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THE ADSORPTION THEORY OF PASSIVITY AND THE FLADE POTENTIAL

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ABSTRACT

From quantitative data reported by various investigators, it is concluded that the primary passive film on iron has the following properties: (1) 25-100 Å thick, (2) equivalent to 0.01 coulomb/cm², (3) can oxidize CrO₂⁻ to CrO₄²⁻, (4) follows the (Flade) potential relation $-0.58 + .058 \text{ pH (volts)}$.

All these properties cannot be accounted for by any of the known oxides of iron. In better accord with the facts is a proposed passive film composed of chemisorbed atomic and molecular oxygen supplemented perhaps by OH and H₂O. The free energy of formation is calculated from potential data of Franck to be -29,900 cal/mol adsorbed O in agreement with independent data for gaseous oxygen chemisorbed on iron surfaces (-30,500 cal/mol adsorbed O). Thermodynamic calculations show that the film is unstable, moreso in acids than in alkalies.

The same kind of film apparently forms on Cr-Fe alloys and on Cr. It is calculated that passivity for these metals is also unstable in acids or alkalies when metal ions or hydroxides are reaction products of the decomposed film. However, spontaneous formation of the adsorbed passive film can occur on exposure of Cr or 20% Cr-Fe alloys to water, contrary to the situation for iron or the low Cr-Fe alloys. It is possible to show that the passive film on iron is able to oxidize CrO₂⁻ to CrO₄²⁻ as

observed, but that this reaction is not thermodynamically possible for the passive film on Cr or on 12% Cr-Fe alloys.

A passive film of chemisorbed oxygen fulfills the conditions of good electrical conductivity and freedom from pores. It is extremely thin (4 to 15 Å) in agreement with Tronstad's optical measurements for the passive film on stainless steels (10 Å). Tronstad's measurements for iron, corrected for a ferric nitrate film forming continuously by corrosion of passive iron in nitric acid, would probably also agree with this lower value. The chemisorbed film decomposes to Fe_2O_3 more than 60 Å thick based on apparent area, which agrees with values reported by others for the decomposed passive film.

THE ADSORPTION THEORY OF PASSIVITY AND THE FLADE POTENTIAL

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The first hint that the passive film on iron might be either an adsorbed film or an oxide film came from Michael Faraday⁽¹⁾ before the word adsorption had been coined. He stated: "My strong impression is that the surface of iron is oxidized, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation, and that having their affinity for oxygen satisfied and not being dissolved by the acid . . . there is no renewal of the metallic surface . . ." Much later, Langmuir⁽²⁾ suggested that passivity of chromium might be caused by an adsorbed film of oxygen chemically bonded to the metal surface (chemisorbed) as was oxygen to tungsten. Tammann used a similar concept to explain passivity of iron, nickel, cobalt, chromium⁽³⁾ and the stainless steels⁽⁴⁾. The present writer proposed that passivators like chromates function by chemisorption on an iron surface⁽⁵⁾⁽⁶⁾.

The primary mechanism of protection, according to the adsorption theory of passivity, is one of satisfying surface affinities of the metal through formation of chemical bonds between adsorbate and metal, but without metal atoms leaving their lattice to form the new lattice of a stoichiometric compound. Metal compounds form in time, and may offer additional protection as diffusion barrier layers, but the primary passive film is thought to be the chemisorbed film. This viewpoint applies, of course, only to those metals on which chemisorption occurs,

and not to metals protected by obvious diffusion barrier layers (e.g. PbSO_4 on Pb).

There are several supporting lines of evidence for the chemisorbed passive film. First, carbon monoxide adsorbs on 18-8 stainless steel immersed in 6.3 N hydrochloric acid saturated with carbon monoxide, reducing the corrosion rate as much as $\frac{1}{470}$ the rate in air-saturated acid⁽⁷⁾. Nitrogen or hydrogen bubbled through the acid has little or no effect on the rate, compared to CO. The effect is not one of increasing hydrogen overvoltage of cathodic areas, because the corrosion potential on admission of CO is shifted in the noble direction, opposite to an effect caused by increased cathodic polarization. Instead, CO, like oxygen, increases anodic polarization, indicating general overall adsorption of the gas. Here, an oxide film is not a possible cause of passivity.

