CCXXXIII.—*The Passivity of Metals. Part VI. A Comparison between the Penetrating Powers of Anions.*

By SIDNEY CHARLES BRITTON and ULICK RICHARDSON EVANS.

PREVIOUS work (Evans, J., 1927, 1020; 1929, 92) has shown that the facility with which chlorine ions penetrate thin films exceeds that of most other anions. It seemed useful to compare the penetrating power of various anions, by measuring the leakage current passing to an anode covered with a film of low electric conductivity. In such a case, the strength of the current should represent the penetration of the film by ions, although where the ion possesses oxidising powers or forms a sparingly soluble salt with the anode metal, the repair thus effected will reduce the apparent penetrating power.

The low electrical conductivity of the film produced by the anodic treatment of aluminium in chromic acid was demonstrated by Bengough and Sutton (*Engineering*, 1926, **122**, 274); the film itself has been isolated by Sutton and Willstrop (*J. Inst. Metals*, 1927, **38**, 259). Until recently it was held, with Günther-Schulze (*Trans. Faraday Soc.*, 1914, **9**, 266), that the anodic behaviour of aluminium was complicated by a gas layer; but recently W. J. Müller and Konopicky (*Z. physikal. Chem.*, 1929, *A*, **141**, 343) have shown the assumption of a gas layer to be unnecessary. An aluminium anode in a chromate solution provides, therefore, a simple means of measuring the penetrating power of anions. Already the work of Callendar (*J. Inst. Metals*, 1925, **34**, 57) has shown that chlorides reduce the resistance of the " scale " on aluminium, whilst nitrates increase the passivity. Moreover, Taylor and Inglis (*Phil. Mag.*, 1903, **5**, 301) and also Bairsto and Mercer (*Trans. Faraday Soc.*, 1911, **7**, 1) have measured the leakage currents due to various anions at an aluminium anode; but the high *E.M.F.*'s employed (12—20 volts) and the character of electrolyte used (sulphuric acid or ammonium phosphate) render it difficult to apply their results to the problems of passivity and corrosion.

Another interesting point is the nature of the potential drop at the anode. W. J. Müller (" Korrosion und Metallschutz," 1929, Beiheft, p. 8) thinks that at an aluminium anode the measured potential merely represents the drop needed to force the small " Rest-Strom " through the high ohmic resistance of the channels threading the layer upon the anode. (At an iron anode, at high *C.D.*'s, a polarisation of a different character is assumed.) It was hoped to obtain some additional information as to whether or not the measured potential is of a purely " ohmic " character, since this is a matter of vital importance in connexion with the theory of corrosion velocity.

EXPERIMENTAL.

Materials.—Three types of aluminium were used : (A) Electrorefined sheet with Si, 0·013 ; Fe, 0·012 ; Cu, 0·014 ; and Ti, 0·004%, kindly supplied by Mr. E. H. Dix of the Aluminum Company of America. (B) Soft annealed sheet of British origin containing Si, 0·33 ; Fe, 0·40%. (C) Hard-rolled sheet of British origin with Si, 0·34 ; Fe, 0·39%.

The salts used were of " A.R." quality, and each was tested for anions of greater penetrating power than the main anion ; the potassium bromide, tested by Chapman-Jones's method (*Chem. News*, 1904, **89**, 229), showed a trace of chloride.

Experiments showing the Variation of Current with Time.—In the preliminary work, electrodes of hard aluminium (C), freshly ground with emery, were clamped vertically in the solution at a distance of 1·1 cm., the immersed area being 1·5 × 1·5 cm. ; 2 volts were applied, and the current measured on a Weston ammeter at various times. With 0·001*M*-potassium chromate, the current rapidly dropped to a very low constant value. When a second salt also was present, however, a considerable current continued to flow indefinitely, the strength depending on the nature and concentration of the second salt, and on the concentration of chromate. In a series of experiments with solutions containing 0·001*M*-potassium chromate and 0·05*M*-potassium chloride, bromide, iodide, nitrate, or sulphate or sodium phosphate, the residual currents recorded were in the (descending) order of the anions Cl', Br', I', SO_4'', HPO_4'', NO_3'.

