A STUDY OF INCIDENCE OF CHEMICAL SLUGS

ABSTRACT

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Dedicated to my wife
The University assumes no responsibility for the accuracy or correctness of statements or opinions advanced in this dissertation.
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A MECHANISM OF
PASSIVATION OF STAINLESS STEEL

I. INTRODUCTION

Stainless steels owe their importance in the industrial world to their ability to resist corrosive attack under oxidizing conditions in spite of the fact that the pure constituents of the alloy are very reactive in the absence of oxygen. The mechanism by which oxygen is deposited upon the surface of this alloy and reduces immensely its reactivity, has been the subject of a large volume of research. Nevertheless, there has been no general agreement among workers in the field.

The purpose of this investigation was to observe the characteristics of the sorption of oxygen upon stainless steel at various temperatures. Type 304 stainless steel, a common austenitic type, was chosen as the stainless alloy to be tested. Particular attention was directed toward the determination of the rate of sorption at room temperature. A comparison of the sorption characteristics of stainless steel with those of Armco iron was made to find the difference in behavior between the manner of formation of "protective" and "non-protective" films.

The evidence as gathered in these studies led to the formation of a new theory of the mechanism of passivation. This theory is believed to explain the conflicting data as observed by workers in this field.
Supplementary work was done in observing the sorption characteristics of oxygen, nitrogen and argon upon stainless steel and iron at 27, -78.6, and -196 C. Confirmation was also made of the breakdown of passivity under high vacuum.

II. SUMMARY AND CONCLUSIONS

A study was made of the sorption characteristics of oxygen and various other gases upon iron and stainless steel. These tests were carried out at a variety of temperatures.

The conclusions to which this study have led are as follows:

1. The sorption of oxygen upon iron and stainless steel, at room temperature, takes place by a two stage mechanism. The initial sorption is very rapid while the secondary process is slow. It is believed that the initial sorption is molecular in character, that is, the bonds between the oxygen atoms are not broken. The second process is believed to be a reaction involving atomic oxygen, either chemisorption or oxidation. As a result of the operation of this duplex mechanism, there is a period of time after the initial passivation of a stainless steel specimen when passivity may be destroyed by a vacuum treatment. If, however, the specimen is exposed to air for too long a period, the secondary process is enabled to cover the surface with a more stable film which is not subject to breakdown under these circumstances.

2. The magnitude of initial rapid sorption of oxygen
upon Type 304 stainless steel is largely dependent upon the presence at which it forms.

3. The rate of the secondary sorption process is only slightly affected by pressure.

4. Neither nitrogen nor argon are appreciably sorbed upon the surface of stainless steel or iron at room temperature.

5. None of the gases, oxygen, nitrogen, or argon, tested in this work, were appreciably sorbed upon the surface of stainless steel or iron at a temperature of -78.6°C.

6. All of the gases; oxygen, nitrogen and argon, were subject to a van der Waals type of sorption at a temperature of -196°C. All of these could be reversibly removed from the surface of iron and stainless steel in this temperature region.

7. Sorption of small amounts of oxygen upon the surface of stainless steel, markedly reduces the ability of that surface to sorb additional oxygen, while sorption of small amounts of oxygen, upon the surface of iron does not readily affect its sorption properties. This would indicate that there is a basic difference between the physical character of the oxides or chemisorbed compounds formed upon these
surfaces. This is in agreement with the work of Gulbransen who found that oxygen could be removed quantitatively from the surface of iron, by reduction with hydrogen at 600°C, while oxygen upon the surface of stainless steel could not be removed in this manner.

8. After exposure to the atmosphere for a period of twenty four hours, stainless steel loses much of its ability to sorb oxygen, while iron still retains that property to a considerable degree.

9. The passive film upon stainless steel is susceptible to destruction under high vacua, if it is subjected to this treatment within 6 hours after the active stainless steel specimen is exposed to the atmosphere.

10. If the partial pressure of oxygen, to which an active Type 304 stainless steel specimen is exposed, is very low, the onset of passivity may be greatly delayed. Exposure of an active specimen to distilled water containing 0.8 parts per million of oxygen, delays the onset of passivity for six hours.
III. LITERATURE SURVEY

A. The Phenomenon of Passivity

Passivity has been the subject of such heated argument, for so many years, that today one finds even its definition is in question. In order not to become embroiled in this controversy, the word passivation will be used in this thesis to denote that phenomenon by which a metal or alloy, theoretically vulnerable to corrosive attack in a given solution, becomes practically immune to such action.

The first observation of passivity is generally attributed to Keir in 1790, but Schonbein in 1836 was the first to describe its characteristics in detail. These early researches were generally made using iron in nitric acid. Faraday made quite an exhaustive study and he is generally credited with the development of the importance of oxygen in the passivation of iron and its alloys.

The characteristic of passivation, as brought out by these men, was not a property of the metal alone but a combination of metallic properties combined with certain influences of the corroding solutions, more specifically, in most cases, it was the oxidizing power of the solution or the ability of the solution to supply oxygen plus the capacity of the metal to retain the oxygen as a protective film, that set up the conditions for passivity.
Since the electrochemical concepts of corrosion have gained such wide acceptance, it has behooved investigators to relate the mechanism of passivity to its effect upon the electrochemical properties of a corrosion system.\textsuperscript{5,6} Means and Brown\textsuperscript{7,8} have given a general review of this problem, in which they relate the behavior of a metal toward a corrosive solution to the polarization of local cathodes and anodes.

In recent years, Pourbaix\textsuperscript{9} has developed a thermodynamical concept of corrosion and passivation. This was done by using a knowledge of the equilibrium between a metal and the different corrosion products which this metal can form by corrosion or passivation. Knowledge of the circumstances of equilibrium permits predetermination of the conditions under which these different compositions are stable in relation to others. From a thermodynamic study of the phenomena, he found he could represent the circumstances of equilibrium by a diagram where the abscissa represents the pH of the solution and the ordinate, the potential of equilibrium "E", of each of the reactions considered. Thus, there is obtained for each metal, a "picture," specific for this metal in which there are certain areas where passivation is the rule. Pourbaix,\textsuperscript{10} makes a distinction between that form of passivation which occurs because the free energy relationships dictate that the metallic surface is stable and that form which results from protection by an oxide film. These
generalized methods of dealing with passivation do not treat the basic mechanism of the phenomenon but merely give methods of visualizing it, in relation to the whole field of electrochemical corrosion.

B. Theories of Passivation

1. Oxide Film Theory

The thought that a layer of metallic oxide at the surface of a metal was the basic reason for passivation, was set forward by Faraday over one hundred years ago. Oddly enough this hypothesis did not receive great acceptance until the last few years. This was due to the fact that the oxide, itself, was not resistant to acid attack. The resolving of this difficulty has been made possible by a line of reasoning which postulates that a thin layer of oxide could be stabilized by the metal.

