LXVI.—*The Passivity of Metals. Part IV. The Influence of Acids in Passivity and Corrosion.*

By Ulick R. Evans.

In general, acids dispel passivity and accelerate the corrosion of iron. Occasionally, however, passivity is obtained with acid media, and it has been argued that in such cases the passivity cannot be due to oxide films, which would—it is urged—be dissolved by the acid. One important case, the action of concentrated nitric acid, has been elucidated by Hedges (J., 1928, 969), who finds that, under the conditions where passivity arises, nitric acid has no appreciable solvent power for ferric oxide, which is therefore regarded as the cause of the passivity. Lately Benedicks and Sederholm (*Z. physikal. Chem.*, 1928, **138**, 123) have advanced direct evidence that the passivity produced by nitric acid diluted with alcohol and water is also due to a protective film; here it is considered that the film is ferrous oxide in the inner portions, and hydrated ferric oxide (FeO·OH) in the outer portions. This seems much more likely than the contention of Fujihara (*Ind. Eng. Chem.*, 1926, **18**, 62), that the passivity produced by alcoholic nitric acid is due solely to ferrous hydroxide, which is supposed to cause passivity by maintaining an alkaline reaction; treatment with nitric acid would scarcely leave an alkaline reaction, whilst in any case ferrous hydroxide is unlikely to escape dissolution or further oxidation in such a medium. There seems no reason to doubt that the passivity is due to an oxide film which—at least on the outside—is in the ferric condition.

Two other cases remain to be explained, *viz.*, the passivity produced (1) by immersion in chromic acid and (2) by anodic treatment in dilute sulphuric acid.

Action of Chromic Acid on Iron.—There seems to be little information available as to the oxide-solvent powers of chromic acid, or the exact conditions under which it produces passivity. Dunstan, Jowett, and Goulding (J., 1905, **87**, 1571) have kept iron bright in chromic acid solution for ten years; but Moody (P., 1903, **19**, 158) states that there is a slow dissolution, whilst van Name and Hill (*Amer. J. Sci.*, 1916, **42**, 301) have found that mixtures of chromic and sulphuric acids (the latter in excess) cause rapid corrosion. Many samples of " chromic acid " contain sulphuric acid, and it was decided to conduct some new experiments with Kahlbaum's " Chromic Acid, free from Sulphuric Acid." For analyses of the specimens of metal employed, see J., 1929, 93.

It was found that *M*/10-chromic acid did not evolve carbon dioxide from sodium or ammonium carbonate, and failed to dissolve freshly precipitated ferric hydroxide, even on standing over it for several days. The solution had no effect on the colours of heat-tinted iron, even after 24 hours, although *M*/10-sulphuric acid produces an appreciable alteration in a few seconds. Apparently, therefore, chromic acid does not dissolve flaky ferric oxide.

Strips of iron H 28, 2 cm. wide, were abraded with French emery No. 1, degreased, and immersed vertically to a depth of 3·5 cm. in 90 c.c. of chromic acid–sulphuric acid mixtures for 6 hours at 14·0°. The mixtures acted rapidly on the metal, producing ferric and chromic sulphates, and the layer of largely exhausted solution, which had an enhanced specific gravity, sank rapidly down the vertical surface, fresh solution being drawn in at the top. Owing to the partial exhaustion, the numbers given in Table I do not indicate the velocity coefficient, but they show very clearly that (*a*) at constant concentration of sulphuric acid, chromic acid increases the attack, evidently acting as a depolariser, since no hydrogen appears when it is present, and (*b*) at constant concentration of chromic acid, sulphuric acid increases the attack; in the absence of sulphuric acid, chromic acid produced no visible change, but the small loss of weight measured was confirmed by experiments with chromic acid from another source.

TABLE I.