In another series of experiments with solutions containing 0·05*M*-potassium chloride, and various amounts of potassium chromate, the residual current first decreased with the chromate concentration, and then quite suddenly began to rise again, finally greatly surpassing the original value. No such phenomenon was found in solutions free from chloride, when the concentration of chromate was varied. No doubt the chromate acts in different ways : it increases the conductivity, decreases the cathodic polarisation, but repairs the anodic film ; since these opposing effects will obey different laws, the fall followed by the rise may be explained. In experiments at constant chromate concentration, the residual current rose as an approximately linear function of the chloride concentration ; this was found true for different values of chromate concentration above and below that which gave the minimum leakage.

Fully annealed aluminium (B) yielded similar time–current curves, but both initial and final values of the current were invariably greater ; also in chloride–chromate mixtures, the sharp angular break in the curve already mentioned occurred at a smaller chromate concentration. Electrolytically refined aluminium (A) gave slightly smaller initial and final currents than the hard-rolled " ordinary " variety (C). Apparently heterophase impurities assist the breakdown of the film, the high leakage obtained with the annealed variety being probably due to the fact that annealing causes the silicon present in solid solution to separate as a distinct phase (compare Röhrig and Borchert, *Z. Metallk.*, 1924, **16**, 398).

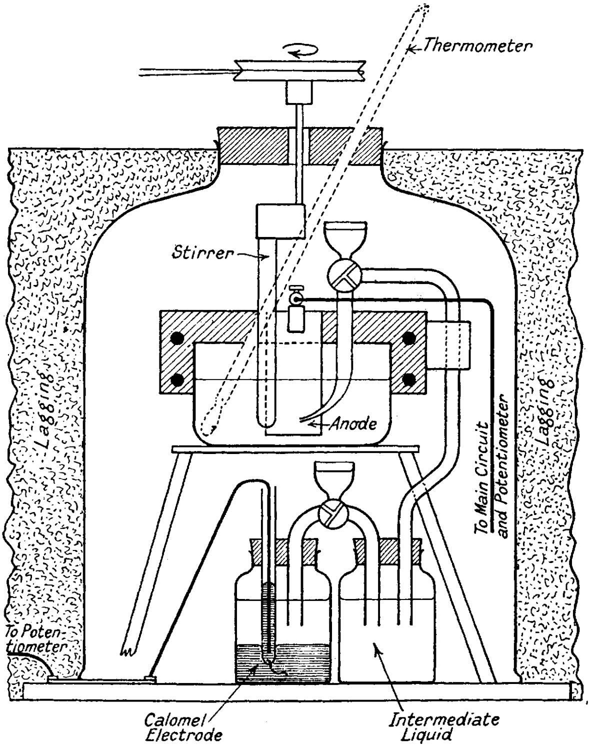
To study the effect of abrasion, a series of experiments carried out with 0·05*M*-potassium chloride and 0·001*M*-potassium chromate showed that the coarseness of the emery paper used affected the final value somewhat; although in most cases a given paper gave fairly reproducible results, the order of the leakage currents was not the order of coarseness. Wire-brushed specimens—in contrast to ground specimens—gave low current values at the moment of immersion, but here the current increased with time to a final value rather similar to those obtained with ground specimens; this indicates that the film formed by exposure to air during wire-brushing possesses a protective character, but becomes more pervious during the anodic treatment. On emery-ground specimens the current sometimes increased and sometimes decreased with the time, according to the abrasive employed and the duration of pre-exposure to air, but these factors did not seriously affect the final constant value of the leakage current.