In recent years, a great deal of work has been done upon the analysis of thin films, which were isolated from the surface of iron and stainless steels. The techniques of this analysis involved the chemical or electrochemical stripping of the base metal away from the film. Although the validity of these methods and, in particular, the effect they have upon the film being stripped, have not been absolutely established, the results have given good indications that under certain conditions an oxide film is obtained upon the surface of passive stainless steel.
According to this theory, the metal oxides, formed upon the surface, give an impervious layer which prevents any contact between the corroding solution and the base metal. Pilling and Bedworth\textsuperscript{12} were able to correlate the protective effect, at higher temperatures, of an oxide film with the relative densities of the metal and the oxide. If the formation of the oxide is accomplished by a decrease of volume, the oxide film must shrink and crack, so providing channels for the further access of oxygen. Such a film will not be protective. When, however, the formation of the oxide involves an expansion, the underlying metal will at all times be covered by the film of oxide which can exert a protective effect. At the same time, if the increase of volume is large, the expansion involved may easily cause cracking of the film and the coating will be poorly protective. From a consideration of the densities of the metals and their oxides, non-protective films are to be expected in the cases of lithium, sodium, potassium, magnesium, calcium, strontium, and barium, all of which, as is well known, can be burned completely in oxygen without difficulty.

2. Electron Configuration Theory.

For some time, it has been believed that certain metals which have passive characteristics do not obtain these because of oxygen or oxides upon their surfaces but instead possess an inate chemical inertness due to a sharing of electrons between
the valence shells and vacancies in lower shells. This would be especially true in the case of transition metals whose shells have vacancies to a greater or lesser degree, depending upon their atomic number. Russell\textsuperscript{13,14} originally proposed that iron was capable of having two states, an active one and a passive one. The electron structures for these species may be represented as follows:

Fe (active) - 2, 8, 14, 2
Fe (passive) - 2, 8, 15, 1

Uhlig\textsuperscript{15} has expanded upon this proposal and supplemented it by experimental work. The major part of his work was done with alloys, in particular, the stainless steels.\textsuperscript{16,17} By assuming that iron is passive when it has only one electron in its valence shell, then a metal or alloy could be passivated by the addition of an alloying element which would absorb electrons into its inner rings. According to this reasoning, chromium, which has five vacancies in the "d" shell, could render passive five atoms of iron. Converting this to weight percent, the percentage of chromium in iron necessary for passivity would be 12\%, which is the approximate composition at which this alloy becomes passive toward some solutions.

This reasoning has been expanded to many alloys, in most cases producing some rather good agreement with factual data.\textsuperscript{18}
During later years, Uhlig,\textsuperscript{19} recognizing some difficulties in his earlier proposals, altered the theory to say, that the electron sharing, mentioned before, was manifested only at the surface of the metal. He further said that oxygen, adsorbed at the metal surface, would aid in passivation, since it would tend to share some of the electrons, while hydrogen would have an opposite effect, tending to lose its electron to the chromium, making that element less effective as a passivation agent.

Although it is probably true that elements with totally filled "d" shells, share their "d" electrons with elements having partially filled shells, it is not at all sure that elements, both of whose "d" shells are unfilled, would also exhibit this property of sharing. Moreover, if it were true, then it would be possible to electroplate this quasi-noble metal at a low potential. This cannot be done. From the standpoint of thermodynamics, any interaction, such as mentioned by Uhlig, would result in a high heat of mixing, which is not observed. In any case Uhlig has recognized that an oxygen layer is necessary to promote passivity so that in essence this fact seems to be the fundamental factor in determining passivity of iron and its alloys.

3. Allotropic Change Theory.
Smits,\textsuperscript{20} in his general theory of allotropy, proposed
that the criterion for passivity is not any of the afore mentioned reasons, but is a consequence of the variety of allotropic forms in which iron may exist at room temperature. At any given time and as a result of its environment, iron may have a number of stable species. The ratio of active to passive forms determines at any given instant whether iron is active or passive. Since this theory has difficulty in explaining many of the occurrences in corrosion, it has been generally disregarded.


The fact that the protective film upon stainless steel is very thin, has led several investigators to conclude that an absorbed oxygen layer is the passivating factor. This fact is supported by observations that oxygen is initially taken on the surface of stainless steel very rapidly. Uhlig has said that one layer of oxygen is all that is necessary to provide a protective surface.

The rapidity of passivation of a stainless steel surface is, indeed, so great in air that Fontana and Beck have proposed a physically absorbed layer of oxygen as the protective film. They have bolstered those arguments by showing that the film may be broken down under high vacuums. Later, these authors, in conjunction with Speiser and Lassettre, produced a theory of "spin adsorption". According
to this model, oxygen possesses what might be termed a residual valence. This is a result of the activation of an electron in the inner shell of the oxygen to produce the well known "sigma triplet state". The oxygen thus possesses some of the properties of a free radical. The interaction of the residual valences of the oxygen with those known to exist on the surface of a metal, produces a bond of intermediate strength between that of physical and chemical adsorption. Such a type of bonding would have a small but definite activation energy.

C. Passivity in Iron

The passive character of pure iron is manifested in only highly oxidizing solutions such as nitric acid. It has been observed that iron after having been immersed in an oxidizing solution such as potassium chromate, potassium permanganate, or hydrogen peroxide is relatively inert or passive, no longer acquiring an immediate deposit of copper when placed in a solution of copper nitrate. The oxide film produced by these treatments is usually assumed to be Fe$_2$O$_3$ or Fe$_3$O$_4$ but other work has postulated FeO$_3$ which is stabilized by the iron lattice. Evans considers the process of destroying passivity of iron to be merely a process of reductive dissolution of the oxide. When oxidized iron is immersed in dilute acid and the

---ferric oxide is destroyed by auto reduction, the rate
of destruction diminishes with an increase in film thickness, with an increase in pH and with a decrease in temperature. Potential measurements show that the polarization increases with a rise in pH which explains why the reduction is so slow at high pH values. According to Evans, chloride ions tend to activate the surface of an iron specimen because they act as a peptizing agent for the hydroxide, formed there.

The subject of an iron specimen to vacuum treatment can bring about the breakdown of the protective film in some instances. This occurrence was noted by Cone, et al. In his tests, the passivation of an iron specimen toward a corrosive solution of chromic acid was destroyed, if the sample was exposed to a vacuum of a few millimeters. This passive film could also be destroyed by a rapid rotation. Other investigators have had difficulty in reproducing these data.

Interesting results have been obtained by Hackerman and Antes for the effect of vacuum treatments upon iron samples. Using the method of Zisman they have investigated the contact potentials of iron under various pressures of oxygen. As the oxygen pressure was increased, the contact potential increased correspondingly, first rapidly and then, after a time, more slowly. Upon subsequent reduction of the pressure, the contact potential was reduced somewhat although not reversibly, indicating the protective
film could be partially removed.

Gatos and Uhlig\textsuperscript{34} have investigated the passivation characteristics of thin pure iron films in nitric acid. In this work they showed that vacuum treatment could be used to remove the oxygen from the surface of iron, thus affecting its corrosion characteristics.

D. Passivity in Stainless Steels.

1. Nature of Stainless Steels.

The addition of chromium to iron in greater than a certain critical amount, confers upon the alloy an abnormal resistance to corrosive attack. The critical chromium content is about 12\%\textsuperscript{35}. There are, in general, three classes of stainless steels, martensitic, austenitic and ferritic.