	H_2SO_4 (mol./l.).	CrO_3 (mol./l.).	Loss of weight, mg.	Mean, mg.
(*a*)	0·05	Nil	9·3, 10·2	9·7
	0·05	0·005	25·0, 26·8	25·9
	0·05	0·01	40·9, 44·5	42·7
	0·05	0·02	76·6, 79·2	77·9
(*b*)	Nil	0·01	0·2, 0·3	0·2
	0·02	0·01	37·6, 38·9	38·2
	0·05	0·01	40·9, 44·5	42·7
	0·09	0·01	54·2, 57·5	55·8

Another series of experiments conducted for 20 hours led to the same conclusions. It was found that immersion in *M*/10-chromic acid for 6 hours rendered the iron passive towards *M*/20-copper nitrate, but not towards copper sulphate, although the latter reagent deposited copper less readily than on the iron merely exposed to air. This was best shown by placing drops of copper sulphate in such a position that only half the drop lay on the area which had been immersed in chromic acid. Copper appeared quickly on the half previously exposed to air, and only slowly on the other half, the line of demarcation being very sharp.

Since chromic acid has powerful oxidising but weak base-dissolving properties, it is easy to understand why it enhances corrosion in the presence of a stronger acid, but produces a protective oxide film when acting alone; the case is completely analogous to that of concentrated nitric acid.

Passivity produced by Anodic Treatment in Dilute Sulphuric Acid.—Tronstad (*Z. physikal. Chem.*, 1929, **142**, 272) has proved optically that an oxide film exists on a nickel anode rendered passive in acid solution, but W. J. Müller (*Z. Elektrochem.*, 1928, **34**, 583; *Monatsh.*, 1929, **52**, 463, 474), whilst agreeing that oxide films play an essential part in many types of passivity, considers that iron oxide could not survive in an acid solution, and cannot therefore be the cause of the passivity of an iron anode. This objection has now been examined experimentally.

The fact that sulphuric acid destroys the first-order temper-colours seems to justify the idea that ferric oxide in the form of films is soluble in the acid; the thinning or removal of the films is easily recognisable at *M*/500-concentration after 1 minute's immersion, and becomes very rapid at greater concentrations. *M*/10-

Sulphuric acid, besides rapidly destroying the thin oxide films, also attacks the metal, and the thicker films (above second-order thickness) peel off in flakes, before they are completely destroyed. Now, *when these oxide flakes pass out of electrical contact with the metallic basis, the solvent action practically ceases ;* flakes have been preserved in *M*/10-acid for long periods without serious change; in one case, they retained their characteristic flake form after standing for 18 days in the acid, although becoming eaten through in places. This suggests that the rapid destruction of the films when in contact with the metal is simply due to the formation, at the various cracks in the film, of the short-circuited cell metal|acid|ferric oxide. The ferric oxide, being the cathode, is rapidly reduced to ferrous oxide, which at once dissolves. Actually, cathodic reduction, conducted with an external source of *E.M.F.*, was employed in earlier work (*Proc. Roy. Soc.*, 1925, *A*, **107**, 228) to bring about the uniform thinning of the films.

If this is the true explanation, it should be possible, by using an oxidising agent, to prevent reduction, and thus retard the destruction of the films. A strip of iron, heated at one side so as to give the complete sequence of tints, was partly immersed in a solution containing sulphuric (*M*/100) and chromic acid (*M*/10). After 24 hours, there was not the smallest alteration of any colour. Yet *M*/100-sulphuric acid, free from chromic acid, causes appreciable change in 5 seconds, and complete destruction of the earlier colours in 1 minute. Experiments with more concentrated sulphuric acid were complicated by the attack on the metallic basis, but here also the life of the colours was greatly prolonged by the presence of chromic acid.

The rational way to prevent cathodic reduction is to submit the specimen, as a whole, to anodic treatment. A series of experiments was performed in which the anode and cathode were vertical strips 2·0 cm. broad, clamped 3·8 cm. apart, and immersed for a depth of 2·0 cm. The cathode was a plain piece of iron, but the anode, after being ground with French emery No. 1 and degreased, was usually given an appropriate oxidising treatment before the experiment. The liquid was *M*/10-sulphuric acid and the *E.M.F.* was 4·0 volts. Except where otherwise stated, the electrodes were connected to the battery *before* introduction into the liquid, so that current commenced to flow from the moment of immersion—a plan previously adopted by Hedges (J., 1926, 2879). The current forced through the cell varied somewhat with the time and pretreatment, but it always rose to about double its previous value when the iron passed from the passive state into the fully active state. Where the back of the anode was protected by nitrocellulose, the current was usually about 0·12 amp. (passive) and 0·24 amp. (active).