Pure aluminium (A) tested with its smooth rolled surface, degreased with carbon tetrachloride but not abraded, gave, in the same chloride–chromate solution, somewhat smaller initial values for the current than the abraded metal, but equally high final values. Here the attack occurred at numerous minute pinholes, situated along the microscopic scratch-lines which are present even on a bright surface, and rather more frequent near the cut edges than elsewhere. It was so intense that, after 30 minutes' treatment, the metal was perforated at the points of attack, although elsewhere the surface was absolutely unchanged.

Some experiments with a solution containing 0·05*M*-potassium chloride and 0·001*M*-potassium chromate were performed in order to ascertain what degree of thermostatic control would be needed in the main series of experiments. It was found that the leakage current rose from 39 milliamps. at 18·5° to 53 at 40·5°, 69 at 55°, and 83 at 80°; with a falling temperature, the leakage current decreased once more to 64 milliamps. at 55° and 52 at 40°—values slightly below those of the rising curve. The temperature coefficient is evidently a small one.

In the experiments at fixed voltage, the fraction of the 2 volts applied falling over the anode–liquid interface varied with the state of the film and the conductivity of the liquid. It was decided, therefore, to conduct experiments with the local anodic potential measured by means of a calomel electrode and potentiometer. The arrangement is shown in Fig. 1. The electrolysis vessel was placed in a bell-jar to prevent complication due to atmospheric impurities, but to ensure that the aluminium salts formed at the anode interacted with the equivalent quantities of potassium hydroxide formed at the cathode, the cell was stirred mechanically by an eccentrically mounted glass rod of 0·52 cm. diameter, which rotated once in three seconds in a circle of 2·2 cm. diameter arranged symmetrically between the two electrodes. The distance between the electrodes was 3·5 cm., and the immersed area 2 × 2 cm. Almost touching the anode at its central point was a glass tubulus containing the electrolyte; the tubulus was a prolongation of a broader tube leading to a vessel containing the intermediate liquid; from the vessel another tube led to the calomel electrode. The intermediate liquid was

FIG. 1.

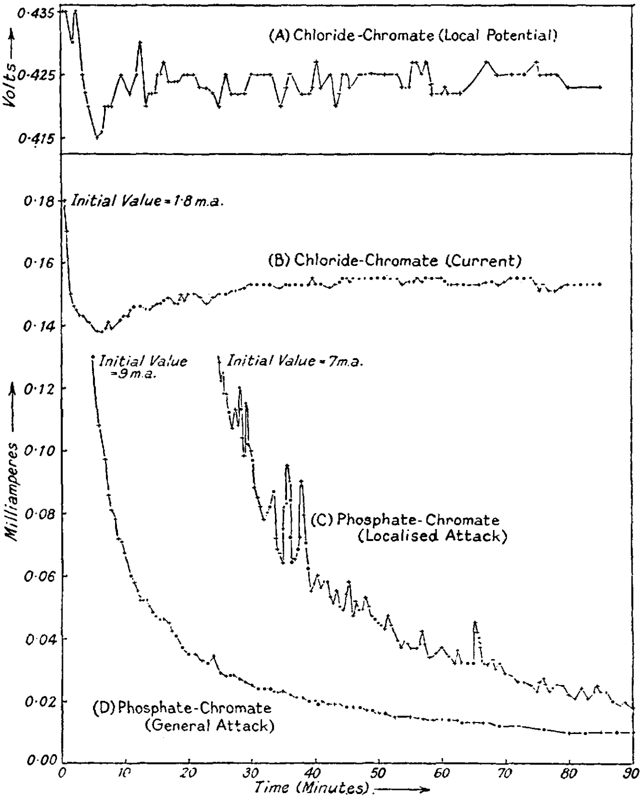


saturated potassium chloride if the electrolyte contained chlorides, and saturated ammonium nitrate in all other cases.