Austenitic stainless steels are fundamentally chromium-iron alloys with nickel added to retain austenite at room temperature.\textsuperscript{35} The resultant alloy possesses optimum properties as to strength, ductility and magnetic permeability.


The formation of a protective film upon stainless steel has been studied for many years from a practical
standpoint. In production plants it has long been thought necessary to treat stainless steel with a nitric acid solution in order to promulgate passivity. Later work has shown that the film formed upon stainless steel while exposed to air exhibits a greater degree of passivity after a time, than that formed when using a nitric acid treatment.

In any case, it appears that a basic understanding of passivity in stainless steels must come from a study of the surface chemistry in an atmosphere containing oxygen. Renshaw and Ferree made extensive studies of the electrode potentials of many types of stainless steel as a function of their surface treatment. In general, they found that all stainless steels possess similar passivation characteristics. After abrasion or etching the surface shows an active potential. After being exposed to air for a short period the potential becomes less basic and finally becomes noble. After nitric acid "passivation" treatment, the potential is initially very noble, but if the specimen is exposed to a conducting solution, the potential falls quickly to a value comparable to that which is found on the specimen exposed to air. Mahla and Nielsen measured the strength of passive films upon stainless steel by using the technique of "break-through potentials." In this work, they arrived at the conclusion that passivation treatments applied in the field are
considerably less efficient and can add little to the corrosion resistance that an already clean stainless steel surface possesses. Initially unclean surfaces and rough handling of the equipment after passivation will prevent and nullify any benefits attributable to purposeful passivation.

Uhlig\textsuperscript{40,41} has also investigated stainless steels extensively, finding that CC upon the surface is a very good passivator. Guitton\textsuperscript{42} has carefully studied the conditions under which stainless steel may exhibit passivity. He concludes that a much more stable film may be produced upon stainless steel if it is first subjected to general corrosion followed by exposure to air, thus confirming the work of Fontana and Beck. This etching process he refers to as "sensitisation". The passivity attained by the sensitized specimen after exposure to air is more protective than that developed upon an abraded sample exposed in the same manner. Berwick and Evans\textsuperscript{43} have also studied the passivation characteristics of stainless steel extensively. According to their work, neither hydrogen, nitrogen, nor argon is capable of conferring passivity upon a stainless steel surface. An interesting part of this work showed that passivity may be instigated by merely bubbling oxygen over an active stainless steel piece in a sulphuric acid solution. The subsequent bubbling of argon over the same surface would reinstate
activity to the specimen, after a period dependent on the
time the oxygen was in contact with the surface. If,
however, the period of oxygen treatment was longer than a
certain critical time, no amount of argon could destroy the
passivity. As a corollary, they found that the higher the
oxygen pressure in solution, the faster was the onset of
passivity in the first case. They concluded that these
phenomena could only be explained by the formation of an
oxide film.

Although there have been several theories of passivity,
as explained previously, the passivity of chromium itself
has still not been fully fitted into these theories. Ryan
and Heinrich have sought to explain chromium's properties
by theorizing that the atoms on the face of the unit cube
of chromium share the electrons in their outermost orbits
in such a way as to bring about a stable condition.
Hackerman and Marshal, on the other hand showed that
chromium readily takes up oxygen and in so doing it enables
its electrode potential appreciably.

In neutral solutions, the passivity of stainless steel
is governed to some extent by the dissolved oxygen content
of the medium. Pratt has shown that oxygen exhaustion
from corrosive solutions, greatly alters the passivity of
nickel-chromium-molybdenum stainless steels.
E. Mechanism of Film Formation

In order to completely delineate the causes of passivity, one must depart from the generalized theories of polarization and treat of the actual mechanism by which oxygen is taken upon the stainless steel.

1. Physical Adsorption.

When a gas becomes attached to the surface of a solid, possibly the weakest interaction possible is that due to van der Waals's Forces. The equation of state of van der Waals for imperfect gases can be put in the form:

\[ P = \frac{RT}{V-b} - \frac{a}{V^2} \]

The equation of state of a perfect gas is:

\[ P = \frac{RT}{V} \]

By definition there are no forces between the molecules of a perfect gas. A comparison of the equations above, shows that the van der Waals equation implicits both attractive and repulsive forces between the molecules of an imperfect gas. The constant in the pressure term is a measure of the repulsion between the molecules. Consider a rare gas atom. This has a spherically symmetrical charge distribution and the electrons form a spherical shell of negative electricity on the outside. Thus a rare gas atom has no external field.

The above equations show that the external pressure is
smaller than the dynamic pressure by the amount $\frac{3}{2}$. This implies attractive forces between the molecules and the van der Waals constant "a" gives a measure of these attractive or cohesive forces. Many of the uncharged molecules have dipole moments, and it was suggested by Keesom that the interaction between those dipole moments is responsible for the van der Waals attraction.

When two molecules, having dipole moments, approach each other, the interaction between the dipoles will manifest itself in two ways. In the first place, the dipoles exert forces upon each other, attraction or repulsion, depending on the relative orientations. If the unlike charges are closer to each other than the like charges, the net effect will be attraction, otherwise repulsion. In the second place each dipole is acted upon by a torque in the field of the other. These torques tend to orient the dipoles parallel to each other, the positive end of one being closer to the negative end of the other.

Debye pointed out that the orientation effect alone can not account for van der Waals cohesion. According to previous equations the attraction potential diminishes linearly with the absolute temperature, but the experimentally obtained van der Waals' cohesion corrections indicate no such
rapid decrease with temperature. He concluded, therefore, that there must be an additional interaction energy which is independent of temperature. Keesom had considered the molecules as rigid dipoles, that is, he assumed that the charge distribution of a molecule does not change under the influence of another molecule in its vicinity. Actually, however, the charge distribution of a molecule is disturbed by the presence of another charged body, the molecule becoming polarized. This is an example of the phenomenon of induction and its manifestation in gas equilibria is known as the Debye induction effect.

Nevertheless, orientation and induction effects can at best account only for van der Waals attraction between molecules possessing permanent dipoles. But many molecules, such as hydrogen, helium, argon, nitrogen, methane etc., do not have permanent dipoles. To explain the van der Waals attraction between two such molecules Debye and Falckenhagen assumed the existence of quadrupole moments. They suggested that the quadrupole moment in one molecule induces a dipole moment in the other and the interaction between a permanent quadrupole and induced dipole gives rise to van der Waals attraction.

A simple example of a quadrupole consists of two similar dipoles laid end to end in such a manner that either the two
positive or the two negative charges coincide in the center. Such an arrangement has no dipole moment since the centers of gravity of the positive and negative charges coincide. Dipole moments can be determined by physical measurements, but quadrupole moments cannot be measured experimentally. Their existence was inferred solely from the fact that attractive van der Waals' forces existed between molecules having no permanent dipoles, and their magnitude was calculated from the van der Waals corrections.

The advent of quantum mechanics offered another possibility however. From calculations based upon this new method, it appeared that rare gas atoms have a charge distribution such that no quadrupole may exist, and that in other atoms the effect was 1/100 of that previously estimated.