When the iron anode had been tinted by heating in air on a lead–tin bath, oxygen was evolved from the moment of introduction, and the anode suffered no corrosion and no change of colour. A short interruption of current (a fraction of a second, and sometimes several seconds) did not dispel passivity; in these cases evolution of oxygen recommenced when the circuit was restored, the anode remaining unattacked. But a longer interruption destroyed passivity, and when the circuit was restored, the current jumped to the higher value, the iron began to dissolve, and no further oxygen was produced. With comparatively thick (second-order) films, an interruption of, say, 15 seconds did not destroy the film entirely, but it allowed attack on the iron to commence at certain points, and a series of such interruptions, with intervening periods during which current was allowed to flow, produced complete undermining of the film, which peeled off in characteristic curling flakes; once out of contact with the metal, the oxide film could be kept in the acid for hours without damage. Thinner (first-order) films were completely destroyed by an interruption of a duration which would only cause undermining of the thicker films; the colour vanished, revealing unchanged iron below, and on restoration of the circuit, the iron became etched without any signs of peeling. On the other hand, in experiments when the circuit was restored at the moment when the film had been destroyed at some points, but not everywhere, the thin film peeled off from the parts where it survived; it could then be washed free from acid, and preserved indefinitely.

Although useless for quantitative purposes, this proved a convenient way of preparing oxide films (especially the thicker films) in a state free from secondary hydroxide. The films showed the same behaviour to reagents as those separated by the iodine method, being turned blue by acid ferrocyanide, but not by acid ferricyanide (except, in some cases, at local spots representing inclusions). The film substance is thus ferric oxide with occasional inclusions (metallic iron, or possibly, in some cases, magnetite); the film fragments showed a very feeble response to the magnet, but this has no significance, since ferric oxide can exist in a magnetic form (Welo and Baudisch, *Phil. Mag.*, 1925, **50**, 399; 1927, **3**, 396).

Unheated specimens simply exposed to air after being ground and degreased showed irregular behaviour when exposed to anodic treatment in *M*/10-sulphuric acid. Occasionally they were active from the moment of immersion; in other cases, after identical treatment, they were passive from the moment of immersion, and after oxygen had passed for a minute, the current could be interrupted for a limited period without loss of passivity. The interruption which could be tolerated without causing activity varied somewhat from one specimen to another, and seemed to depend on the time during which current had been passing, but the following observation appeared to provide the explanation. After the current had been interrupted, small oxygen bubbles continued to be evolved for some seconds, slackening as the supercharge of oxygen became exhausted. If the circuit was restored *before* this evolution of "residual" oxygen ceased, the iron remained passive and a lively production of oxygen set in again as soon as the current began to flow; but if the interruption was prolonged until the slow evolution of "residual" oxygen had completely ceased, the iron became active, and began to dissolve, without oxygen evolution, when the circuit was restored; evidently a considerable supercharge of oxygen is needed to prevent the reduction of the film during the interruption. On some specimens, after a few seconds' interruption, small oxygen bubbles continued to stream from certain points after they had ceased to come off from the specimen as a whole; if, at this stage, the circuit was restored, small bubbles continued to rise from the points in question, although elsewhere the electrode became rapidly attacked. In such cases the strength of current passing was intermediate between the ordinary active and passive values.

The irregular behaviour of the air-exposed electrodes provided another example of the variable character of the film produced by the action of air at low temperatures; on some specimens, a weak point would chance to be included in the electrode area, whilst on others there would be no spots sufficiently faulty to cause breakdown under the prevailing conditions. Specimens exposed to $M/10$-potassium chromate for five days evidently possessed a more uniform skin; without exception, these behaved as "passive" electrodes, provided that the circuit was completed before the specimen was introduced into the acid. Immersion in $M/10$-chromic acid for the same period afforded even better protection; here it was possible to place the specimen in the acid for short periods before the current was turned on, and yet to obtain oxygen evolution immediately the circuit was completed. In four experiments in which the current was started respectively 1, 1, 2, and 4 seconds after immersion, passivity was obtained; but in a fifth experiment, where a period of 5 seconds was attempted, the electrode had become active.