With this arrangement, the electrode remained in the liquid for some minutes before the current was applied; this caused the film to be in comparatively good repair at the commencement of the experiment, and the tendency for the current to rise with the time was greater than in previous series. Experiments were conducted with aluminium (B), abraded with French emery No. 1, in a solution containing 0·05*M*-potassium chloride and 0·025*M*-potassium chromate. When the total *E.M.F.* was 0·30, 0·42, or 0·58 volt the current fell with the time; at 0·71 or 0·82 volt, it rose for the first three minutes and then gradually dropped; at 0·91 and 1·32 volts the rise was very pronounced and the drop hardly apparent. But apart from the *general* rise or fall, the curves showed numerous fluctuations of current strength, which at 0·3 volt were extremely violent. The absolute value of these fluctuations varied considerably from one specimen to another in duplicate experiments; but, at higher *E.M.F.*'s (1·3 volts), since the fluctuations represented a smaller proportion of the mean current flowing, the curves, which were very jagged at 0·3 volt, became practically smooth. Even where the fluctuations on the current–time curve are only slight, the fluctuation of local anodic potential is often still marked. This is shown in Fig. 2, where curves A and B represent respectively the change of anodic potential and of current with time. Evidently the fluctuations represent local breakdowns of the film, followed by its repair. Where a breakdown happens to occur close to the tubulus, its effect on the potential may be marked, even if it is too small seriously to increase the current, whereas a breakdown far from the tubulus, even if sufficient to cause an appreciable increase of current, may hardly alter the measured potential. Thus, although the two curves show general agreement, many features on the one are not represented on the other; this was found in other cases also. The phenomenon demonstrates the already-known fact that the corrosion of a material covered with a protective film is an occurrence discontinuous both in space and in time. The reproducibility is necessarily worst when the occurrence of breakdowns is infrequent; when they are very numerous, the " law of averages " ensures better reproducibility, and complete reproducibility may be looked for when the corrosion becomes uniform.

Numerous other time–current and time–potential curves were plotted and the results agreed well with the scheme suggested. Instructive data were obtained with a solution containing 0·05*M*-sodium phosphate and 0·001*M*-potassium chromate with a total *E.M.F.* of 2·0 volts. In one experiment, the current fluctuated violently with time (curve C, Fig. 2), and the anode afterwards showed a limited number of pronounced pits; in another experiment, carried out with a different anode but under identical external conditions (curve D, Fig. 2), the violent fluctuations were quite absent and the anode was almost uniformly attacked. The mean final value of the current reached practically the same value in both cases (0·011 and 0·010 milliamp. respectively), but it was reached more quickly in the experiment giving a smooth curve. Probably the existence of a few points specially liable to serious breakdown reduces the general leakage through the film substance, which would otherwise occur; this may explain the marked contrast between the behaviour of identically treated specimens.

FIG. 2.



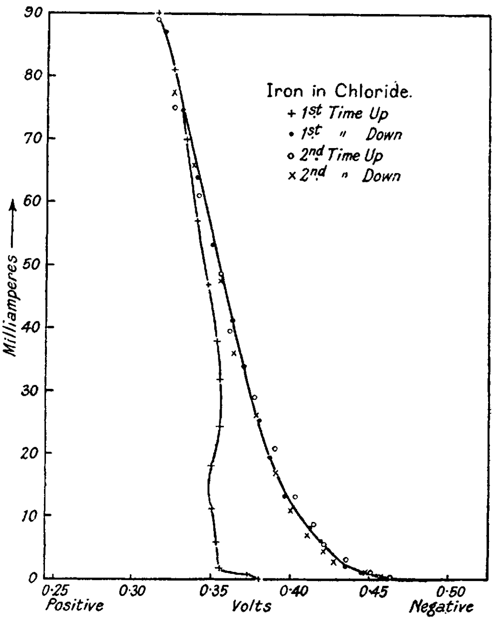
Curves showing variation of current and potential with time. All potentials are measured on the normal hydrogen scale and lie on the negative *side of the zero value* (i.e., *the same side as potassium*).