To account for the attractive force previously attributed to quadrupoles, London\(^5\) developed the theory of a "dispersion effect". Consider, for example, an argon atom as an example of a non-polar molecule. Since there are 18 electrons moving around the central nucleus in various directions, it is very unlikely that at any instant the electrons should be so arranged as to give exactly zero dipole moment. The dipole moment will be constantly fluctuating in magnitude and direction. This will create a fluctuating electric field
around the atom, which produces displacements of the charge in a near-by atom. The force exerted by the fluctuating field on the displaced charge will not average zero, because there is a tendency on the part of the fluctuations of the dipole and the induced dipole to move in phase with each other. There will result a net attraction. Thus, we see that the interaction known as van der Waals adsorption is the sum of several interactions all of which, by their very nature, are weak in character. Since van der Waals forces are those which cause gases to condense, it would be expected that the energy change involved in an adsorption involving these forces would be of the order of the energy change when liquefaction of a gas takes place. Moreover, since the adsorption would take place with no sharing of electrons nor other serious rearrangement of the molecular structure, the process would be very rapid in attaining equilibrium. Both of these facts have been observed, during adsorption experiments.

The "secondary" forces being rather weak, it is to be expected that this type of adsorption would occur to a great degree only near the liquefaction point of the gas. Many systems exhibit physical adsorption. For instance, hydrogen upon nickel at temperatures below -200 °C and CO upon copper at low temperatures. The review of literature thus indicates that physical adsorption is a type associated with weakly
attractive forces; it is rapid and has a low heat of adsorption.

2. Chemisorption.

In 1930 H. S. Taylor suggested that, just as an activation energy is necessary to bring about co-valent combination of atoms, so the process of chemisorption requires an activation energy. In particular it was considered that one and the same gas could often be adsorbed on one solid at two different temperatures in the two forms of van der Waals adsorption and chemisorption. Owing to the much smaller activation energy of the former it took place at very low temperatures; as the temperature rose, owing to a small heat of adsorption, gas was removed more or less completely. At still higher temperatures adsorption recommenced, but in a different form, as chemisorption, the molecules having now attained considerable energy of activation required to combine by co-valent forces with the surface.

The conception that chemisorption requires an activation energy is not obscure; most chemical reactions require this. Polanyi points out that free valencies at a surface would not attract molecules, until these have jumped over a potential barrier; therefore only these molecules which have a certain energy may be expected to combine chemically with the surface. On the other hand, reactions in which free atoms take part, generally have a very small true activation energy, that is, an activation energy in excess of any energy needed to supply
the heat absorbed in an endothermic reaction, such as a
dissociation of hydrogen on a surface. If this is correct,
there need not be any appreciable energy of activation for
a chemisorption involving dissociation into atoms on the
surface.

The adsorption of gases on the plane surface of metals
has been extensively studied. It has tremendous
importance in the field of catalysis, where metal catalysts
have many applications. The studies of adsorption in this
area, however, cannot be directly applied to this subject
since they generally involve finely divided powders which
have features not evident in plane surfaces, i.e. capillary
pores. To accurately study the adsorption phenomenon upon
plane surfaces involves very careful measurements of small
amounts of gas. Perhaps the most widely studied metal, until
this time, has been tungsten whose adsorption characteristics
greatly influence its performance as an incandescent filament.
In a series of papers, J. K. Roberts, outlines the
mechanism by which he believes that oxygen is adsorbed upon
tungsten. According to his analysis, oxygen exhibits
peculiar properties on being adsorbed by tungsten because
it is larger than the site available upon the quadratic
lattice. He, therefore, developed a theory for the purpose
of building up an immobile film by the adsorption of the two
atoms of a diatomic molecule on neighboring solid atoms and he shows that such a film necessarily has gaps. Adsorption of a second film corresponds to adsorption upon these gaps. Using the heat of adsorption values, he established the fact that the first layer is atomic while the second is molecular. The properties of the initial film make it immobile, that is, the oxygen is attached at fixed points on the tungsten lattice. The secondary, molecular film, is mobile, however, and it is considered to be much less stable than the atomically bonded film. These views are born out by the work of Miller who applied statistics to the problem. Rideal and Trapnell give the phenomenon, occurring upon tungsten, a somewhat different interpretation. According to their views the take up of oxygen upon the surface of tungsten is initially molecular chemisorption. This is followed by a second process, identified by them as oxidation, which slows very rapidly as gas is taken up. If the experiments are performed at a somewhat elevated temperature, the oxide may be readily identified by electron diffraction. These authors state that a majority of chemists in England now accept the fact that chemisorption of simple gases such as oxygen, hydrogen and carbon monoxide upon clean metal surfaces, proceeds without an appreciable activation energy.

Schmitt and DeBoer rather extensively investigated the adsorption characteristics of hydrogen upon a nickel catalyst.
Previously it had been reported that the adsorption of hydrogen was very rapid. Using nickel from reduced nickel compounds these men found that although some of the adsorption was very rapid, a great deal of it was slow. Their explanation of this matter revolved around their hypothesis that the surface used was a heterogeneous one with the more active centers adsorbing more rapidly while weaker centers had an appreciable rate.

Possibly the most extensive investigation of the adsorption properties of iron was made by Armbruster and Austin. In a series of papers\textsuperscript{65,66,67,68,69} they described a complete study on the adsorption of argon, neon, hydrogen, nitrogen, carbon monoxide and carbon dioxide upon the smooth surface of steel at temperatures of 20, -78, -183 and -145 C. These investigators used a method of differential pressure determinations similar to the procedure used in the experiments described in this thesis. They initially studied the adsorption of ethyl iodide upon steel surfaces. The resultant isotherms did not correspond to monolayer adsorption. Next they studied the adsorption of argon, nitrogen, oxygen, carbon monoxide and carbon dioxide. Their results indicated that argon, nitrogen, and carbon monoxide were adsorbed at -195 and -183 C but were not adsorbed at -78 and 20 C. CO\textsubscript{2} on the other hand showed some adsorption at -78 C and lower but none at 20 C.

Oxygen was rapidly adsorbed at -195 and 183 C but above
this range the process became much slower and at higher temperatures, the process was shown to be irreversible. The properties as observed on smooth silver were rather similar to those which they found for steel. The properties of a hydrogen reduced surface were shown to closely resemble those of a surface which is merely heated under vacuum.

The adsorptive power of stainless steel (Type 304) was also investigated and its properties shown to be the same as plain carbon steel.

A new method in the study of adsorption has been the use of "contact potentials." This method is based on a principle that two dissimilar metals when placed close together and connected electrically act as a condenser. The amount of charge collected on the metals may be measured by discharging them through a sensitive galvanometer. This charge is sensitive to the conditions prevalent upon the metal surface. Antes and Hackerman have studied the contact potential variation on freshly condensed metal films at low pressures. Their results upon iron films are of a special interest. They found that when oxygen was admitted to the surface of iron its contact potential, with reference to a platinum standard, rose rapidly at first but after a time the rate became much slower. Upon raising and lowering the
pressure above the system, the adsorption process was found to be partially reversible. It appeared from their results that there was a reversible type of adsorption taking place upon the surface which accounted for a major part of the initial adsorption but at the same time, at a much slower rate, there was an irreversible type of adsorption taking place, possibly involving molecules already in the irreversibly adsorbed state.