The objections raised to the "film theory" of anodic passivity in acid solutions can thus be answered as follows.

(1) The statement that the oxide film on iron is rapidly destroyed

by acid is true of ordinary conditions, but not of anodic conditions. Under suitable anodic conditions, these films are unaffected by the acid (best observed if the films are thick enough to produce interference tints).

(2) The statement that the nature of the film does not affect the time which elapses before passivity appears is only true of experiments in which the film is dissolved away before the current is turned on. If the circuit is completed before introduction of the specimen, the nature of the film may make all the difference between immediate passivity and serious corrosion.

(3) The statement that iron rendered passive by anodic treatment behaves differently from iron rendered passive, *e.g.*, by simple immersion in a chromic acid solution is perfectly true; the reason is clearly found in the fact that the anodically polarised iron possesses a supercharge of oxygen, which serves to keep the oxide film repaired and in the fully oxidised condition.

Experiments conducted at higher current densities, which permitted the electrode to revert to the passive state after once it had become active, confirmed several of the observations of W. J. Müller (*Z. Elektrochem.*, 1927, **33**, 401; 1928, **34**, 572; 1929, **35**, 656) and of Hedges (J., 1926, 2878; 1927, 2710; 1928, 969). A visible brown coat often appeared on the electrode prior to the arrival of oxygen bubbles; if, for any reason, this brown coat appeared first at one particular region, bubbles were subsequently observed first at that region; in general, the evolution of bubbles started first at the bottom, and spread upwards, producing the **U**-shaped area described by Hedges. W. J. Müller is undoubtedly right in thinking that saturation of the liquid with ferrous sulphate must be attained before passivity can set in; the difficulty of obtaining passivity with vertical electrodes is explained by the fact that heavy ferrous sulphate solution—clearly distinguishable by reason of its different refractive index—sinks continuously down from the anode, and this circulation hinders the attainment of saturation.

Principles governing Anodic Passivity in Acid Solution.—When a metal is subjected to anodic treatment, its surface layers are converted *in situ* into a compound with the principal anion of the liquid. If this compound is freely soluble, it will dissolve, exposing a fresh surface of metal to attack; but if sparingly soluble, it will remain *in situ*, protecting the underlying metal. Thus, lead in a sulphate solution, silver in a chloride solution, and iron in a hydroxide solution escape attack almost from the first; the protective layer, being in optical contact with the metal, is frequently invisible. But ferrous sulphate is readily soluble, and a film-free iron anode in a sulphuric acid solution will dissolve freely at first. If, however, the layer of liquid next to the metal should become saturated with ferrous sulphate, the behaviour of iron will be analogous to that of lead, and if now the surface portions are converted into sulphate, this will no longer dissolve and will temporarily protect the metal. This *protective* sulphate is probably invisible; it is fairly certain that the visible deposit is not the protective layer, but the result of spontaneous crystallisation of hydrated sulphate from the liquid which is locally supersaturated with respect to that salt; its importance lies in furnishing a sure sign that saturation has been reached. When once the whole anode surface is converted into sulphate, any further discharge of SO''_4 ions cannot cause further attack on the iron, and must (as on a platinum anode) lead to evolution of oxygen. The bubbles of oxygen, however, will soon stir up the liquid, and the visible layer will gradually dissolve or flake off (a phenomenon observed by Hedges and by W. J. Müller). Meanwhile, however, the metal will have become supercharged with oxygen, and, at high current densities, this may be sufficient to produce and maintain an oxide film on the surface which (as shown) will *not* be dissolved by the acid under anodic conditions; in that case passivity will persist indefinitely, and the current will be expended on the production of oxygen. At lower current densities, the oxide film may not be maintained, and the electrode may revert to the freely dissolving condition; if so, periodicity may be set up. At still lower current densities, a state of saturation in the anodic layers will never be reached and the electrode will remain active indefinitely; this is most likely to occur if the conditions are favourable to convection.

