the current I, when we can write

$$\varphi = K + \log\frac{I}{S}. \qquad (9)$$

It follows from Eqn. (9) that the constancy of φ is a consequence of that of the quantity I/S. This hypothesis is consistent with data obtained for aluminium, whose critical solution potentials in acid chloride, bromide, and iodide solutions are more negative than the corresponding values of the reversible hydrogen potential. Tomashov and Modestova[41] have shown that in this case a shift in the electrode potential to the critical value is accompanied by an increase not only in the overall rate of dissolution but also in the rate of spontaneous dissolution, which is shown in an increase in the amount of gaseous hydrogen evolved (negative differential effect). It was clearly established that the rate of hydrogen evolution increases linearly with increase in the polarising current. Since in this case the corrosion has a well-defined local character, and the evolution of hydrogen is strongly retarded at the passive portions of the surface, such a relation between current and rate of hydrogen evolution evidently indicates that the effective surface of the active sites increases linearly with increase in the polarising current. This conclusion agrees with visual observations of these workers, indicating a growth in the number of pits with increase in the current.

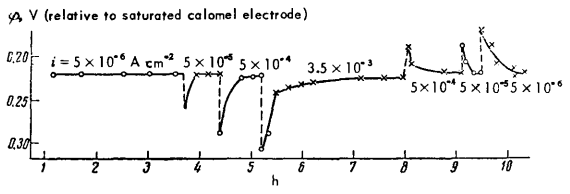


Fig. 6. Variation of potential with time when the current density is increased or decreased during the anodic dissolution of zirconium in 1.0 *N* HCl.

The observed momentary deviations of the potential from the critical value immediately after the current has been stepped up or down are obviously due to the fact that, with a rapid change in polarisation, the quantity S has insufficient time to keep pace with the growth in I.

It can be concluded from the experimental coincidence of the forward and reverse polarisation curves that depassivation of a metal surface by halide ions is reversible in the sense that, when the factors producing activation of the surface are eliminated, the latter again passes into the passive state. Hence it appears that two competing processes are occurring on the metal surface under these conditions — the passivating adsorption of the oxygen of water (8b) and the activating adsorption of chloride ions — which can be represented schematically as follows

$$\text{M}(\text{O}^{2-}\cdots\text{H}^{+})_m + p\text{Cl}^- \rightleftharpoons \text{M}(\text{Cl})_p^{p-} + m\text{H}_2\text{O}. \qquad (10)$$

The possibility of displacing such an equilibrium to the right should obviously depend not only on the electrode potential but also on the concentration of halide ions near the metal surface. Engell and Stolica[37] have recently shown that the activating influence of chloride ions on the corrosion of a passive iron electrode (accompanied by pitting) is observed only when a certain critical concentration of these ions in the solution is reached.

Naturally the question arises as to why the dissolution of a metal under these conditions has a well-defined local character. In the reviewer's opinion the experimental dependence of the area of active sites on the polarising current is of considerable importance for an understanding of this phenomenon. The existence of such a relation can be understood and explained if it is assumed that the supply of chloride ions to the metal surface is effected by transport by the current. This hypothesis agrees well with experimental data showing that the corrosive effect of chloride or other halide ions can be diminished or completely eliminated by raising the concentration of the main electrolyte in the solution. Thus, Gil'man[40] has recently shown that the effect of chloride ions on the anodic dissolution of zirconium in sulphate solutions disappears completely when the concentration ratio of sulphate to chloride is brought close to 5. If, however, perchlorate, whose anion is singly charged, is employed as the main electrolyte, the critical concentration ratio is practically doubled, *i.e.* it is brought close to 9–11.

Such a hypothesis is supported also by the data of Engell and Stolica[37], who showed that, with passive iron at a specified potential, the activating effect of chloride ions on the anodic dissolution of this metal is not observed immediately after chloride has been introduced into the solution, but only after the lapse of a period of time, which is longer the lower the chloride concentration in the solution. Under conditions such that the bulk concentration of chloride remains below the critical value, the appearance of such an induction period may be due to the time required for the Cl^- concentration next to the electrode to reach the critical value.