Uhlig\textsuperscript{71} has also investigated the effect of oxygen on the contact potential of iron. His measurements indicated to him that oxygen was greatly facilitated in adsorbing upon iron when water vapor was present.

Mignolet\textsuperscript{72} has measured the adsorption of some gases on evaporated nickel films by this new method. He has found several indications of chemisorption at room temperature.

Rideal\textsuperscript{73} has shown that appreciable decomposition of chemisorbed compounds may occur if that material is subjected to a high vacuum. Moreover, he says that many investigators ignore the possibility of lateral mobility in surface films. According to his work practically all films have some ability to move over the surface of the adsorbent from the spot where they were initially deposited.
Benton and White have studied the adsorption of hydrogen upon nickel over a range of temperatures. Specifically, they investigated the adsorption of hydrogen by reduced nickel at pressures from zero to one atmosphere and at eleven temperatures from 110 to -210 C. They found that at a given pressure, the adsorption is relatively large at the lowest temperatures. Upon increasing the temperature to -200 C the adsorption decreased to a minimum. Further increases in temperature caused a maximum at -100 C and finally a continual decrease. The major results of the work are interpreted on the hypothesis that, at low temperatures, the adsorption is of a secondary or molecular type, while at higher temperatures, a progressively larger fraction of the nickel surface is capable of holding the hydrogen by adsorption of the primary type, involving a marked activation of the gas.

In order to measure the rate of adsorption of even the fastest process, the oscilloscope has been used. Johnson and Vick have measured the adsorption in certain systems and report that the time is in the order of microseconds.

3. Oxidation.

Since the time of Faraday the primary thinking on the character of metal surfaces has been tied up with the fact that oxides readily form there. Frequently workers have attempted to correlate the structure of metallic oxides
formed at higher temperature with the protective film formed upon metals at room temperature. The data for the stability of metallic compounds show that practically no metal would remain completely unaffected by a gaseous environment. The problem, therefore reduces to a consideration of the extent to which coatings, formed by reaction with the gas, are protective. In other words that is the manner and rate of growth of the oxide layer.

Kinetic theory is concerned primarily with the progress of a reaction with time. Thus, a first consideration is the relation of weight gain and time. A number of these have been discovered empirically. First there is the linear relationship:

\[ w = k \cdot t \]

which is the simplest equation that was found to express experimental data. If a surface layer is non-protective and offers no resistance to the continued contact between metal surface and gas phase, the actual thickness of the layer has no significance on the reaction rate, and the oxidation is governed by a linear law.

There are two groups of metals and alloys which have been found experimentally to 'obey this relationship, namely those that form porous or volatile oxidation layers. There is one
criterion that enables us to predict whether a porous layer will be formed. If the volume ratio is smaller than unity, that is, if the surface compound has a smaller specific volume than the metallic phase, the linear time law has been found to apply for the reason that the surface compound is not able to form a coherent layer, and thus fresh metal surface is being continuously exposed. This fact was first pointed out by Pilling and Bedworth.12.

If the volume ratio is greater than unity and volatile compounds are absent, the linear relationships are no longer applicable and the growth of a continuous coherent surface film must be considered. If, in these layers, a diffusion process is rate-determining76 then one may expect the increase in film thickness with time to be inversely proportioned to the film thickness or we find the following relationship to apply:

\[(w)^2 k_2 t\]

The rate of oxidation is thus parabolic.

In addition to these two laws, there is a third called the "logarithmic law", which may be represented by:

\[w k_3 t\]

In fairness it must be said that any process which tends to come to a standstill will follow, in general, a logarithmic
relation. So that this law is not able to accurately fit the experimental curves with any exactness. This law has a special application in any "oxide film" theory of passivity since it has been found that many thin films react by this law.

More particularly, it has been proposed by Mott\textsuperscript{77,78} that a thin oxide film forms on aluminum according to this logarithmic relation. He proposes a mechanism that applies quantum mechanical laws to the system. According to this theory, the oxide of aluminum is not a conductor, therefore there must be another mechanism by which the electrons are enabled to cross the barrier and be shared with the oxygen. The idea of a "tunnel effect" is used by Mott to explain this phenomenon. Since the potential walls of the metal boundaries are not of infinite height, an electron is able to penetrate the barrier on a statistical basis. Thus it is possible to build up a thin film of oxide upon the aluminum surface. As the film thickens, eventually no further growth is possible.

Gulbransen\textsuperscript{79,80,81} has done a great deal of work upon the take up of oxygen upon iron and stainless steel at room temperature. He employed a technique involving a vacuum microbalance. Using this method, he studied the oxidation of pure electrolytic iron from 25 to 400 °C and at various pressures of oxygen. According to the observed reaction rate,
he proposed that the mechanism is the sum of three separate reactions. These are (1) a rapid initial rate; (2) an intermediate reaction which involves the logarithm of the difference between an extrapolated parabolic law and the experimental value as a function of time; and (3) a parabolic law which is found to hold above a certain temperature and film thickness.

In his work upon stainless steel, Gulbransen found that the film formed by oxygen upon iron may be quantitatively reduced by hydrogen at 600 °C, while that formed upon stainless steel is not susceptible to this type of treatment, thus, giving some indication of the differing physical character of the oxides upon the surface. In later work Gulbransen has developed the transition state theory for the formation of oxide films upon metal surfaces. This transition state theory is the same as that of Eyring which is normally called the "Absolute Reaction Rate Theory."

He shows two terms to be important in the rate equations: (1) the energy factor and (2) the entropy factor. The difference between the oxidation rates of stainless steel and iron is shown to be due largely to an energy factor while the difference between copper and iron is one of an entropy factor. This would imply that the mechanisms of oxygen take-up upon stainless steel and iron are similar while that of iron and copper
are different.

The analysis of films formed at high temperatures has been a problem which has been worked on by many people. Phelps, Gulbransen and Hickman have carried out experiments on the electron diffraction analysis of films formed on a good many metals at moderate temperatures. In each of the cases studied, definite crystalline patterns were found. However, investigators are not agreed as to the structure of films formed upon stainless steel at room temperature. Many contend there is no discernible crystalline structure to be found upon the surface and these same investigators conclude that the film is either amorphous or it is too thin to be detected.

Yamaguchi is among those who feel that the oxide formed at room temperature must be similar to that formed at higher temperatures. Some recent evidence has implied that this is not correct. Early investigators such as Mahla and Nielson stripped films from stainless steel that had been subjected to high temperature oxidation. According to the analysis of this material, the oxide was enriched in several of the constituent base elements, in particular, chromium. Later results by Rhodine, who used a much more detailed technique, showed that the composition of films formed at room temperature has approximately the same ratio
of metallic elements as was present in the base alloy. This would tend to indicate a substantial difference between the oxides formed at the various temperatures.