A theory that the anodic passivity of iron in a sulphate solution may be initiated by a protective layer of *ferric* sulphate has been put forward by McCulloch (*Trans. Amer. Electrochem. Soc.*, 1929, **56**, 325). He points out that ferric sulphate dissolves only slowly in water, and that such a film might persist even in unsaturated solution. McCulloch is undoubtedly right in thinking that salts, as well as oxides, may constitute protective films. Moreover, it is not impossible that the slow dissolution of ferric sulphate by water may itself be the cause of the slow dissolution of ferric oxide film by dilute sulphuric acid; but it is not easy to explain the facts set forth above on the hypothesis that the protection is due solely to a film of ferric sulphate.

Function of Carbon Dioxide in Corrosion by Condensed Moisture.—Many early workers and one recent writer (Fujihara, *Chem. Met. Eng.*, 1925, **32**, 810) have ascribed to carbon dioxide a special rôle in rusting; this idea may have arisen from the serious damage produced by the combustion products of coal, now commonly attributed to oxides of sulphur. The researches of Dunstan, Jowett, and Goulding (J., 1905, **87**, 1548), Tilden (J., 1908, **93**, 1356), and Hicks (*J. Physical Chem.*, 1929, **33**, 781) have definitely proved that the presence of carbon dioxide or other acidic substance is not necessary for rusting; but the measurements of Hicks indicate that moist oxygen does produce rust more quickly if carbon dioxide also is present.

Apart from the scientific, historical, and economic interest of the matter, the question whether carbon dioxide—in amounts normally present in air—constitutes a serious cause of corrosion is important to experimenters, since the detailed observation needed for detection of vital microscopic occurrences becomes almost impossible if the work has to be conducted exclusively in closed vessels. Some experiments have, therefore, been performed to elucidate this point.

Specimens, 5·5 cm. square, were degreased with carbon tetrachloride and then alternately ground and degreased three times. Into each of a series of beakers, 8·5 cm. high and 4 cm. in diameter, a small quantity of water (2 c.c. in the main series) was placed, and one of the specimens was cemented over the mouth of each beaker with nitrocellulose. After the seal had set, the bottoms of the beakers were placed in warm water (50°), and a metal dish containing ice was placed on the upper side of the specimen. Water then distilled without ebullition, condensing on the lower side of the specimen in droplets, fairly large in the centre and microscopic around the edges. In other parallel experiments saturated carbon dioxide solution or $N/100$-sodium hydroxide solution was used instead of water; four different materials were employed, *viz.*, steel H 28, electrolytic iron E 28, commercial zinc containing lead, and electrolytic zinc; abrasion with four different grades of emery, and also scraping with a knife, was studied in different series.

The fact that the presence of carbon dioxide may affect results is clearly shown by the experiments on zinc : the distillate from dilute alkali produced, in practically every drop, a microscopic circle or sphere of membranous zinc hydroxide surrounding a tiny dark point representing the seat of corrosion; in the presence of carbon dioxide, however, the white hydroxide did not appear, but there was general darkening of the metal.

On iron and steel, the result was identical whether distillation was conducted from $N/100$-sodium hydroxide, distilled water, or carbon dioxide solution; in every case, some of the drops developed rust, whilst others remained perfectly clear. On many specimens, the frequency of rust-developing droplets varied from one part to another in a manner not depending on the drop size. Thus no accurate count could be made of the proportion of drops developing rust, but this appeared to be highest in the coarsely abraded specimens. There was no evidence that the presence of carbon dioxide increased the probability of rust formation in a drop, although, where rust appeared at all, it seemed to be developed more quickly if carbon dioxide was present, thus confirming Hicks's results. After time had been allowed for the development of rust in those drops which were able to produce it, the specimen could be taken off the beaker and exposed to a stream of carbon dioxide (or to carbon dioxide and air alternately) without causing any rust in the clear droplets; indeed the specimen could conveniently be dried in a stream of carbon dioxide without fear of increasing the number of rust spots. Apparently the presence of carbon dioxide is incapable of causing rusting in places which have escaped rusting in its absence. On the other hand, exposure to the vapour of hydrochloric acid for only 15 seconds caused rapid rusting, in the places which had previously escaped. There seems no doubt that the corrosive qualities of the air of many laboratories—frequently attributed to carbonic acid—are really due to other acids.