Second, evidence comes from typical patterns of data for metal surface concentration of a passivator as a function of passivator concentration in solution, such data having the typical shape of adsorption isotherms for gases on solids. Data, for example, have been obtained for chromates on iron using radioactive chromium⁽⁸⁾ or through potential measurements⁽⁶⁾. Potential data have also shown Langmuir adsorption-isotherm behavior for 18-8 stainless steels as a function of dissolved oxygen concentration in a solution of 3% NaCl plus 0.3 M NaOH⁽⁶⁾. Additional measurements show that oxygen uptake from water on a pickled oxide-free 18-8 stainless steel surface follows at first a rapid rate and then a slow rate, typical of gases chemisorbing on metals⁽⁹⁾. Furthermore, the slow rate follows the Elovich equation (amount adsorbed is linear with log time) typical of the behavior of gases chemi-

sorbing on metals or oxides⁽¹⁰⁾.

Third, of all metals that show a tendency to form chemisorbed films, the transition metals predominate. These metals with high heats of sublimation and with unfilled d-electron energy bands, or vacant atomic d orbitals, favor strong bonding to adsorbates. They are the metals that show typical passivity both as pure metals (e.g. chromium, molybdenum, nickel, etc.) and as alloys within specific composition ranges (e.g. iron-chromium, nickel-copper, nickel-molybdenum, etc.) accompanied by invisible surface films. The correspondence of unfilled d energy bands with chemisorption and passivity has made it possible to predict approximate passive compositions for some alloys⁽¹¹⁾⁽¹²⁾. Further details concerning the foregoing correlation of adsorption with passivity are summarized in reference (13).

Properties of the Passive Film

Appreciable quantitative data have been reported by several investigators within the last several years, particularly for iron and the chromium-iron stainless steels, which bear on the properties and behavior of the passive film. Among such results are the following:

(1) The passive film on iron measured optically is about 25 to 100 Å thick⁽¹⁴⁾. Indirect measurements by electrochemical⁽¹⁵⁾⁽¹⁶⁾⁽¹⁷⁾ or chemical^(17A) techniques agree with this order of thickness.

(2) The electrochemical equivalents of substance making up the passive film are about 0.01 coulomb per square centimeter of apparent surface. This was shown by Olivier⁽¹⁸⁾ for high Cr-Fe alloys anodically passivated in 10% H_2SO_4 (average value: .010 coulomb/cm² for 12 to 18% Cr-Fe alloys), and more recently by King⁽¹⁹⁾ in 4% Na_2SO_4 (average value:

.009 coulomb/cm² for 6 to 30% Cr-Fe alloys)*. Through extrapolation of potential and coulometric measurements on anodically passivated iron, Weil⁽¹⁷⁾ calculated that the primary passive film on iron is equivalent to .008 coulomb/cm² apparent surface, which is the same order of magnitude as for the Cr-Fe alloys. It is of some consequence that the amount of oxygen adsorbed by a pickled 18-8 stainless steel from water containing dissolved oxygen is also about 0.01 coulomb/cm² apparent surface, indicating that the passive film on stainless steels formed directly from dissolved molecular O₂ is of about the same thickness as that on iron or on stainless steels formed by anodic polarization.

(3) The passive film on iron is capable of oxidizing CrO₂⁻ to CrO₄⁻⁻ in concentrated NaOH. The oxidizing capacity is equivalent to formation of a maximum of about 2×10^{-8} mole of CrO₄⁻⁻/cm² of passive iron surface⁽²¹⁾.

This oxidizing capacity, as discussed later, is equivalent to .012 coulomb/cm², and hence is of the same order as the estimate of Weil for the primary passive film on iron.

(4) Franck⁽²⁰⁾ showed that the potential of passive iron at the point immediately preceding rapid loss of passivity (the Flade potential E_F) depends on pH according to the relation (American Chem. Soc. Sign Convention):

* For iron, and also low Cr-Fe alloys the specific composition range of which depends on pH and temperature, the number of coulombs equivalent to the amount of passive film includes formation of a temporary insulating surface layer⁽²⁰⁾ (perhaps FeSO₄). Hence the measured value for iron in 1 N or 10% H₂SO₄ is 1.7 coulombs/cm²⁽¹⁸⁾⁽²⁰⁾. For higher Cr-Fe alloys, this preliminary insulating film does not form, and the measured number of coulombs corresponds to the primary passive film.

$$E_F = -0.58 + .058 \text{ pH}$$

such that the potential is less noble the higher the pH. Rocha and Lennartz⁽²²⁾ showed that for the Cr-Fe alloys, including chromium, a similar dependence on pH occurred below 15% chromium, and that potentials followed a coefficient of $2 \times .058$ for alloys containing 15 or more % chromium. Previously, Müller and Cupr⁽²³⁾ had provided data showing that E_F for chromium is also linear with pH, with a slope of .058 for self-activation, and twice this value for cathodically-activated specimens.