Experiments showing Variation of Current with Local Anodic Potential.—In another series, an attempt was made to obtain anodic polarisation curves. The local potential was adjusted, and the current measured after it had flowed for 5 minutes at that potential. The potential was then moved to the next value, and after a further 5 minutes the current was read again. In this way numerous potential–current curves were obtained with liquids containing chromate and chloride in different proportions. On the whole, the potential where the current began to rise was found to move in a negative direction with increasing chromate, but a given solution did not give identical curves in duplicate experiments. One experiment with 0·05*M*-potassium chloride and 0·025*M*-potassium chromate was repeated seven times with different anodes. Each anode gave a different curve, and a given anode did not give the same curve with rising current as with falling current. The potential at which the rising curves left the horizontal axis was nearly the same in different experiments, but the gradient showed great variation. This is explained by the fact that in some experiments the tubulus may happen to be opposite a point of breakdown, whilst in others it is far away from a point of attack; in the latter case, the measured drop of potential corresponding to a given current will be abnormally high, just as though the tubulus had been placed at a distance from the anodic surface. It has already been shown that at a fixed *E.M.F.*, the current varies discontinuously with the time (increasing or decreasing according as the area of breakdown extends or diminishes); it is not surprising, therefore, to find that the potential–current curves are not quite smooth. The fact that the descending curve does not coincide with the ascending curve, indicates that the healing which should follow a reduction of the current requires an appreciable time.

To ascertain whether the explanation suggested for the irregularities is correct, analogous experiments were carried out with other metals. A zinc anode in chloride–chromate was attacked locally, not uniformly, and it was found that the same irregularities were present to an even greater extent; there was an entire lack of concordance between ascending and descending values. But with an iron anode in a chloride solution, the attack soon became general; in this case, the first rising curve, obtained whilst the attack was still local, showed abnormal values, but when once the attack had become uniform, it was found that the *E.M.F.* could be moved up and down and the points always fell on the same curve (see Fig. 3): here, since the whole surface was bare, the tubulus necessarily opened on to a bare part, and reproducibility was to be expected.

It must be remembered that whilst the curves for iron (Fig. 3) show the connexion between the true *C.D.* and the true anodic potential, this is not true of curves obtained on an aluminium anode; on this metal only a small fraction of the surface is being attacked, and therefore the true *C.D.* is far greater than the apparent; moreover, since the tubulus is not in general in close contact with a point of attack, the apparent potential includes a considerable fall due to an ohmic resistance. Indeed the abrupt rise of the steepest curves for aluminium rather suggests that on aluminium the apparent polarisation is almost entirely of this character, although the rounded curves obtained for iron after the corrosion has become general suggest that here polarisation of a different character must be taken into account; these conclusions agree well with the results obtained by Müller (*loc. cit.*).

Fig. 3.



Comparison between the Penetrating Powers of Different Anions.— The fact that the local anodic potential varies in time and space makes it impossible to measure penetrating powers under conditions of constant local potential; the benefit of the "law of averages" is best obtained by maintaining a constant value for the total *E.M.F.*, and measuring the leakage current. The consistency of the results thus obtained was found to depend largely on the ratio of the concentration of chromate and the second anion. If the latter was added in large amount, giving a big breakdown area, the reproducibility was good, but the conductivity of the liquid was clearly affected. If the addition of the second anion was kept so small that the conductivity was hardly increased, a great lack of agreement was noted between duplicate experiments, especially with ions of low penetrating power. This is quite in accord with the principles already established. With a chromate concentration of 1·0*M* and a chloride concentration of 0·001*M*, the reproducibility was too poor to render measurements of value, but with a chromate concentration of 0·001*M*, and 0·05*M* concentration of the second salt, satisfactory reproducibility was obtained with the more penetrating ions; the less penetrating ions, although showing no greater absolute deviation, naturally gave a greater percentage deviation. The results are shown in Table I. It will be noticed that the fluorine ion has less penetrating power than the other halogen ions; it has, of course, also a lower mobility, and the cause of the latter (whether hydration of the ions, or the formation of complex ions such as HF_2') is probably also the cause of the low penetrating power. In the experiments with nitrates, the current fell fairly quickly to about 0·3 milliamp., and after an almost constant period, a gradual fall set in ending at a final value of about 0·1 milliamp. This low value is no doubt due to the oxidising and film-repairing character of the nitrate ion, already noted by Callendar (*loc. cit.*).