The observations are explained by the fact that iron specimens are covered with an invisible film of ferric oxide with irregularly distributed weak spots (Evans, J., 1929, 117). The chance of rust formation will depend on the "probability" that the drop area includes a place on the skin sufficiently "weak" to admit the most penetrating anion present. In pure water this will be the hydroxyl ion, and the ferrous hydroxide formed as the anodic product will interact with dissolved oxygen at a distance to form the less soluble ferric hydroxide ("rust"). The presence of carbon dioxide will certainly not increase the probability of initiation of rusting, since it is unlikely to dissolve the film of ferric oxide, whilst it will decrease the hydroxyl-ion concentration; the penetrating power of the HCO_3' or CO_3'' ions can probably be neglected. But if it be assumed that the weak spot *does* exist under a droplet, the carbon dioxide may accelerate the electrochemical action, by enhancing the conductivity and hydrogen-ion concentration.

In some of the early experiments, a small proportion of the previously rust-free droplets developed rust after the vessels were opened; this may have been due to traces of acid fumes, but was probably due to the bending that accompanied opening. It was found that if a specimen was cut with small shears when the droplets were in position, the drops near the shear-lines, although quite untouched by the shears, quickly developed rust, clearly because the cutting stresses fractured the protective film.

Droplets produced by distillation from ammonia caused no true rust, evidently owing to the presence of sufficient alkali to depress the solubility of ferrous hydroxide; some attack did occur, however, since, after the drops had been removed by evaporation, interference tints were noticed.

It was observed (before the opening of the vessels) that droplets which developed rust tended to " dry up "—partially or completely —and that the clear drops situated close to a drop which had developed rust frequently disappeared altogether; on the other hand, in regions where no rust appeared, the drops showed no signs of evaporation. This confirms the early view of Crum Brown (*J. Iron Steel Inst.*, 1888, ii, 129) that rust is essentially hygroscopic —a matter recently discussed by Hudson and others (*Trans. Faraday Soc.*, 1929, **25**, 207, 485, 487, 493).

Corrosion of Iron immersed in a Carbonic Acid Solution.—Some confusion exists regarding the effect of carbon dioxide in " immersed corrosion." In *hard, natural* waters containing calcium bicarbonate, it is unquestionable that excess of carbonic acid increases the corrosive character; in the absence of free carbonic acid such waters, when they act on iron, necessarily deposit calcium carbonate on the cathodic areas, and the deposit obstructs diffusion of oxygen, bringing the action to a standstill (Tillmans and Klarmann, *Z. angew. Chem.*, 1923, **36**, 94, 103, 111, 113; Baylis, *Ind. Eng. Chem.*, 1927, **19**, 177; Evans, *J. Soc. Chem. Ind.*, 1928, **47**, 57T); in the presence of excess of carbonic acid, this deposition does not occur, and the corrosion continues. The indirect action of " aggressive " carbon dioxide may be serious even with metals where its direct action is undoubtedly inhibitive; thus the corrosion of lead by distilled water is retarded by the presence of carbon dioxide, but waters containing sufficient calcium bicarbonate to have no permanent action on lead become distinctly plumbosolvent if much excess carbon dioxide is present.

The action of dissolved carbonic acid *in the absence of calcium compounds* is quite different. The normal product is soluble ferrous bicarbonate, as indicated by Crum Brown (*loc. cit.*); the bicarbonate is formed very quickly if the carbon dioxide is under 50 atm. pressure (E. Müller and Henecka, *Z. anorg. Chem.*, 1929, **181**, 159), but at ordinary pressures the action is much slower, quite small quantities of iron rendering the liquid supersaturated with respect to ferrous carbonate (Tillmans and Klarmann, *loc. cit.*). If oxygen is present, the iron is likely to be precipitated as ferric hydroxide (rust) in a form which will hinder diffusion; indeed Bauer's tests (*Stahl u. Eisen*, 1921, **41**, 37, 76) indicate that distilled water containing carbon dioxide may produce less corrosion than distilled water free from carbon dioxide, owing to the obstructive character of the rust produced.