There have been attempts to explain the Flade potential on the basis of special oxides⁽²⁴⁾ or double oxides⁽²⁵⁾. But the large difference of about 0.6 volt between the Flade potential and the potential calculated for any of the known oxides of iron in equilibrium with iron poses a difficult problem and, as Vetter states⁽²⁶⁾, attempts at an explanation have not yet succeeded.

The Chemisorbed Passive Film

We might consider as a next step to what extent the adsorption theory of passivity can be applied in explaining the Flade potential. Lord's data⁽⁹⁾ make clear that only dissolved oxygen, water and the metal take part in building up the passive layer on 18-8 stainless steel. We shall assume first, since coulombs of substance per unit area are not different within experimental error, that the same type film forms on low chromium alloys and on iron as occurs on the higher chromium-iron alloys. Because oxygen has higher affinity than water for an iron or chromium surface, and since oxygen is known to chemisorb on iron⁽²⁷⁾, a

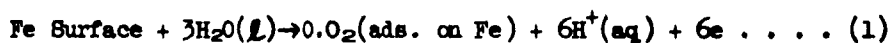
film of chemisorbed oxygen is expected to compose the initial primary film. How much oxygen adsorbs can be calculated from the coulombs/cm² equivalent to the passive film. Based on absolute surface, this value for 18-8 stainless steel was shown by Lord to be 0.27 microgram oxygen or .003 coulomb/cm² which corresponds to greater than a monolayer of oxygen atoms*. There must be, therefore, a multilayer film on the surface. Recent observations on the system oxygen-tungsten⁽²⁸⁾ by Becker indicate that for tungsten there are two kinds of adsorption sites, the first with energy of bonding equal to about 90,000 cal and the second to about 45,000 cal. Greenhalgh, Slack and Trapnell⁽²⁹⁾ have obtained similar evidence for adsorption of N₂ on W, Mo, Ta, Nb, Cr and Fe, and propose that on Fe the gas less tightly bonded is also chemisorbed but probably in molecular rather than atomic form. The same situation probably applies to chemisorption of oxygen on Fe or Cr-Fe alloys. Evidence for an outer layer of adsorbed molecular oxygen on 18-8 is derived, for example, from potential measurements⁽⁶⁾ showing a linear dependence of $\frac{\sqrt{p}}{\Delta E}$ vs $\sqrt{p}$ rather than a linear dependence of the expression for atomic adsorption, $\frac{\sqrt{p}}{\Delta E}$ vs $\sqrt{p}$. (p = partial pressure of oxygen, ΔE = change of potential in 3% NaCl + 0.3 M NaOH.)

Accordingly, if we assume a close-packed layer of O atoms of covalent radius 0.7 Å on top of which is chemisorbed a close-packed layer of O₂ molecules of radius 1.2 Å, we obtain the observed value 0.27 microgram adsorbed O₂/cm² abs. surface. The actual adsorbed film structure

*The number of iron atoms/cm² approximates 1.9×10^{15} . If each Fe atom constitutes one site for adsorption of an O atom, the number of coulombs/cm² = .0006.

probably differs from this simple model, and more likely is composed of a first layer with one-to-one correspondence of O with Fe atoms through gaps of which O₂ molecules are chemisorbed. It is also likely that OH radicals or H₂O molecules participate to some extent in the passive film structure beyond the first layers of oxygen, since OH⁻ discharges on passive anodic areas, and it seems logical that OH should compose the thicker passive films corresponding to potentials more noble than the Flade potential*.