TABLE I.

Leakage currents between aluminium electrodes in 0·001*M*-potassium chromate + 0·05*M*-second salt: immersed area 2 × 2 cm.; distance 3·5 cm.; temp. 15°.

Second salt.	Leakage current (milliamps.)					
Potassium chloride	15·4,	14·9,	16·0,	15·6	Mean	15·5
Potassium bromide	14·0,	14·2,	14·2,	14·0	,,	14·1
Potassium iodide	11·8,	11·7,	11·1,	11·3	,,	11·5
Potassium fluoride	3·95,	2·78,	3·25		,,	3·3
Potassium sulphate	0·58,	0·51,	0·58		,,	0·56
Potassium nitrate	0·11,	0·12,	0·14		,,	0·12
Sodium phosphate	0·018,	0·011,	0·010		,,	0·013

The question arises as to whether, in these circumstances, the leakage current is a satisfactory measure of penetrating power. It may be argued that, since the conductivity of the different solutions is not the same, the comparison is not a valid one; actually, however, the specific equivalent conductivities of the chloride, bromide, iodide, and nitrate at 0·05*M*-concentration, all lie between 1·04 × 10^{16} and 1·15 × 10^{16} *C.G.S.* units, whilst that of the fluoride lies only slightly lower (above 0·8 × 10^{16}, not known accurately). These differences are hardly larger than the variation between individual readings. The sulphate has a specific equivalent conductivity of 0·89 × 10^{16} or a molecular conductivity of 1·79 × 10^{16} *C.G.S.* units as compared with 1·04 × 10^{16} for the nitrate. Here the current may not afford a satisfactory comparison of penetrating powers. If it is assumed that in these solutions nearly the whole of the potential is banked up at the anode, and that the liquids retain their characteristic conductivity in the pores, it would seem that the ratio of the effective cross-section of the pores in sulphate and nitrate solutions is not 0·56 : 0·12 but 0·56/1·79 : 0·12/1·04, or about 2·7 : 1.

Another possible criticism is that with a salt causing great leakage, such as chloride, most of the *E.M.F.* is spread over the bulk of the solution, whereas with anions of low penetrating power, it is largely banked up at the anode surface. It might be urged that a juster comparison would be to examine salts under conditions of equal values for the anodic potential drop; but this potential drop varies from point to point, and actually some purely arbitrary definition of "anodic potential" would have to be adopted. Evidently, however, measurements made on a basis of constant anode potential would show a bigger contrast between halogens and the larger ions than the measurements made above.

No doubt microscopic measurements of the area actually undergoing visible attack might be regarded as a good criterion of penetrating power, but it was found that the area increased with the time, even after the current had become constant. Some experiments were performed upon the pure aluminium (A), which shows such well-defined areas of attack that the area can be measured. In all cases the potassium chromate concentration was kept at 0·001*M* and the experiments were continued until 12 coulombs had passed. Those solutions which gave the smallest areas of attack naturally produced the greatest numbers of points of complete perforation. When the solution contained potassium chloride, the fraction of area corroded (about 1% when the chloride concentration was 0·05*M*) was much greater than when the solution contained potassium fluoride. Reproducibility was poor, and there was no direct proportionality between area corroded and current passing, although it was found that there was a tendency for the area to increase with rising chloride concentration. The results confirmed the view that the penetrating ions increase the leakage current by increasing the area undergoing attack.