To elucidate this matter further, new experiments have been performed. A number of strips of iron H 28, 2 cm. wide, were cut, abraded, degreased, and immersed vertically to a depth of 4 cm. for 15·5 hours at 14° in 65 c.c. of liquid in beakers 8·5 cm. high and of 4 cm. diameter. The loss of weight produced by different liquids is shown in Table II; it will be noticed that within this time saturated carbon dioxide has produced more corrosion than distilled water but much less than *M*/20-sulphuric acid; the water "condensed on silica" was a sample prepared by L. C. Bannister and S. C. Britton for work on electrode potentials, the special object being to exclude traces of metals.

TABLE II.

Liquid.	Loss of weight, mg.	Mean, mg.
M/20-K_2SO_4	2·9, 3·3, 3·5	3·2
M/20-H_2SO_4	20·1, 20·5, 20·6	20·4
Saturated CO_2 solution	5·9, 7·0, 7·0	6·6
Laboratory distilled water	1·5, 1·7	1·6
Laboratory distilled water, redistilled and condensed on silica	1·0, 1·3	1·1

A series of qualitative experiments, interrupted at different stages, showed the action of carbonic acid solution to be as follows. Freshly immersed specimens are attacked by carbonic acid just as by any dilute acid, hydrogen being evolved slowly; the bubbles appear mainly at the edges and a few favoured spots on the faces (evidently points of low over-potential); but the actual attack commences at quite different points (evidently weak spots on the skin). For a time the liquid remains clear, though containing a considerable quantity of iron dissolved as ferrous bicarbonate; after about 2 hours, rust (ferric hydroxide) begins to appear along the water-line, and gas evolution gradually ceases, as the p_H value rises from about 4·0, where hydrogen production is appreciable, to a range (5·0—6·0) where direct hydrogen evolution is almost negligible. Meanwhile the oxygen absorption type of attack is increasingly hindered by the formation of rust over the water-line zone. The conditions thus become less favourable for corrosion than in a neutral sulphate or chloride solution, where the corrosion is of the differential aeration type from the first moment, and where the cathodic zone near the water-line remains comparatively free from rust, so that oxygen can continue to reach the place where it is required for corrosion. It is to be expected, therefore, that over long tests carbonic acid would produce a smaller amount of corrosion than a salt solution; and it was found in a 39-day test by the author (*J. Soc. Chem. Ind.*, 1928, **47**, 77T) that actually the corrosion by saturated carbonic acid was less than that produced by *M*/20-

sodium sulphate or chloride. Probably Bauer's results, mentioned above, can be explained in the same way. In effect, carbonic acid solution is not a serious corroding agent.

It would appear that, with carbonic acid, the "hydrogen-evolution type" of corrosion lasts just long enough to produce rust at a point unfavourable to subsequent attack of the "oxygen-absorption type." The apparent exhaustion of hydrogen ions occurs long before the quantity of iron dissolved is stoicheiometrically equivalent to the carbonic acid present; some experiments conducted with sulphuric acid showed that here the attack persists rapidly even when most of the acid has been used up. The difference between the action of sulphuric and carbonic acids is easily understood by considering the movement of p_H during titration of these acids with alkalis; with sulphuric acid, the p_H value remains very low (below 3·0) until the end-point is approached, whereupon it suddenly rises; with the weak carbonic acid, the p_H value is higher at the first (about 4·0) and commences to rise even with the first addition of alkali. The p_H value alters in much the same way when the acid is used up on the corrosion of iron; thus sulphuric acid continues to evolve hydrogen almost to the last, whilst with carbonic acid, the evolution of hydrogen—weak even from the first—soon dies away.