Since the dissolution of solid metals always takes place irregularly (even when they are passive), so that the current is always distributed irregularly over the surface, it is reasonable to assume that the critical concentration of Cl^- ions will be reached soonest close to those portions of the metal surface which dissolve at the greatest rate. If the current is maintained constant, the activation of these portions which has already begun will inevitably lead to a still greater localisation of the current, and hence to a still more rapid supply of activating ions to them, which will result in a self-accelerating dissolution process. It is very probable that the dissolution of metal at active sites will be limited by diffusion‡, so that further increase in the anodic current will inevitably result in an increase in the area of these portions.

It is easy, with the same postulates, to explain the formation and development of pitting in the absence of external anodic polarisation, *i.e.* under conditions such that corrosion is due to the reduction of an oxidant present in the solution, in particular, of oxygen. Data on the electrochemical properties of passive metals show that it is reasonable to suppose that the cathodic reaction will occur mainly on the passivated part of the surface. A local current then inevitably arises, which can play the same part as an external current.

It follows that pitting can develop on a metal surface in the presence of Cl^-, Br^-, or I^- ions in the solution only if the critical solution potentials (φ_c^{Hal}) for the metal in the presence of these ions are more positive than the passivation potential (φ_p) of the metal. This evidently implies that the affinity of the metal for oxygen should considerably exceed its affinity for the corresponding halogens. If the opposite relation holds ($\varphi_p > \varphi_c^{Hal}$), the adsorption of halide ions will obviously prevent the passivating adsorption of the oxygen of water and favour dissolution of the metal in the active state. With zirconium such a condition is realised by introducing into the solution fluoride ions[42], which possess a greater affinity for this metal than has oxygen. The zirconium surface is then completely activated in acid solution, and its rate of dissolution considerably increased. It follows from what has been said that analogous conditions are realised also in the dissolution of silver, cadmium, lead, and indium amalgam in acid solutions of chlorides, bromides, and iodides.

The condition formulated above ($\varphi_p < \varphi_c^{Hal}$) is necessary but not sufficient for pitting to develop in the absence of external polarisation. Even when this condition is satisfied, introduction into the solution of a corrosive anion can obviously lead to pitting only if the steady-state potential of the corroding metal is more positive than φ_c^{Hal}, *i.e.* if the following relation holds: $\varphi_{st} \geq \varphi_c^{Hal} > \varphi_p$. Since the value of φ_{st} depends on factors which determine not only the kinetics of the anodic but also that of the cathodic reaction, the realisation of this latter condition may depend on the concentration of the oxidising component in the solution, on the rate of supply of this component to the metal surface, and finally on its true rate of reduction. This conclusion agrees well with numerous experimental observations showing that, in the presence of aggressive anions in the solution, the development of pitting corrosion is favoured by the presence of an oxidant in the system, in particular molecular oxygen, ferric ions, etc. The maximum permissible concentration of oxidant should obviously depend on several conditions, including the nature of the corroding metal, the pH, the nature and concentration of the aggressive anion, the temperature, and the rate of stirring of the solution.

The relation between φ_p and φ_c^{Hal} may be affected by a change in composition of the solution. According to numerous data, the value of φ_p for any given metal or alloy depends on the pH of the medium, becoming more positive with increasing acidity of the solution[25,43-45]. The value of φ_c^{Hal}, however, varies appreciably with a change in concentration of the aggressive anion, and is practically independent of pH. Thus according to Gil'man's results[40], obtained with zirconium, a tenfold increase in Cl^- concentration is accompanied by a shift in φ_c^{Hal} of approximately 58 mV towards more negative values (see Fig. 7).

