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Chemistry. — "*The Passivity of Chromium*". (Second Communication). By Dr. A. H. W. ATEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of Jan. 26, 1918)

In the first communication on this subject¹⁾ the potentials were discussed, which different kinds of chromium present, when they are in contact with an electrolyte in a currentless condition. This second paper gives the results of determinations of the potential presented by chromium in anodic and cathodic polarisation.

1. *Anodic polarisation of electrolytic chromium in solutions of chromous-sulphate.*

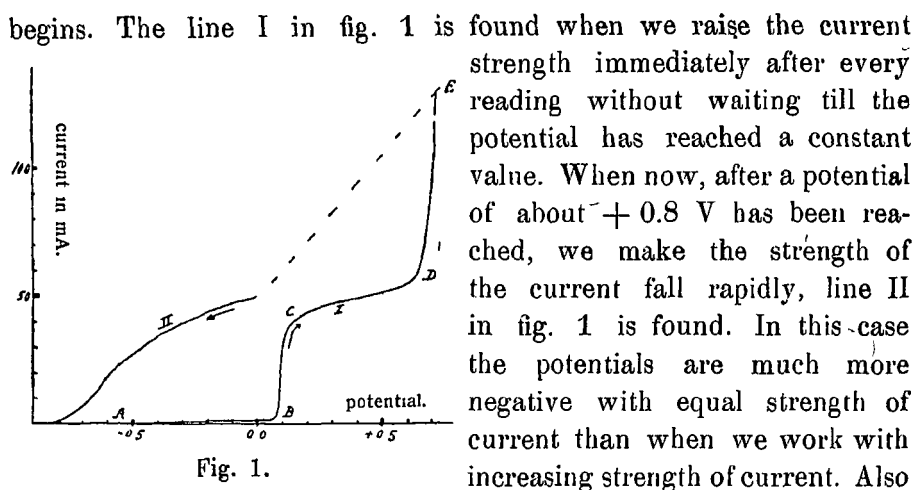
The phenomena that make their appearance on anodic polarisation of electrolytic chromium, are dependent on the nature of the metal on which the chromium has been deposited. The results given below refer to chromium that has been deposited from a solution of chromic chloride on copper. The measurements took place according to the method of LE BLANC²⁾. The commutator used in this was arranged so, that the electrode was polarized during a certain time, was then currentless for a time of equal duration, was then connected with the compensation apparatus, and was finally currentless again.

The potential as function of the strength of the current had in this the following course. In currentless condition the potential was -0.55 . With a very feeble current the potential rose to $+0.1$, and increased only little when the current was strengthened.

Above a certain limiting value of the strength of the current the potential rapidly rose again to $+0.7$ V, and increased but little on further strengthening of the current. This course is represented by line I in figure 1. It appears from the shape of the line that from *A* to *B* a slowly progressing reaction takes place at the anode, from *B* to *C* a rapidly proceeding reaction. Between *C* and *D* the limiting current for this reaction is reached. At *D* a new reaction

¹⁾ These Proc. Oct. 1917.

²⁾ Zeitschr. für physik. Chemie. 5, 469 (1890).



in currentless condition the electrode is much more negative than before the polarisation, viz. -0.8 V as against -0.55 V.

When the strength of the current is not rapidly increased, but when we wait after every increase of the strength of the current, till the potential has become constant, we obtain a line lying between the first mentioned. In fig. 2 the line for rapid increase of the strength of the current is given by I, that for rapid decrease by II, the line for slow increase of the strength of the current by III. Line III is also found when the strength

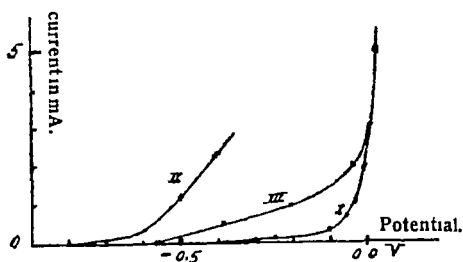


Fig. 2.

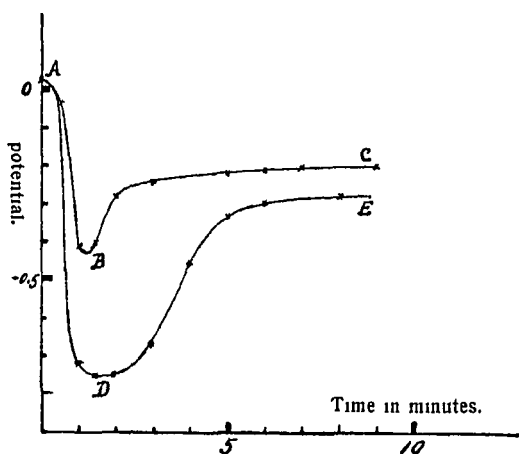


Fig. 3.

of the current is made to decrease slowly. In this last mode of procedure we get from a point on line I to a point of line II, and then the potential rises slowly to a point of line III. In consequence of this the potential as function of the time presents a peculiar course, which is represented in figure 3. The upmost line was found when the current was rapidly changed from 5 mA to 1 mA.