We can then write as the reaction for formation of the primary passive layer of arbitrary composition O.O₂ the following:



The standard potential for the above reaction at 18°C from Franck's⁽²⁰⁾ measurements is -0.58 volt. This value, as was shown by Flade⁽³¹⁾, changes only 30 millivolts in the active direction on going from 15° to -3°C. Hence we can write for reaction (1) the corresponding Flade potential at 25°C:

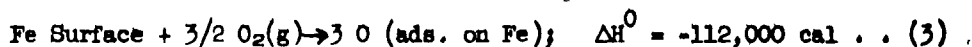
$$E_F = -0.58 + .0592 \text{ pH}$$

which agrees with Franck's relation. The free energy corresponding to chemisorption of the passive film can then be calculated from reaction (1) employing the value of -56,690 calories for the standard free energy of formation for water⁽³²⁾.



* Heumann and Rösener⁽³⁰⁾ from anodic polarization behavior in H₂Cr₂O₇-K₂Cr₂O₇ mixtures propose that the passive film on Cr is CrOOH, but they assume only one of several possible initial surface states consistent with interpretation of their data. If the passive film on Cr is considered to be similar to that on passive Cr-Fe alloys, which is a reasonable assumption, the measured equivalence of film thickness (.01 coulomb/cm²) is greater than can be accounted for by assuming CrOOH alone.

The large negative free energy of formation for the adsorbed passive film is typical of values for chemisorption. Trapnell⁽³³⁾ quoting Tompkins provides thermal data for oxygen chemisorbed on iron as follows:



The entropy change for the above reaction is not available, but for 1 mole nitrogen chemisorbed on iron, the value corresponds to -46.2 e.u. (standard state equals half-surface coverage)⁽³⁴⁾. Hence, using this value of entropy for adsorbed oxygen, and noting that ΔH is not sensitive to amount of surface coverage⁽³⁵⁾, we calculate for 3/2 mole oxygen chemisorbed on iron:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -112,000 + 3/2 (46.2 \times 298) = -91,400 \text{ cal} \dots (4)$$

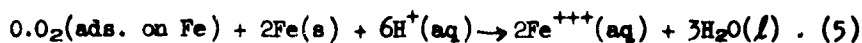
The close correspondence of the above value to -89,700 calories calculated from potential data (Reaction (2)), although in better agreement than the approximations warrant, supports the premise that the passive film is chemisorbed, and that the important component of the passive film is chemisorbed oxygen.*

Decomposition of Passive Film

Eventual decomposition of the passive film on iron is observed in acids or alkalies, with instability being more pronounced in acids. Just as chemisorbed oxygen on carbon decomposes mostly with formation of CO and not O₂, it is probable that the passive film decomposes accompanied

* This conclusion is not altered by the assumed number of chemisorbed oxygen atoms or molecules for unit area of passive surface. Reaction (1) indicates that the average free energy of adsorption is $\frac{-89,700}{3}$ or 29,900 900 ✓
cal. per mole adsorbed O, regardless of the amount of oxygen chemisorbed per unit area, in agreement with the value per O atom calculated from reaction (4).

by reaction with the underlying metal. If we assume that the decomposition reaction follows in accord with:



the standard EMF equals + 0.616 volt, making use of equation (1) and

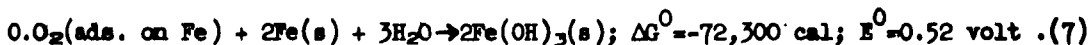
$\text{Fe} \rightarrow \text{Fe}^{+++}(\text{aq}) + 3\text{e}$, $E^0 = +.036$ volt. Therefore:

$$E = .616 - \frac{.059}{3} \log (\text{Fe}^{+++}) - .059 \text{ pH} \quad (6)$$

This equation shows that the tendency for the passive film to decompose forming ferric salts is greater in media of low pH, and that increased concentrations of ferric salts should help stabilize passivity.

In alkaline media, passivity breaks down with formation of Fe(OH)_3 .

The corresponding reaction is:



where the free energy is calculated from the standard free energy of formation for Fe(OH)_3 (-166,000 calories /mole) and the previously cited value for water. Since the free energy change is negative, the passive film tends to decompose in alkaline media as well as in acids, but the tendency is now independent of pH.

The Adsorbed Film on Cr and Cr-Fe Alloys

When Fe is alloyed with Cr, the chemical bond between metal and adsorbate becomes stronger. At about 20% Cr, the standard Flade potential becomes zero⁽²²⁾ and ΔG^0 for $0.0_2(\text{ads. on 20\% Cr-Fe})$ equals -170,000 cal. For Cr, the standard Flade potential equals + 0.2 volt and ΔG^0 for $0.0_2(\text{ads. on Cr})$ equals -197,600 cal. This means that the reaction:

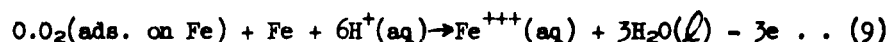


can go spontaneously as written for 20% Cr-Fe alloys, and that the corresponding reaction for Cr is also possible thermodynamically.