Following these ideas and assuming, as in Eqn. (10), that the activating effect of halide ions on the anodic dissolution of metals with pitting is due to the participation of these ions not only in the depassivation of individual portions of the surface but also in the elementary act of ionisation of the metal atoms, we could reasonably expect that the process would be retarded by the slowness of supply of aggressive anions to the metal surface. Experimental data do not, however, confirm this conclusion. Experiments with zirconium have shown that, even with comparatively low concentrations of chloride ions, an increase in the anodic polarising current density (calculated on the apparent surface) right up to 10^{-1} A cm^{-2} produces no appreciable deviation of the electrode potential from the critical value. In the reviewer's opinion this result can be understood and explained, bearing in mind that pitting can develop only when the affinity of the metal for oxygen exceeds its affinity for the corresponding halogen. The stable form of the metal ion in the bulk of the solution will then be its oxygen complex of the type ZrO^{2+}.

It is very probable that under normal conditions dissolution of a metal involves the direct formation of such ions, whereas when the critical potential is reached conditions are created which favour the formation of complex ions of the metal with the aggressive anion as primary product. As such ions diffuse from the metal surface into the solution, however, they can be expected to hydrolyse completely with

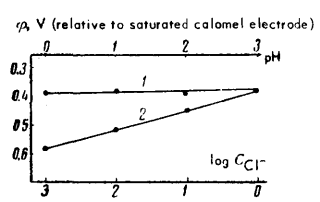


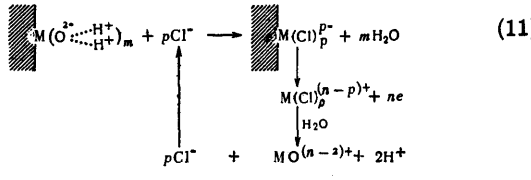
Fig. 7. Dependence of critical solution potential of zirconium on:
1) pH value at constant Cl^- concentration;
2) concentration of chloride ions at constant pH.

‡ Such a hypothesis is quite reasonable if it is remembered that the potentials at which pitting occurs are usually appreciably more positive than the corresponding passivation potentials. On the assumption that the kinetics of metal dissolution is characterised by roughly the same Tafel straight line at pitted regions as on the active metal in the potential range of the preceding passivation, it can be easily shown that the true rate of dissolution of the metal will then considerably exceed the rate of diffusion of the reaction products from the metal phase into the solution.

TABLE. Solution potentials of some metals in the presence of halide ions (N).

Metal	Potential, V (relative to saturated calomel electrode)		Ref.
	Cl^-	Br^-	
Magnesium	−1.419	−1.269	46
Aluminium	−0.509	−0.369	41
Zirconium	+0.380	+0.660	40

the formation of oxygen complexes and free halide ions, which can take part in the process afresh. Under such conditions the concentration of halide ions at the metal surface, as also in the bulk of the solution, will remain unchanged, and they will act as a kind of corrosion catalyst. The mechanism of the dissolution of a metal under such conditions can obviously be represented by the scheme:



(11)

The fact that the corrosive effect of halide ions is exerted in each case only when a definite electrode potential is reached indicates that their chemical activity increases with increase in the positive charge on the metal surface, the role of which is evidently to polarise such ions. Hence the potential at which ions of a given halogen are able to displace the passivating oxygen from the metal surface should vary with the zero-charge point of the metal and its affinity for oxygen§, and consequently should depend not only on the nature and concentration of the halide ions but also on the nature of the metal itself. This conclusion agrees well with available experimental data.

It is clear from the Table that, of the three metals compared, zirconium, which possesses the greatest affinity for oxygen, is characterised by the most positive solution potentials in the presence of chloride and bromide ions.

In conclusion, halide ions are not exceptional in their ability to cause pitting. Results obtained by Kabanov and Vanyukova[38], for iron[39], and recently by Gil'man[40] for zirconium show that perchlorate ions also possess a similar ability, but the solution potential then has considerably more positive values.

§ Since in this case we are dealing with a specific interaction between the surface atoms of the metal and oxygen, the affinity between them can be usefully measured not by the total energy of interaction but only by the part of it associated with the covalent bond.