The potential was at 5 mA *A*, descended on transition to 1 mA to *B*, and then rose slowly to *C*. The lower line was found when the current was rapidly changed from 5 mA to 0.1 mA. This line exhibits the same course, but more pronounced. The course of the lines in figure 3 can be accounted for by the assumption that the anodic polarisation has two kinds of influence on the potential. In the first place the potential is much more positive than the end-potential *during* anodic polarisation; in the second place the potential is more negative than the end-potential *after* anodic polarisation. There is, therefore, a passivating action, which manifests itself during the polarisation, and there is at the same time an activating action, which shows itself after the polarisation. Both actions are the stronger as the strength of the polarising current is the greater, as will be more fully discussed later.

When the current is broken after anodic polarisation, the potential descends to about -0.8 V, then a *slow* rise to -0.55 V takes place again.

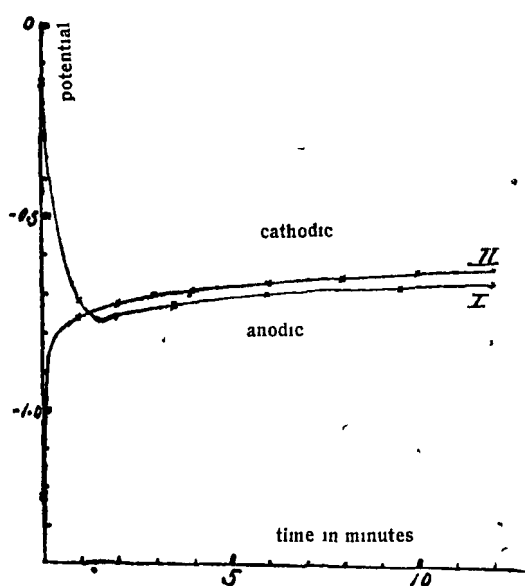


Fig. 4.

This course is shown by line I in figure 4. Here the current was brought from 5 mA to 0.

In the same figure line II gives the course of the potential after cathodic polarisation with 5 mA. Here the potential is very strongly negative at first, after one or two minutes the potential has already risen to -0.75 V, and from this point the line for cathodic polarisation coincides about with that for anodic polarisation. I.e. through anodic polarisation

the potential is at first too positive, through cathodic polarisation too negative, after a few minutes, however, the condition after anodic and cathodic polarisation has become the same.

As was already observed, it follows from line I in figure 1 that two different reactions take place on anodic polarisation of chromium. One at about $+0.1$ V, another at about $+0.7$ V. The latter is undoubtedly the anodic formation of chromate. What reaction takes

place at $+0.1$ V is still to be investigated. There exist here three possibilities. 1. the chromium can go here into solution as chromous-ion (perhaps also as chromic-ion). 2. oxidation can take place in the solution from Cr^{++} to Cr^{+++} , 3. the copper on which the chromium has been precipitated, can go into solution. This last possibility must be considered, as the chromium does not very firmly adhere to the copper. The chromium might, therefore, present cracks, and this might be the reason that the copper went into solution.

That the reaction at $+0.1$ V is not an oxidation from chromous- to chromic-ion appears from this, that pretty much the same course was found for the current potential line when as electrolyte a solution of KCl was used. Only the potential, for which a great increase of the strength of the current was found, lay somewhat lower, viz. at from -0.1 to 0.0 V. The same thing appears from the following experiment: A naked, and a platinized electrode were anodically polarized in a solution of chromous-sulphate. No rise was noticeable at $+0.1$ V. The strength of the current rose at once with a potential of -0.5 V; hence oxidation evidently takes place here from Cr^{++} to Cr^{+++} . The limiting current had already been reached at 2 mA, and a further rise of the strength of the current did not set in before $+1.0$ V (oxygen generation). For comparison the anodic oxidation of FeSO_4 was examined. Here the limiting current was not reached before 90 mA. In figure 5 the current

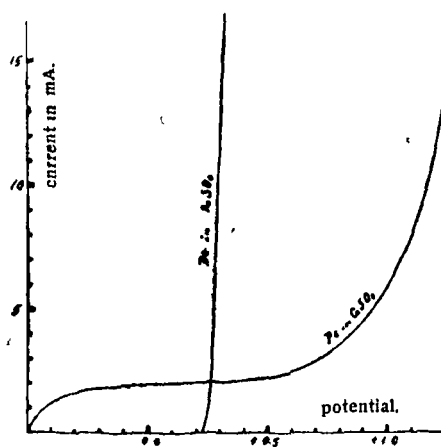


Fig. 5.

solution of copper.