Many years ago, Friend and Marshall (J., 1914, **105**, 2776) measured the amount of sodium carbonate needed to stop corrosion of iron by solutions containing a second anion in *N*/20 concentration. The numbers obtained may be regarded as a basis for comparing the power of the various anions to penetrate the "protective" skin on iron. The order was Cl′, I′, Br′, NO_3', SO_4'', F′; at $N/100$ concentration, it was slightly different, and further modification occurred when borax was substituted for sodium carbonate as the inhibitor.

Experiments with Lead.—It is clear that anions which form an insoluble salt with the anode metal are likely to show abnormally low penetrating power; in fact, they are more likely to repair breakdowns than to cause them. Some experiments were made with lead electrodes at an *E.M.F.* of 2·0 volts. The final values of the leakage currents are shown in Table II.

TABLE II.

Leakage currents between lead electrodes in 0·05*M*-solution. Immersed area 2 × 2 cm.; distance 3·5 cm.; temp. 15°.

Salt.	Leakage current (milliamps.)		
Potassium nitrate	19·3, 19·1	Mean	19·2
Potassium chloride	18·9, 18·2	,,	18·5
Potassium bromide	6·45, 7·05	,,	6·75
Potassium iodide	2·85, 2·62	,,	2·73
Sodium phosphate	1·58, 0·80	,,	1·19
Potassium sulphate	0·56, 0·44	,,	0·50

The results emphasised the effect of the formation of sparingly soluble salts in repairing the film; thus, in contrast to aluminium, nitrates gave a higher current than chlorides, and sulphates a very low current. The current–time curve obtained in the iodide solution showed a very rapid initial fall in the current, followed by a marked rise, and then a rather slow fall to the final value; yellow lead iodide separated at the anode surface, but it is not certain whether this visible film actually constituted the obstructive layer.

The solubility of lead salts also affects the behaviour of lead immersed in solutions without applied *E.M.F.* It is already known (Friend and Tidmus, *J. Inst. Metals*, 1924, **31**, 177) that sulphate solutions attack lead far less quickly than nitrate or chloride solutions, and this is undoubtedly due to the low solubility of lead sulphate. A white deposit is often observed on lead immersed in a potassium sulphate solution, and it was thought that this might be lead sulphate. Since, however, the deposit was found to be easily dissolved by acetic acid, it would appear to be lead hydroxide. Presumably it is produced in the same manner as the "Type A" zinc hydroxide in the experiments on zinc (J., 1929, 113), *viz.*, by interaction between lead sulphate and alkali produced at microscopic anodic and cathodic areas practically adjacent; this type of corrosion, although slow, will not be completely prevented by the low solubility of lead sulphate, since the lead ions will be removed continuously by the alkali produced close at hand. The later stages of the corrosion of zinc (which produce zinc hydroxide of types B and C, by interaction of cathodic and anodic products formed far apart) can have no close analogy in the case of lead, since such a type of attack would soon convert the surface layers into solid sulphate.

Summary.

The penetrating power of different anions has been compared by measurement of the leakage current at an aluminium anode, with potassium chromate as a film-producing solute. The initial current is influenced by the pre-treatment of the metallic surface, but the final constant value is almost independent of this. Apart from a general rise or fall of the current towards the final value, there are fluctuations, due to alternate breakdown and repair of the anode film. When the mean value of the apparent current density is low, these fluctuations are violent; but they become unimportant at high (apparent) current densities, owing to the operation of the " law of averages." The breakdowns are occurrences discontinuous in time and space, and the results explain why reproducibility is good in some conditions and poor in others. Some measurements of the variation of potential with time and with current density also throw light on the principles governing reproducibility. The (decreasing) sequence of penetrating power of ions for aluminium is Cl', Br', I', F', SO_4'', NO_3', HPO_4''. The order of leakage currents at a lead anode is quite different, being affected by the repairing power of those anions which give sparingly soluble lead salts; the sequence here is NO_3', Cl', Br', I', HPO_4'', SO_4''.

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