F. Surface Characteristics of a Metal.

Chemisorption is often called "specific", van der Waals adsorption "non-specific". The term "specific" is somewhat vague, it has never been accurately defined. Consider that adsorption in the first layer depends on two factors: the extent of the surface area and the energy of interaction between the surface and the gas. The former is the "non-specific" factor, the latter the "specific" factor in adsorption. In van der Waals adsorption, the energies of interaction between a given gas and different adsorbents are not very different and so the surface factor is of greater importance than the energy factor. In chemisorption the reverse is true, the energy factor is more important. Strictly speaking it is incorrect to say, therefore, that one adsorption is non-specific, the other specific; it would be more correct to say that van der Waals adsorption is only slightly specific while chemisorption is strongly specific.48

If physical adsorption were completely non-specific, the nature of the adsorbent would be entirely immaterial and only the extent of the surface area would matter. Whether one measures the adsorption on an ionic crystal like sodium
chloride, on a semi-conductor like graphite, or on a metallic conductor like iron, the adsorption per unit surface would be the same. Of course, this does not happen. The isotherms do not coincide, because even the slight differences in the heats of adsorption bring a certain amount of specificity into van der Waals adsorption.

If one should inspect the adsorption isotherms of nitrogen and argon upon graphite, he would see that the amount adsorbed falls very sharply, at first, with the amount of gas adsorbed, then attains an almost constant value. The adsorption of the first part of the gas takes place on a strongly heterogeneous surface, but beyond that the surface is approximately homogeneous. Barrer's work shows that the initial part covers less than one-sixth of the surface of graphite, in this instance more than five-sixths of the surface can be characterized by a uniform heat of adsorption. This example illustrates the fact that the surfaces of adsorbents can usually be divided into two parts: a heterogeneous part possessing higher heats of adsorption and a homogeneous part with a smaller, approximately constant heat of adsorption.

According to Brunauer, adsorption above the critical temperature is probably always unimolecular. All data available at present on adsorbents of known surface area
indicate less than a complete layer absorbed. Data obtained on adsorbents with unknown surface areas suggest unimolecular adsorption by the shapes of the isotherms.

Most isotherms obtained for gases above their critical temperatures represent adsorption on the heterogeneous part of the surfaces. If the adsorption of a gas is measured considerably above the critical temperature, saturation of the surface with a unimolecular layer is attained only at high pressures.

The heterogeneity of the adsorbent surface has a much more marked effect on chemisorption than on van der Waals adsorption. Brunauer and Emmett found that if part of the surface of an iron catalyst is covered with a layer of oxygen the physical adsorption of nitrogen proceeds just as readily on the oxygen covered part as on the unoxidized iron atoms of the surface, but the chemisorption of hydrogen or of carbon monoxide is eliminated on the oxidized portion and proceeds only on iron atoms. If the entire surface is covered with oxygen, the chemisorption of hydrogen and carbon monoxide at low temperatures is almost completely eliminated, but the physical adsorption of nitrogen remains practically unaffected by the oxidation.

Although the effect of the non-uniformity of the surface
on van der Waals adsorption is not as pronounced as on chemisorption, it is by no means negligible. Previously it has been said that the theoretically calculated heats of adsorption of a gas on the surfaces of carbon, a metal, or anionic crystal are not very different, and that experimental evidence corroborates the theory for the less active homogeneous part of the surface. However, even though the heat of adsorption of a molecule is about the same on the plane surfaces of carbon and iron, it makes a great difference whether the molecule is attracted by two carbon surfaces or by one. In other words, the heat of adsorption in narrow cracks and crevices differs strongly from that on a plane surface.

There are other causes besides narrow pore spaces that can give rise to high heats of adsorption. Atoms located on the edges and corners of crystals have different degrees of unsaturation from those located in the surface planes, therefore their interaction energies with a gas molecule will be different. Even plane surfaces of a crystal will have different heats of adsorption depending on the distances and geometrical configurations of the atoms composing the plane. The attraction of a molecule by the (100), (110) and (111) faces of the same crystal will obviously be different.

Beside such causes as are inherent in the structure of the adsorbent itself, there are other extraneous causes
producing heterogeneity in the surface. Impurities adsorbed on parts of the surface create differences in the heats of adsorption. The effect of an impurity is usually to cut down the physical adsorption of a gas or to leave it unchanged. The effect of impurities is greater on chemisorption than on van der Waals adsorption. As one would expect, the effect on van der Waals adsorption is most marked at lower pressures but small at higher pressures. Brunauer and Emmett found that the isotherms of nitrogen on iron catalysts at -183 °C were the same whether adsorption took place on the pure surface or on surfaces covered with chemisorbed hydrogen, nitrogen, or oxygen atoms. Atomic chemisorptions do not cut down appreciably the extent of the surface area of the catalyst, and they do not change much the heat of adsorption on the less active part of the surface.

The purpose of evacuation prior to any adsorption run is to remove adsorbed impurities from the surface. The importance of thorough evacuation has been emphasized by many investigators. Raising the temperature helps to remove the impurities.

IV. PROCEDURE AND APPARATUS

A. Preparation of Specimens.

Three types of specimens were used for this investigation:

1. For the study of the sorption characteristics of stainless steel, a coil of Type 304 stainless steel strip was
obtained from the Driver-Harris Co. The composition of this material as analyzed was found to be chromium 13.9%, nickel 8.3%, carbon .04, balance iron. The strip was 3 x .005 inches and was received in the dead soft condition. This type of stainless steel was chosen because it is a typical austenitic steel which is used extensively.

Strips 0.5 x .005 x 6 inches were cut from this coil and the surface areas measured. A typical sorption determination was made using 103 of these strips, whose projected surface area was approximately 0.423 square meters.

To obtain an initially active surface, the strips were first subjected to an etching treatment. This etch consisted of exposing the specimens for one minute to the action of boiling 10% sulphuric acid. Following this treatment, the material was rinsed several times in double distilled water and then in acetone. The specimens were allowed to dry in air for fifteen minutes before being placed in the sorption bulb.

(3) For sorption studies upon iron, a number of sheets of cold rolled Armco iron were obtained from the Armco Iron Company of Middletown, Ohio. The material analyzed as .001 carbon, balance iron. The sheets were cut into 4 inch strips and sent to Battelle Memorial Institute where they were rolled to a maximum of 0.006 inches. Sorption specimens were prepared
by cutting this material into strips of 0.5 x 0.006 x 3 inches. A stress relief anneal was performed upon the iron by heating at 600°C for 1 hour. To simulate a surface comparable to that used for the stainless steel, the iron was also etched for 1 minute in boiling 10% H₂SO₄, rinsed in distilled water and also in acetone and then dried in air for 15 minutes before enclosure in the sorption bulb.

(3) Stainless steel specimens for use in vacuum break-down tests and in studies relating to the active-passive transition point, were of Type 304 stainless steel which was analyzed as chromium 18.9%, nickel 8.8%, carbon 0.04%. The specimens normally used were approximately 3/8 x 1/4 x 1 inch. They were ground upon #180 grit belt grinder with the corners being rounded to avoid edge effects.