That the metal on which the chromium has been electrolytically precipitated, plays a part in anodic polarisation, appears from the following observations. Chromium that has been deposited on silver, presents about the same current potential line as chromium on copper.

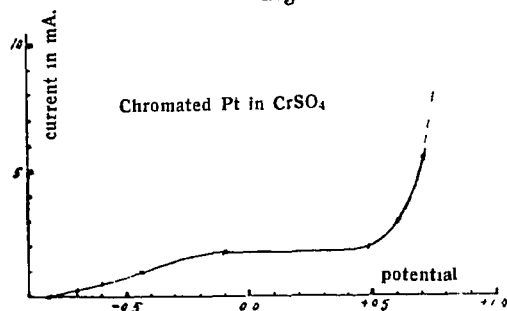
potential lines of platinum in chromous sulphate and ferrous-sulphate have been drawn.

When an electrode of copper is anodically polarized in a solution of KCl, a current potential line is found, which, as regards the first portion, agrees pretty well with the line for chromium precipitated on copper. Hence it is possible that the first vertical part in the chromium line is caused by the going into

The only difference is, that the first vertical portion lies at a more positive potential, viz. $+0.4$ V.

For chromium on platinum or on gold the shape of the current potential line is different. Figure 6 represents the behaviour of chromium

Fig. 6.



on platinum, when the strength of the current is quickly increased. From -0.8 V a slow increase of the strength of the current takes place till a potential of about -0.1 V has been reached. Then the line has a very flat course, till the formation

of chromate begins at $+0.7$ V. When now the strength of the current is slowly raised, and we wait every time till the potential has become constant, we find a line with a much flatter course, for which already at 0.1 mA the potential rises to $+0.7$ V. It appears from this, that electrolytic chromium cannot continue to go into solution at a potential that lies in the neighbourhood of the potential of equilibrium. It may be, that the ascending course that the line exhibits at -0.8 V in figure 6, does not correspond with the solution of chromium, but with the solution of hydrogen present in the electrolytic chromium.

Immediately after the current has been broken, the chromium on platinum or gold is not activated, but presents a potential of $+0.7$ V. This phenomenon is treated more at length under 2.

2. The activation of chromium by anodic polarisation in solutions of chromous sulphate.

Chromium that has been deposited electrolytically on silver, presents

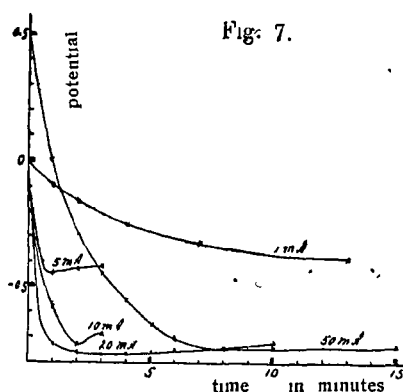


Fig. 7.

like chromium on copper, an active potential after anodic polarisation. Immediately after anodic polarisation the potential is fairly positive. It descends, however, in a few minutes, to a pretty great negative value. In figure 7 the course of the potential has been drawn as function of the time, when the current of 1, 5, 10, 20, and 50 mA is suddenly broken off. The general

course of these lines is as follows: When the current is interrupted, the chromium is still somewhat passive, the potential moves however quickly to more negative values, and finally approaches a value of about -0.5 V.

The way in which this value of -0.5 V is reached, is however different for different strengths of current. For feeble anodic polarisation, 1 mA, the potential falls gradually from 0.0 V. At 5 mA a faint minimum is reached, after which the line begins again to ascend slowly. For 10 mA this minimum lies lower, for 20 and 50 mA still somewhat lower (-0.75 V). For these last two lines the rise following on the minimum, is much slower than for the others. Hence it appears from this, that the activation of chromium on silver is the stronger and the more prolonged as the strength of the current, with which the anodic polarisation takes place, is the greater.

The same phenomenon is observed for chromium that has been precipitated on gold, but the potentials are much more positive here. In figure 8 these lines are drawn, which indicate the course of the potential with the time, when the current is suddenly broken off. Here too the potential that is reached, lies at the current has been the stronger.

more negative values as the polarising current has been the stronger. Hence it appears here, that activation makes its appearance after anodic polarisation with chromium that has been deposited on copper, silver, or gold.

The potentials that are reached in this, are most negative for the least noble of these metals¹⁾.