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METHODS FOR INCREASING THE RESISTANCE OF POLYMERS TO LOW-TEMPERATURES

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CONTENTS

1. Introduction 167
2. Reduction of the glass point in polymers by plasticising 167
3. Reduction of the tendency of polymers to crystallise 169
A. Copolymerisation 169
B. Modification 170

1. INTRODUCTION

The rapid growth of technology places increasing demands on the properties of polymeric materials; in particular, an increase in the temperature limits of their applicability is needed.

This article reviews the methods for increasing their low-temperature resistance, *i.e.* the ability of parts made from polymeric materials to retain their serviceability at low-temperatures. An insufficient low-temperature resistance in polymers may be due to vitrification or crystallisation†, which produce increased hardness, brittleness, and loss of elastic properties. According to modern views[1,2], the vitrification of polymers is caused by a sharp decrease in the intensity of the thermal motion of the polymer chains, a decrease in their flexibility, closer approach of the molecules, and an increase in their interaction. The temperature at which the polymer becomes vitreous is called the glass point (T_g). Polymers typically show a range of glass points, and not a single temperature T_g, since the values of T_g obtained by different methods do not coincide. Moreover, as Aleksandrov and Lazurkin[3], Lazurkin[4,5], and Bartenev[6-8] have shown, the temperature at which the material loses its properties can vary by several tens of degrees, depending on the rate of deformation: T_g increases with the rate of deformation; thus in evaluating T_g for polymers, the actual conditions of use must be taken into account‡.

As the temperature is reduced, the tendency of crystallising polymers to vitrify increases. Crystallisation takes place over a range of temperatures, and its rate increases sharply over a definite section of this temperature range[2]. Thus for unstretched natural rubber this range extends from +15° to -50°, with a maximum rate of crystallisation at -26°. No crystallisation occurs below -50°, since the mobility of the macromolecular chains is too small to form orderly structures. Polychloroprene polymers crystallise over the temperature range +32° to -32°, with a maximum rate of crystallisation at 0°.[2]§

Articles made of polymeric materials often cannot be used even at temperatures above the glass point, because of crystallisation. Thus goods of natural rubber, which has a glass point of the order of -73°, sometimes cannot be used at -10° to -40°, because of incipient crystallisation and loss of elastic properties. Methods are now known for reducing the glass point and decreasing the extent of crystallisation in polymeric materials.

2. REDUCTION OF THE GLASS POINT IN POLYMERS BY PLASTICISING

Until recently the only method for increasing the low-temperature resistance of polymeric materials was by plasticising them, which comprises compounding the polymer with substances which reduce the glass point of the initial polymer. The most widely used plasticisers were phthalic, sebacic, and phosphoric esters.

For a long time, however, the experimental data on the plasticising of polymers had no theoretical foundation, because of the absence of any clear views on the structure of polymers. The investigation of the physical basis of plasticising became possible after the studies of Kobeko[1], Aleksandrov and Lazurkin[3], and Kargin and Slonimskii[15] on the structure of polymers and their behaviour on deformation.

According to modern views there are two mechanisms for the action of plasticisers, for polar and non-polar polymers. After studying the plasticisation of polar polymers by polar or easily polarised plasticisers, Zhurkov[16-19] concluded that the plasticising effect is independent of the chemical nature or molecular dimensions of the plasticiser. The plasticising effect was directly proportional to the molar concentration of the plasticiser:

$$\Delta T = kn,$$

where ΔT is the plasticising effect and n is the molar concentration of plasticiser. k was constant for several plasticisers (tetrachloroethane, acetone, benzyl alcohol, and others). Zhurkov explained this action of plasticisers on polar polymers as the blocking of the individual active centres in the polymer molecule, and showed that this should be determined only by the number of molecules introduced, irrespective of their nature or shape. This is known as the Zhurkov rule of molar concentrations.

† For polymers which crystallise.

‡ The processes occurring in vitrification have been described in more detail in special publications[9,10].

§ The processes occurring in crystallisation have been described in more detail[2,11-14].