The rapid exhaustion of carbonic acid stands in contrast to the view of Crum Brown (*loc. cit.*) that a limited quantity of carbonic acid "can carry on the process indefinitely," being regenerated in full when the ferrous bicarbonate is oxidised to ferric hydroxide. Actually the conception of "regeneration in full" is inadmissible, since the precipitation of ferric hydroxide is inconsistent with concentrations of hydrogen ions such as are present in pure water saturated with carbon dioxide at normal pressure. Only if the concentration of carbon dioxide is kept low, can ferric hydroxide be produced. Since, however, the oxidation of ferrous bicarbonate to the ferric condition occurs at the water-line, the dissociation of any ferric carbonate that may temporarily be formed is quite to be expected, the carbon dioxide passing out into the gas phase (where the partial pressure of carbon dioxide is usually low) as quickly as oxygen is taken in. This accounts for the fact that, in 24-hours experiments, practically no carbonate was found in the "rust," which was mainly hydroxide, and practically no free carbon dioxide was found in the liquid, although this still contained much ferrous iron in solution. The facts do not support Crum Brown's idea of the cyclic regeneration of carbonic acid.

Recently, theories based on liberation of acid by hydrolysis of ferric salts have been suggested for other types of corrosion.

McCulloch (*Trans. Amer. Electrochem. Soc.*, 1929, **55**, 268) considers that, in corrosion by chloride solution, the ferrous chloride first produced " may be oxidized to ferric chloride by absorption of oxygen, and ferric chloride may hydrolyze to give hydrochloric acid. This hydrochloric acid may attack the steel." It seems difficult to understand how any considerable increase of acidity can be produced by the action of oxygen on ferrous chloride, since in addition to ferric chloride, this oxidation itself must produce ferric hydroxide or basic ferric chloride. Whilst the hydrolysis of ferric salts undoubtedly is responsible for the formation of rust in the final stages of the action of acids on metals, it is doubtful whether regeneration of acid plays any serious part in prolonging the attack.

Summary.

Chromic acid has strong oxidising and weak base-dissolving properties; it produces passivity when present alone, but stimulates corrosion if sulphuric acid also is present.

The ferric oxide film usually present on iron is rapidly destroyed by dilute sulphuric acid owing to the formation of the circuit iron|acid|oxide; the ferric oxide suffers cathodic reduction to ferrous oxide, which is rapidly dissolved by the acid. If the reduction is prevented by the presence of excess of chromic acid, or by anodic treatment of the specimen as a whole, the film can remain in contact with $M/10$-sulphuric acid for hours without change. This explains why iron can remain passive in acid solution during anodic treatment.

The explanation of anodic passivity in acid solution is as follows. When lead is anodically treated in sulphuric acid, the conversion of the metallic surface into sulphate will protect the metal below, but with an iron anode this will only occur when the liquid has locally become saturated with ferrous sulphate. At that stage, any further current must be expended on the production of oxygen, and although the bubbles stir the liquid, dispelling the saturated layer, the metallic surface may in the meanwhile have been converted into ferric oxide, which will protect the metal so long as the current continues to flow. Indeed, a short interruption of current can also be tolerated without resumption of activity, and this seems to depend on the presence of an oxygen supercharge, which prevents reduction to the rapidly soluble lower oxide.

The corrosive qualities of carbon dioxide have been exaggerated in the past, and probably the damage attributed to carbon dioxide has really been due to sulphur dioxide or hydrogen chloride. If water is allowed to condense in droplets on iron, some of them develop rust, whilst others (which do not happen to rest on a weak point) remain clear; this is true whether carbon dioxide is present or absent, and the clear drops may be dried up in a current of carbon dioxide without developing rust; hydrogen chloride vapours quickly produce rusting. A solution of carbonic acid causes at first slight corrosion of the hydrogen-evolution type, but the p_H rapidly rises and the formation of hydrogen ceases; the ferrous bicarbonate produced yields ferric hydroxide at the water-line, and this obstructs diffusion of oxygen and prevents attack of the oxygen-absorption type. In effect, therefore, a solution of carbonic acid is not dangerously corrosive; but it must be remembered that the presence of excessive free carbonic acid in a hard natural water may prevent the deposition of calcium compounds which would otherwise bring the action to a standstill.

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