It was noticed in these experiments that chromium on gold or on platinum, after anodic polarisation, becomes less active when it has been cathodically polarised shortly before. Lines 1 and 2 in figure 9 give the potential after the current has been interrupted, when the electrode had not been

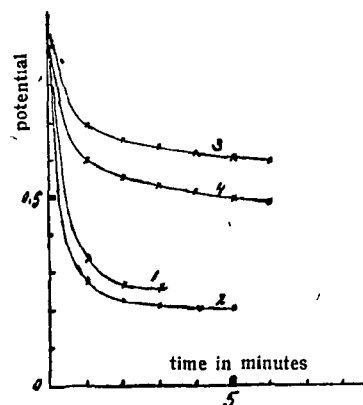
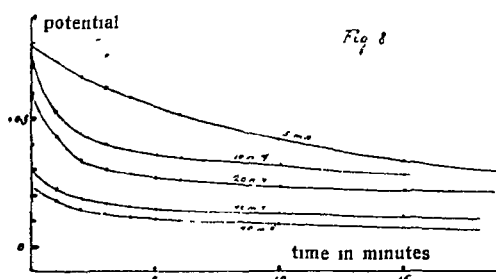


Fig. 9.

¹⁾ RATHERT. Zeitschr. f. physik. Chemie 86, 567 (1914) observed the same phenomenon for Cr that had been precipitated on Cu and on Pt.

cathodically polarised beforehand, lines 3 and 4 when this had been done.

This activating action of the anodic polarisation still comes to expression in a very peculiar way in this, that for chromium on gold a current potential line is found with a retrogressive part. With increasing strength of the current, the potential descends

Such a current potential line has been drawn in figure 10. At 5 mA the potential is $+0.94$; this *descends*, on increase of the strength of the current to 100 mA, to $+0.82$ V. This peculiar course is easily accounted for on the ground of what precedes.

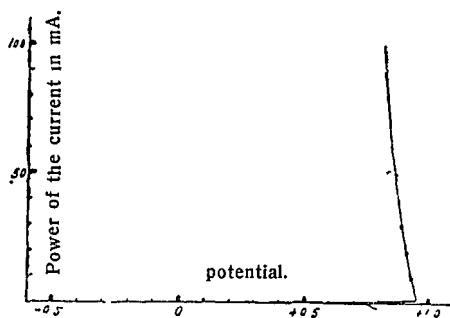


Fig. 10.

current than for a small. Now in this method of procedure the potential is not measured during the passage of the current, but shortly after (about $\frac{1}{100}$ sec.).

That the current potential line is found to be retrogressive, is therefore again a consequence of the activation *after* anodic polarisation. When these considerations are true, this retrogressive line will only be found when we work with a commutator, not when we measure the potential with a siphon *during* the polarisation. This proved actually to be the case. For chromium of GOLDSCHMIDT, which likewise gives a retrogressive current potential line in solutions of KCl, H_2SO_4 , and HCl, when we work according to LE BLANC's method, a normal line was found when the potential was determined by means of a siphon.

Two lines have been traced in figure 11 for measurements with commutator and with siphon in HCl. The activation by anodic polarisation appears here very clearly.

At 100 mA the potential descends in $\frac{1}{100}$ sec. from $+1.22$ V to $+0.83$ V,

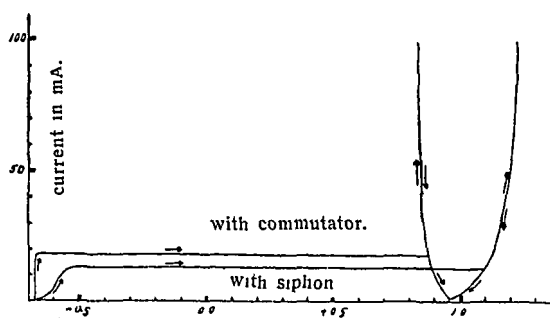


Fig. 11.

hence 0.39 V; at 5 mA it descends only 0.1 V, viz. from $+1.03$ to $+0.93$ V. With these potentials formation of chromate takes place. But also when the chromium goes into solution as chromous ion, the activation is very apparent after interruption of the current. Here e.g. the potential that is found according to LE BLANC, is for 10 mA about 0.1 V more negative than when measured with a siphon. In the first case the current potential line up to 18 mA has the course of a normal line, in the second case the current potential line proves that also the anodic solution in hydrochloric acid as chromous ion is a reaction that proceeds slowly.

In virtue of the difference found here between the current potential line that is determined with a commutator and one that is determined by means of a siphon, it might be imagined that the above described activation by anodic polarisation takes only place during the moments that the current is broken, hence only after, not during the polarisation. That activation takes place also *during* the anodic polarisation appears from the experiments with chromium of GOLDSCHMIDT described below.

3. *Anodic polarisation of chromium of GOLDSCHMIDT.*

The passivation and activation of chromium of GOLDSCHMIDT has been closely examined by HITTORF, especially with regard to the different factors that act in a passivating or activating way. It then appeared, as was already said in the introduction of the preceding paper, that oxidizers (HNO_3 , bromine water), like anodic polarisation, make chromium passive. Cathodic polarisation on the other hand makes chromium active. In the same way the hydrogen generation, which chromium gives in active state in diluted acids (especially HCl) is able to make the active state permanent. Chromium is also made active by being placed in melted chlorides, (Zn Cl_2 , $\text{KCl} + \text{NaCl}$). Chlorine ions have a specific activating action, hence chromium is more strongly active in hydrochloric acid than in sulphuric acid of the same concentration.