B. Experimental Apparatus

1. Sorption Apparatus.

The equipment used in the study of the sorption characteristics of iron and stainless steel is pictured in Figure 1. A schematic diagram is shown in Figure II. This apparatus is modeled after that of Armbruster and Austin who in turn used the equipment of Bawn as a guide. In essence, it consists of two carefully calibrated volumes, one of which contains the specimen and the other of which is connected to an accurate pressure measuring device.
Initial evacuation of the sorption bulb and gauge was done with a standard mercury diffusion pump backed up by a Duo-Seal mechanical pump from the Welch Manufacturing Company. This combination of pumps was easily able to attain pressures of the order of 0.61 μm (μm = 0.001 mm of Hg) within a few minutes after being started, if the interior of the system was clean and dry.

To facilitate expansion of the gas from one part of the system to another, mercury cutoffs were employed. They consisted of small "U" tubes into which mercury could be raised at will and which, when filled with mercury, effectively sealed off one part of the equipment from another. This was necessary, to avoid the use of stopcocks, since the vapor pressure of the stopcock grease could not be tolerated in this work. To maintain accurate volume checks at all times, it was necessary to be able to raise the mercury levels to certain prescribed points which would be the same for each determination. To accomplish this, tungsten leads were sealed into the glass in such a manner that when the mercury level reached the designated height, an electrical circuit was "made" and a light informed the operator of this fact. The three cutoffs were operated remotely by use of a vacuum manifold which enabled the operator to measure out gas additions, expand the gas into various portions of the apparatus, and read the pressure, all from a central position.
A gas measuring burette was used to admit small amounts of gas to the gauge compartment. This burette could measure within one percent, an amount of gas less than $1 \times 10^{-7}$ moles.

All pressure measurements were made using a three stage U-bend gauge constructed in this laboratory. This instrument could accurately measure pressure from $1 \times 10^{-6}$ to 0.3 millimeters of mercury. The gauge was calibrated by weighing the water which could fill the various volumes. Data for this instrument are:

- Area of capillary: 0.385 mm$^2$
- $V_1$ bulb: 69.3 cm$^3$
- $V_2$ bulb: 4.86 cm$^3$
- $V_1$ bulb: 0.324 cm$^3$

Pressure readings could be reproduced to about three percent, with all readings being made using a cathetometer.

The gas purification train was used for the purification of hydrogen and for the drying of argon and nitrogen "tank" gas. It consisted of a drying tower of magnesium perchlorate, followed by a furnace containing platinized asbestos, which was in turn followed by a concentrated sulphuric acid bubble bottle and another magnesium perchlorate drying tower. The furnace, containing platinized asbestos, was operated at 600°C.

Several standard cold traps were a part of the equipment. A large one near the left of Figure 3 served to protect the
absorption specimen from any mercury which might condense upon its surface. Standard "Dewar" type flasks surrounded these traps. When tests were made at room temperature or at $-78.5^\circ C$, the traps were filled with a dry ice and acetone mixture while if the test were made at $-196^\circ C$, the traps were filled with liquid nitrogen.

2. Vacuum Breakdown Apparatus.

The equipment used in experiments relating to the breakdown of passivity at high vacuums is essentially similar to that of Beck.$^{36}$ It is pictured in Figure 3 and a schematic drawing is shown in Figure 4. The apparatus may be evacuated by means of a standard mercury diffusion pump operating in conjunction with a "Cenco-Vac" forepump. This combination could easily attain vacuums of the order of $0.01 \mu$ upon a clean dry system. Pressure measurements were made using a small McLeod guage. Accessory equipment was so arranged that, at any given moment, the specimen could be sealed off from the pumps and a specified acid admitted to test the specimen for activity or passivity. As shown in Figure 4 there was also a means of admitting selected gases to the specimen before the acid was let in.

3. Active-Passive Transition Point Apparatus.

The determination of the active-passive transition point required a minimum of formal equipment. Tests for passivity were made using $10\% H_2SO_4$ in a constant temperature bath. This
bath was made to hold a temperature of 40 °C within 1 degree, using a medium of ethylene glycol. The equipment used for the analysis of oxygen is that of Winkler. 89

C. Experimental Procedures

1. Sorption Experiments.

The types of sorption experiments performed were many and varied, but the general procedure was the same for all of the tests. After the specimens had been dried in air for 15 minutes, as previously described, they were sealed into the sorption bulb. With all the mercury cutoffs in the "down" position and the entrance to the gas reservoir also open, the forepump was started and allowed to "rough down" the system for 15 minutes. The mercury pump was then started. With these pumps operating, all of the "Dewar" flasks surrounding the cold traps were filled with an appropriate medium according to the temperature at which the test was to be conducted. The usual procedure was to attain a vacuum of less than $1 \times 10^{-5}$ mm of Hg and maintain that pressure for 24 hours, before any sorption determination was made. In most cases, and especially in those instances where the apparatus was exposed to air for only a short time between runs, this order of vacuum was easily attained within the first hour. Upon other occasions when such speeds of evacuation could not be had, the entire system was gently heated by a torch. Trouble was sometimes found in evacuation of the small capillary of the McLeod gage since water vapor would often condense there. An
electric spark coil, used in leak detection, proved effective in this case, because it could ionize the gases adsorbed upon the inner walls of the capillary by merely holding it against the outer wall of the glass. In extreme cases, it was necessary to "rinse" the system with purified hydrogen and then reevacuate. Deploying these methods, the ultimate vacuum could always be brought to a value of less than 5 x 10^-6 mm of Hg.

Immediately prior to each sorption determination, #1 stopcock, as shown in Figure 3, was raised, and left in that position for 1 hour after which, a pressure reading was taken. If, during this period, the pressure had risen to a value greater than 1 x 10^-5, the run was discontinued and the leak repaired.

The gases used in this study were oxygen, hydrogen, argon, and nitrogen. Since hydrogen is sorbed by neither the specimens nor the glass at these temperatures, it was used for all calibrations of the volumes involved. The purification of hydrogen was accomplished by passing electrolytic "tank" hydrogen through a bubble bottle containing concentrated sulphuric acid, then, through the platinized asbestos furnace which converted any oxygen to water and finally through a drying tower containing magnesium perchlorate. In preparing for a sorption run, hydrogen was passed through this system for four hours before any gas was admitted to the reservoir.
The oxygen used in these experiments was prepared by heating chemically pure potassium permanganate. This material was always freshly prepared before each experiment in the following manner. First the gas reservoir was sealed off from the remainder of the evacuated system and a glass apparatus was connected. This attachment had a small tube of dry potassium permanganate at one end, with a cold trap between it and the gas reservoir. The cold trap was immersed in liquid nitrogen following which, the gas reservoir, the cold trap, and the tube containing potassium permanganate were evacuated. Heating the tube allowed oxygen to expand into the gas reservoir with all water vapor being condensed in the cold trap. This heating was continued until a pressure of about three millimeters of mercury was reached, as registered upon the manometer, shown in Figure II.

Argon and nitrogen were high purity materials although not "spectroscopically pure". They were both treated in the same manner as the hydrogen previously described.