Passivity, as for iron, is unstable in acids or alkalies for the situation where the film reacts with the base metal. The large negative free energy of formation of $\text{Cr}(\text{OH})_3$ overbalances the increasingly negative free energy value for $\text{O}_2(\text{ads. on Cr-Fe})$, thereby maintaining an overall negative free energy for the decomposition reaction. For example, in acids the standard EMF for decomposition of the passive film on Cr with Cr^{+++} as end-product is 0.51 volt compared to 0.616 volt for iron (reaction (5)). With $\text{Cr}(\text{OH})_3$ as end-product, $\Delta G^0 = -62,400$ cal compared to $-72,300$ cal for iron (reaction (7)).

Slope of E_F vs. pH

The following equilibrium involving the passive film is also possible:



the standard potential for which, from data cited previously, is calculated to be + 1.20 volt. It follows that:

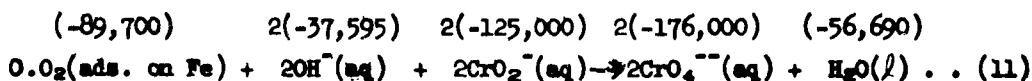
$$E = 1.20 - \frac{0.059}{5} \log (\text{Fe}^{+++}) - 0.059 \times 2 \text{ pH} \dots (10)$$

A similar reaction is possible for chromium or chromium-iron alloys and provides a possible suggestion for the fact that Müller and Cupr's data show a dependence of Flade potential with pH with a slope of 0.058 for spontaneous activation of chromium in acids, but with approximately twice this slope (0.058×2) for chromium activated by cathodic polarization. It would seem, if this idea is right, that cathodic activation may favor an equilibrium of the passive film with Fe^{+++} or Cr^{+++} because of many pores introduced by thinning of the film through cathodic reduction thereby allowing the metal to corrode, whereas with self-activation, the measured potential is essentially that of the pore-free film (reaction (1))

just at the point where the film decomposes very rapidly starting from a single pore or area of activation. At the point where passivity rapidly breaks down, the initially exposed bare surface acts as anode of a passive-active cell the current flow of which reduces adjacent film acting as cathode, thereby continuously enlarging the anode area.

Oxidation of Chromite

We have still to account for oxidation of chromite ions by passive iron in concentrated sodium hydroxide, as measured by O'Connor. We can assume the following reaction:



for which we obtain $\Delta G^0 = +6200$ calories. Hence this reaction will not go.

Instead we can write the following reaction:



This reaction is spontaneous, the free energy ΔG^0 being $-33,020$ cal. It follows that $K = \frac{(\text{CrO}_4^{--})}{(\text{OH}^-)(\text{CrO}_2^-)} = 1.3 \times 10^{12}$ and reaction (12) goes to completion. Hence this is the probable reaction, results for which O'Connor reported. Instead of Fe(OH)_3 as end-product, formation of $n \text{ OH(ads. on Fe)}$ where n represents the number of adsorbed OH radicals can undoubtedly also account for reaction (12) going spontaneously as written.

Calculations analogous to those carried out above show that the passive film on stainless steels is not able to oxidize CrO_2^- to CrO_4^{--} . The upper limit of Cr content in the alloy for which this oxidation is thermodynamically possible lies at about 12% Cr ($E_F^0 = -.29$ volt) assuming formation of Fe(OH)_3 and Cr(OH)_3 in the molal ratio corresponding to Fe/Cr in the alloy.