In the first place a quantitative comparison was then made between the activating action of hydrochloric acid and sulphuric acid by determination of the strength of the current required to make the metal in these solutions passive. It then appeared that the current strength required for passivation was about proportional to the concentration of the acid, as figure 12 shows. The values found for the current strength of passivation, are rather divergent; this causes the points in figure 12 to lie rather scattered.

It appears clearly from the lines found that hydrochloric acid

acts more strongly activating than sulphuric acid, with the same concentration about three times as strongly. Accordingly besides the hydrogen ions, also the chlorine ions have an activating action. This follows also from this, that the strength of current of passivation

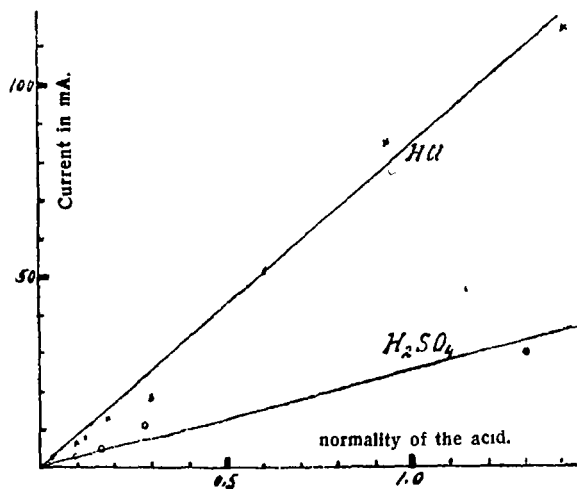


Fig. 12.

in hydrochloric acid to which potassium chloride has been added, is greater than in hydrochloric acid alone. In two experiments this amounted in 0.1 n HCl + n KCl to 14.5 and 16.5 mA, in 0.1 n HCl to 5 and 7 mA. By making the concentration of the chlorine ions ten times greater, the activating action is increased two and a half times.

The chlorine ions, however, do not act here independently of the hydrogen ions, for in 1 n KCl without hydrochloric acid chromium already becomes passive under ordinary circumstances with the smallest strength of current.

In the second place the anodic behaviour was investigated of chromium that had been activated by placing it in melted salts. The activating action of molten NaCl + KCl may appear from the following experiment.

A piece of chromium of GOLDSCHMIDT in a saturated solution of KCl gave a potential of -0.47 V, and already became passive at 0.1 mA.¹⁾ After this electrode had been for half an hour in molten NaCl + KCl, the potential was -0.640 . Now the electrode bore a current of 8 mA without becoming passive on slow increase of the strength of the current.

¹⁾ These and the following experiments were not carried out with a commutator, but the polarisation voltage was measured by means of a siphon, hence during the polarisation.

After the current had been broken, the potential was more active than before the polarisation viz. -0.667 . In this the activating action of the anodic polarization *after* the interruption of the current manifested itself again. When after this the current was suddenly again raised to 8 mA, the electrode became passive. Hence, while on slow increase of the strength of the current the electrode resisted 8 mA, it could not bear this strength of current with rapid rise to 8 mA, notwithstanding the electrode was very active in currentless condition. This is in harmony with the phenomenon described before, that on quick increase of the current an electrode at first presents a too positive value, which afterwards becomes less positive. By quick increase of the current the potential can now become so positive, that the electrode becomes passive. If the current had been slowly made stronger, so that the potential had every time an opportunity to go back to less positive values, no passivity would have set in.

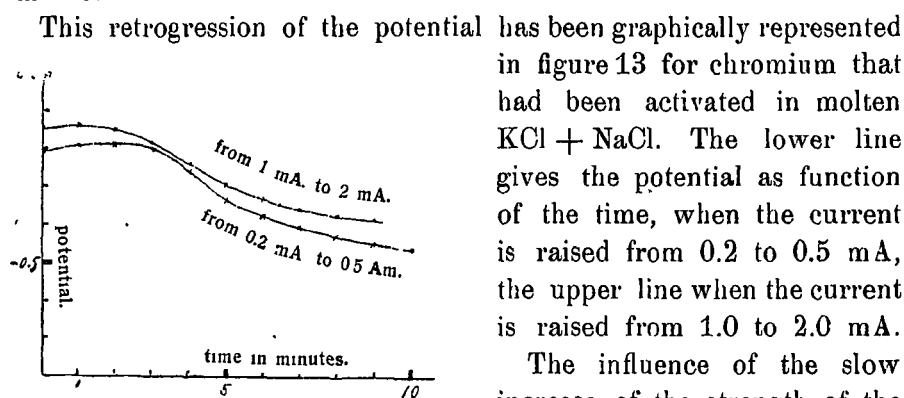


Fig. 13.

This retrogression of the potential has been graphically represented in figure 13 for chromium that had been activated in molten $\text{KCl} + \text{NaCl}$. The lower line gives the potential as function of the time, when the current is raised from 0.2 to 0.5 mA, the upper line when the current is raised from 1.0 to 2.0 mA. The influence of the slow increase of the strength of the current was still more apparent for a piece of chromium that had been activated in ZnCl_2 . This resisted a strength of current of 14 mA, when the current was increased by 1 mA every three minutes. After interruption of the current this electrode was more active than before the polarisation. When after this the current was at once brought to 5 mA, the electrode became passive¹⁾.

Another electrode was likewise activated in molten ZnCl_2 . The potential was -0.542 in saturated KCl. The electrode was anodi-

¹⁾ The influence of the interruption or enfeebling of the polarizing current appears in a very peculiar way from the following experiment. A piece of chromium, which was anodically polarized with 7 mA. in KCl-solution, was brought in contact with a piece of zinc. This caused the potential to fall from -0.538 to -0.750 . Then the current passed into the solution chiefly through the zinc, which caused the density of the current, with which the chromium was polarized, to

cally polarized, and the strength of current was slowly raised to 2 mA., at which the potential amounted to -0.405 Volt. When air was blown through along the electrode, the potential did not change more than 10 mV; the same occurred when the liquid was stirred, from which follows that the activity of the chromium was not caused here by a change in concentration of the liquid in contact with the metal. After the current had continued to pass throughout the night, the strength of the current had increased to 3.28 mA., and the potential had fallen to -0.513 . Accordingly the electrode was very active now. The solution of KCl was then siphoned off, and replaced by fresh solution. The electrode remained active, though the potential rose a little, viz. from -0.513 to -0.472 . Here too it appears that the activity of the chromium was not the consequence of a change in the concentration of the liquid. The chromium generated small bubbles of hydrogen. Also when the metal was brought in contact with a platinum wire, it remained active. In this the hydrogen continued to develop at the chromium. When the current was broken, the potential was -0.613 , and fell to -0.642 in 15 minutes.

Now the electrode could resist 1 mA without becoming passive, and the current could be made stronger pretty quickly, in 20 minutes from 1 mA to 3.6 mA, without the activity being lost.

Accordingly the anodic current could remain interrupted for this electrode for 15 minutes, the activity being maintained.

After the anodic current had been first carried up to 3.6 mA again, at which the potential amounted to -0.421 , it was cathodically polarized with 50 mA for 15 minutes. This took place in another solution of KCl. The anode was placed in a porous vessel, so that the liberated chlorine did not get in contact with the chromium electrode. When the electrode was again brought in the original solution of KCl, the potential was strongly negative in consequence of the hydrogen charge, -1.09 V. Then this electrode was anodically polarized with 0.5 mA. In an hour the potential rose to $+0.512$ V. While therefore without previous cathodic polarisation the electrode could bear anodically 1 mA without becoming passive, it already became passive with 0.5 mA after cathodic polarisation. After interruption of the current this electrode again obtained an active potential, viz. -0.614 V.

become smaller. When afterwards the zinc was removed, the potential rapidly rose to -0.35 V, after which it fell again to its original value -0.54 in three minutes.

The decrease of the anodically polarizing current had consequently given rise here to a very considerable rise of the potential.

Just as HITTORF has found, it appeared also in these experiments that chromium is more strongly activated by molten zinc chloride than by molten $\text{KCl} + \text{NaCl}$.

In molten $\text{K}_2\text{Cr}_2\text{O}_7$, and also glowed at the air, chromium becomes very little activated, but yet it is a little more active than chromium that has not been heated. In molten KCN the metal is perceptibly, though feebly activated, it bore 1.5 mA without becoming passive.

It is remarkable that not always the electrode that has the most negative potential in currentless condition, is made passive with the greatest difficulty. Thus chromium that had been immersed in molten KCN presented a potential of -0.44 V before polarisation, after polarisation -0.58 V. Yet this chromium was less easy to make passive than chromium from molten $\text{K}_2\text{Cr}_2\text{O}_7$, which showed -0.56 before polarisation, -0.64 V after polarisation.

All the electrodes that had been treated with molten salts, were covered with a layer of green or black oxide. From molten ZnCl_2 and $\text{KCl} + \text{NaCl}$ the metal generated hydrogen. The chromium that had been glowed at the air, exhibited blue annealing colours.

The treatment that the chromium electrode has been previously objected to, is therefore of great influence on the passifiability.

The same thing applies to the concentration of the solution in which the chromium is examined.