Properties of Chemisorbed Film

It is evident, therefore, that a passive film composed essentially of chemisorbed oxygen accounts for much of the observed behavior of passive iron. The film is not stable but tends to break down both in acids and in alkalies. The calculated oxygen dissociation pressure is higher than any at the normal oxides of iron, as predicted by Bonhoeffer⁽³⁶⁾. Its structure, however, is not the same as the adsorbed film formed by exposing iron to molecular oxygen. The passive film contains more oxygen, and can be formed only by processes like anodic polarization or by reactions analogous to that occurring with HNO_3 , which, as Bonhoeffer and his school have shown, produces an active cathodic depolarizer HNO_2 which sets up currents that polarize anodic areas of iron to the required high values for anodic passivation. With 18-8, however, the passive film formed by direct adsorption of dissolved molecular oxygen appears to be identical with the passive film formed by anodic polarization and it is plausible that this should also be true of all Cr-Fe alloys of about 12% or more Cr, including pure Cr, which form stronger adsorbate-metal bonds with oxygen the higher the Cr content. The thickness is approximately the same as that of the primary passive films on iron and the low Cr-Fe alloys, and the structure is probably also similar. Vetter⁽³⁷⁾ showed that the passive film on iron behaves as a good electrical conductor and is essentially pore-free. The chemisorbed passive film, like adsorbed oxygen on platinum, fulfills the conditions of a good conductor, and since adsorption occurs over all the surface, the film is essentially pore-free.

The minimum thickness of the adsorbed passive film of oxygen atoms over which oxygen molecules are chemisorbed is perhaps (adding previously quoted radii): $2(0.7) + 2(1.2) = 3.8 \text{ \AA}$ based on absolute

surface, and approximately $15 \text{ \AA}$ based on apparent surface assuming a roughness factor of $4^{(38)}$ (within the limitations of defined thickness for a rough surface). Thickness would be increased by adsorbed OH or H_2O less tightly bound than the oxygen layers, but, in any event, the film is extremely thin. It should be noted that previously reported values for the passive film thickness much greater than $3.8\text{--}15 \text{ \AA}$ were calculated mostly for the decomposed passive film which is thicker. One exception were the measurements by Tronstad, employing optical techniques, who reported the thickness in situ of the passive film on iron immersed in concentrated HNO_3 . But his measurements included a surface film of $\text{Fe}(\text{NO}_3)_3$, which forms continuously through reaction of the metal with acid*. For stainless steel in concentrated HNO_3 , the corrosion rate for which is much less than for iron and for which a surface film of metal nitrate is less pronounced, his measured value for the passive film was only $10 \text{ \AA}$ in agreement with the estimated thickness for the adsorbed film. It is probable that Tronstad's measurements of film thickness on anodically passivated iron, as for iron in HNO_3 , were also too large by the amount of surface compound formation during measurements. His

* By analysis of HNO_3 for Fe^{+++} , the corrosion rate of iron in stagnant concentrated $\text{HNO}_3 = 23 \text{ mg/dm}^2/\text{day}^{(39)}$. The continuous corrosion of passive iron in concentrated HNO_3 can be explained by the equivalent continuous slow reaction of iron with overlying chemisorbed oxygen at specific sites, forming Fe_2O_3 . The rate of conversion of chemisorbed oxygen to oxide is sensitive to temperature, as is expected, but less so to applied potential, in agreement with data of Vetter⁽³⁷⁾ who measured the corrosion rate of iron in conc. HNO_3 at various temperatures and applied potentials. Fe_2O_3 so formed immediately dissolves in acid forming $\text{Fe}(\text{NO}_3)_3$, whereupon anodic polarization of exposed iron at sites where oxide dissolves immediately restores the adsorbed passive film. If the exposed area is so large that galvanic currents reduce the adjacent passive film to a potential below the Flade potential, passivity, instead of repairing itself, breaks down.

were the only direct measurements of the passive film thickness.

According to reaction (7), every mole of passive film substance on decomposition yields 2 moles of $\text{Fe}(\text{OH})_3$ or 1 mole $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. The 2×10^{-8} mole $\text{CrO}_4^{--}/\text{cm}^2$ apparent surface, in turn, found by O'Connor⁽²¹⁾, is equivalent according to reaction (12) to 2×10^{-8} mole of passive film substance. Hence the passive film on iron breaks down forming $\frac{2 \times 10^{-8} \times 159.7}{5.12} = 62 \times 10^{-8}$ cc Fe_2O_3 where 159.7 is the molecular weight and 5.12 the density of anhydrous Fe_2O_3 . This corresponds to a film thickness of $62 \text{ \AA}$ based on apparent area and would be still thicker for the hydrated ferric oxide. This value is in good agreement with thickness measurements obtained by Schwarz^(17A) ($80 \text{ \AA}$) and by Gulbransen⁽⁴⁰⁾ ($78 \text{ \AA}$).

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