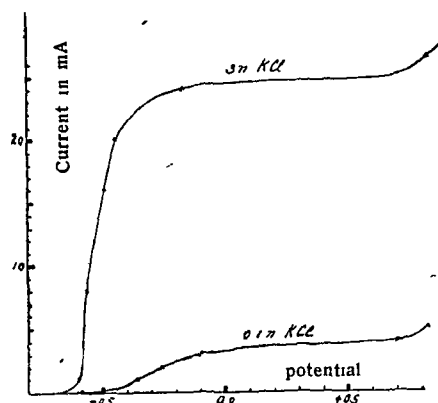


Fig. 14.

The metal is very easy to make passive in a solution of Na_2SO_4 ; not so easy in a solution of KCl .

In this the strength of current of passivation is the greater as the KCl -content of the solution is the greater. Figure 14 represents the line of passivation for a same chromium electrode in a saturated solution of potassium chloride, and in a 0.1 n solution.

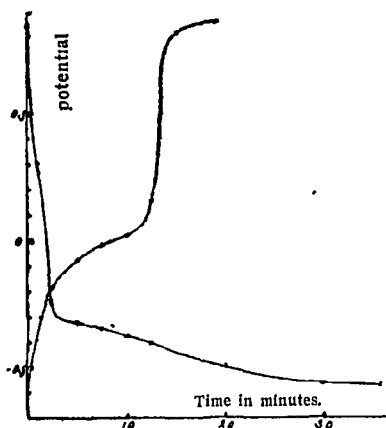
When an electrode that has been activated in molten ZnCl_2 , is anodically polarized with a sufficient density of current, it becomes passive, and presents potentials which are the same as for an electrode which has lain in nitric acid beforehand for a long time, and has become passive through this. After the current has been broken off, the electrode from ZnCl_2 becomes again active after a short time, that from HNO_3 remains passive. Also an electrode

that has been first activated by ZnCl_2 , becomes passive through HNO_3 .

In the experiment the potential rose from -0.65 to $+0.1$.

After vigorous anodic polarisation the electrode had become active again and presented a potential of -0.49 .

When a piece of chromium is brought into hydrochloric acid, it becomes active, and generates hydrogen. After it has been rinsed and conveyed into a saturated KCl -solution the activity continues, but is by no means so strong as the activity obtained in molten ZnCl_2 , so that the electrode already becomes passive e.g. at 1 mA. When, however, the current is slowly made stronger, the activity continues to exist. Thus a strength of current of 12 mA could be reached for a potential of -0.35 V in ten days. Here too it was always observed that on increase of the strength of current the potential first increased greatly, and diminished later again. The electrode continually developed hydrogen, sometimes with a crackling sound. The liquid contained a large quantity of chromhydroxide



and had become alkaline in consequence of the cathodic formation of NaOH . After breaking of the current the electrode was active -0.66 V. When after 8 minutes the current was suddenly brought to 3 mA, the electrode became passive. After interruption of the current the activity returned. In Fig. 15 the passivation with 3 mA and the activation after the current had been broken off, is represented as a function of the time.

When chromium of GOLDSCHMIDT, which had not been previously activated, is anodically polarised in a saturate solution of KCl with a current strength of 1 mA, it becomes passive. When we begin to heat, activation sets in at a certain temperature. With a strength of current of 1 mA this took place at about 60° . Then the potential fell to -0.55 V. When the temperature is lowered during passage of the current, the electrode remains active, during which the potential rises to -0.4 V. With higher current strength the same behaviour is found; here the temperature at which activation occurs, lies higher, for 25 mA e.g. at 75° . With lowering of the temperature the electrode remains active in this case; the potentials found here, are the more positive as the strength of the current is the greater.

If this is too great, e.g. 50 mA, the electrode becomes passive on cooling.

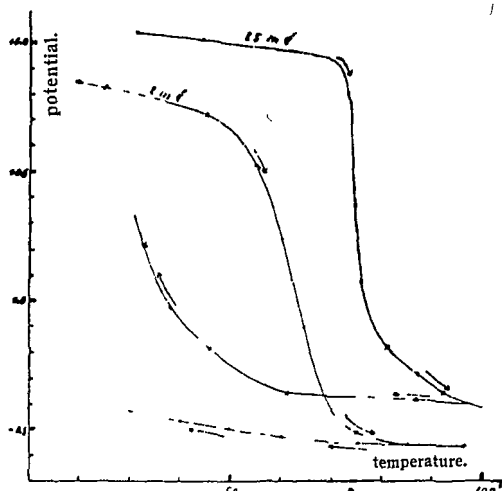


Fig. 16.

Figure 16 gives the course of the potential as function of the temperature on heating and cooling of a chromium electrode, when this is anodically polarized with 1 mA and 25 mA.

After the current had been broken, the potential was very active, at 1 mA — 0.60 V, at 50 mA — 0.66 V.

When the electrode has remained active after cooling during the anodic polarisation, and the current is broken,

a very active potential is found. When after a short time e.g. after 20 sec. the current is closed again, the electrode cannot bear this current, but becomes passive. In harmony with this is the phenomenon that a chromium electrode which has become active through heating in a solution of KCl, on anodic polarisation, and is cooled then after the current has been broken, preserves indeed an active potential, but can resist only a very feeble anodic current without becoming passive.

Finally the influence of molecular hydrogen and of hydrogen that had been generated cathodically on the passifiability of chromium was examined. Molecular hydrogen has no influence here, as was already known from earlier researches. When a chromium electrode is brought in an atmosphere of hydrogen in a saturate KCl-solution, the chromium gets a potential of about —0.5 V, a platinum-electrode presenting —0.68 V under the same circumstances. The chromium is, therefore, not able to assume the hydrogen potential. When the chromium is cathodically polarized, so that hydrogen is vigorously generated, the metal at first shows a strongly negative potential, which is the consequence of the acquired hydrogen charge. The chromium pretty soon loses this hydrogen charge, at which the potential gradually rises to —0.5 V. Both before and after cathodic polarisation, this electrode became passive on anodic polarisation with 0.2 mA. Accordingly the cathodic polarisation had not been able to activate the electrode perceptibly. This electrode *did* become active when brought in strong hydrochloric acid. Now the potential

amounted to -0.7 V in a saturate KCl. solution, and no passivation took place on anodic polarisation with 1.2 mA. Hence it appears from this that cathodic polarisation activates the chromium less strongly than treatment with hydrochloric acid. It appeared from further experiments that cathodic polarisation *diminishes* the activity.¹⁾ Thus an electrode which had been in a solution of KCl for two days, and had remained active in it, exhibited a potential of -0.57 V. On anodic polarisation with 0.3 mA the chromium remained active with a potential of -0.46 V. Then this electrode was cathodically polarised with 50 mA for $1\frac{1}{2}$ hours. The potential was -0.79 V after interruption of the current, and rose to -0.192 in $1\frac{1}{4}$ hours. Hence the activity had greatly diminished *after* cathodic polarisation, which also appeared from this, that the electrode became passive already on anodic polarisation with 0.01 mA in this case.

On strong cathodic polarisation other electrodes obtained a much more negative potential, down to -1.22 V. Notwithstanding such an electrode was strongly active as far as the values of the potential are concerned, it could not withstand anodic polarisation with 0.1 mA without becoming passive. After activation in strong hydrochloric acid the electrode easily resisted 0.4 mA, at which the potential was -0.55 .

4. Summary of the results.

1. Electrolytic chromium becomes passive in chromous sulphate on anodic polarisation with a sufficiently great strength of current. After breaking of the current the potential of the electrode is more negative than before the polarisation.

2. When the polarising current is made stronger the potential at first assumes a too positive value, which slowly falls to a more negative value. When the current is made feebler, the same thing takes place in reversed order.

3. The activation to which chromium is subjected by anodic polarisation, is the stronger as the electrode is polarized more vigorously.

4. GOLDSCHMIDT Chromium, which has been activated by treatment with molten ZnCl_2 or $\text{KCl} + \text{NaCl}$, can be anodically polarized in a solution of KCl without becoming passive. The strength of current which the chromium can resist in this, is greater when the current is gradually strengthened than when the strength of the current is rapidly increased.

¹⁾ This appears already from the experiment described on p. 1129.

5. Previous cathodic polarisation makes the anodic current strength which this chromium can resist without becoming passive, smaller.

6. The increase of the activity on continued anodic polarisation is caused by a change in the metal surface.

7. Chromium of GOLDSCHMIDT that has become passive through anodic polarisation in a solution of KCl, becomes active on heating of the solution, also during the passage of the current. On cooling the activity remains preserved, at least if the current is not too strong.

When the chromium cools down in the solution without becoming anodically polarized, the activity which it retains after cooling, is smaller than when the current continues to pass on cooling.

In the literature a few more examples are found of the activation through the anodic polarisation observed here. Thus FLADE¹⁾ states that a nickel electrode as negative pole of an element, the positive pole of which was platinum in chromic acid, gave a stronger current (hence was more negative) when it had first been strongly *anodically* polarised.

The same thing was found by RATHERT²⁾. A nickel electrode which in NiSO₄ presented a potential of + 0,237 V, had a potential of - 0,125 V after anodic polarisation, of + 0,64 V after cathodic polarisation. He attributes this phenomenon to changes in the concentration in the liquid. That for chromium such an explanation is not valid, has already been demonstrated above.

In the following paper we shall endeavour to give an explanation of the above described phenomena.

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¹⁾ Zeitschr. f. physik. Chemie **76**, 513, (1911).

²⁾ Zeitschr. f. physik. Chemie **86**, 567, (1914).