A typical sorption experiment was always preceded by calibration of the volumes involved. All experimenters working in this field have found that, at room temperature, hydrogen is neither sorbed by iron or by glass. These facts have been verified in this work. The inert quality of hydrogen makes it ideal as a calibrating agent.
When the initial evacuation treatment had been completed, the gas reservoir was sealed off from the other parts of the system and hydrogen was admitted to pressure of approximately three millimeters. At this point, mercury cutoffs #1 and #2 were raised to the "up" position. By suitable manipulations, hydrogen was allowed to enter the gas burette where a small amount was metered out. This gas was then expanded into the main part of the system, whereupon, cutoff #3 was raised. As can be seen from Figure 3, the hydrogen was then contained in a space between the three cutoffs. This volume was accurately known from prior work which involved measuring the weight of water which would fill this apparatus and also other calibrations of the type being discussed. This space was designated as the "measuring volume".

Upon measuring the pressure of the hydrogen so enclosed, the number of moles of gas could be accurately calculated for the temperature used. Lowering of cutoff #2 permitted the gas to expand into the specimen chamber. Since hydrogen is not sorbed upon glass or the specimen, the lowering of the pressure due to this expansion, accurately reflected the "dead space" in the system. This space varied with the differing volumes of the specimens introduced and it also changed from run to run due to alterations introduced when the sorption bulb was sealed off. When experiments were first initiated, the calibration was always made after a run had been completed. This procedure
was rather awkward and subsequently a change was made so as to complete the calibration just after the system had been evacuated and before the 24 hour evacuation period was begun.

Thus with the system calibrated and the specimen given the standard twenty four hour evacuation treatment, a sorption experiment would be begun. Oxygen was delivered to the reservoir as described previously and as in the calibration, cutoffs #1 and #2 were placed in the "up" position. A suitable amount of oxygen was metered out through the gas burette and cutoff #3 was raised. After a short period for the attainment of equilibrium, a pressure reading was made and the number of moles of oxygen calculated. At this low pressure, gases follow the perfect gas laws rather closely and these laws were used in all calculations.

Lowering cutoff #2 permitted expansion of the oxygen into the specimen bulb. After fifteen minutes for equilibrium to be set up, a second pressure reading was taken. The amount of pressure lowering, not accounted for by the simple expansion into the dead space of the sorption bulb, was attributed to sorption upon the surface of the sorbent and was easily translatable into moles of gas sorbed.

At low temperatures, the equilibrium was always attained instantaneously. That is, after the first pressure measurement, taken fifteen minutes after expansion, there was no
further lowering of the pressure. Room temperature tests, however, always necessitated a longer period for sorption to cease. In fact, at higher pressures many specimens did not attain an equilibrium state at all, within the time that pressure measurements were taken. This period was often as long as 48 hours. In a case of this sort, pressure measurements were taken as often as was necessary to define the shape of the "time-sorption" curve.

After equilibrium had been attained or, in the case where the time effect is noted, when the shape of the "time-sorption" curve had been defined, cutoff #3 was raised and cutoff #5 was lowered. By suitable manipulation, another quantity of gas was admitted to the measuring space and cutoff #3 placed in the "up" position. A pressure reading served to determine the total number of moles of gas present in this volume, while another calculation gave the number of moles of gas trapped in the dead space of the sorption bulb when cutoff #5 was raised. Thus the total amount of gas present in the measuring space and in the sorption bulb was known and the theoretical pressure which should be manifested when cutoff #3 is again lowered could be calculated. The difference between this pressure and that actually measured was attributable to sorption and the amount found to be sorbed in this step was added to that found to be taken up in the first step. In such a way the complete isotherm could be built up without any
To show that sorption was reversible in some cases, desorption studies were made in the following manner. After an isotherm determination had been completed, cutoff #2 was raised and cutoff #1 was lowered, permitting evacuation of the "measuring volume". The cutoff was left in the "down" position until the pressure was below $5 \times 10^{-6}$ at which time it was raised. Lowering of cutoff #2 permitted expansion of the gas, trapped in the sorption bulb, back into the measuring volume. Any increase in pressure over that which was dictated by the expansion itself, was attributed to a description of gas sorbed upon the surface of the specimen being studied. The raising of cutoff #2 and subsequent reevacuation of the measuring volume allowed another desorption to be made and in such a manner an entire desorption isotherm could be built up. This operation was very time consuming, however, and the usual technique was to find only one or two points on the desorption curve to check the reversibility of the sorbed product.

2. Vacuum Breakdown Tests

The work upon the breakdown of a passive film under high vacuum essentially followed the work of Beck. Specimens to be subjected to this treatment were given an etch in boiling 10% sulphuric acid as previously described. After drying in air for a time dictated by the particular conditions of the
test, the specimen was placed in a test tube fitted with a standard taper joint and this tube was then affixed to the vacuum apparatus as shown in Figure 4. The equipment was "roughed down" for fifteen minutes using the mechanical pumps and the mercury pump was then turned on. After attainment of a vacuum of less than $1 \times 10^{-5}$ mm. of mercury, the specimen was subjected to the vacuum for two hours. During this period, several hundred cubic centimeters of 10% sulphuric acid were brought to a temperature of 40°C in the constant temperature bath. Just prior to the time when it was desired to test for the specimen's activity or passivity, the acid, contained in a specially constructed bulb, was transferred to position just above the acid inlet as shown in Figure 4.

At the end of the two hour period, a stopcock was closed, sealing off the specimen from the pumps and the gage, but maintaining an evacuated condition above the specimen. At the appropriate moment, the valve was opened allowing acid to flow into the specimen chamber. As soon as the acid could be seen to completely cover the specimens, air was admitted above the acid to avoid unnecessary loss of oxygen in solution in the sulphuric acid.

When the pressure above the system was atmospheric, the test tube containing the specimen immersed in acid was removed and placed in a holder in the constant temperature bath. The
specimen was kept under observation until it could be definitely established whether the specimen was active or passive. If it were active, bubbles of hydrogen were seen soon after exposure to the acid and after about one hour, the solution turned a perceptible green. On the other hand, if the specimen were in the passive state, there were no hydrogen bubbles in evidence and the solution remained clear. Let it be said here, that the transition from active to passive forms was on a go or no-go basis. If the specimen was passive the corrosion rate, over any time period, was substantially nil, while in the active condition, corrosion rates approached several hundred mils per year. There was no gradual transition between them and for this reason there were no corrosion rates recorded as such, only the observation of activity or passivity according to appearance.

3. Active-Passive Transition of Stainless Steel

In the study of the period necessary to induce passivity upon the active surface of stainless steel, the procedure generally followed this pattern. Small rectangular specimens abraded in the manner mentioned before, were "activated" by boiling for three minutes in a 10% sulphuric acid solution. The corrosion products were then rubbed off and the specimen rinsed several times in double distilled water. According to the conditions of the experiment, the specimens were then either rinsed in acetone and dried in air or they were exposed to distilled water whose oxygen content was
accurately known. After the prescribed exposure under these conditions, they were tested for activity or passivity by the methods described in the previous section.

Analysis for oxygen in distilled water was done according to the standard Winkler method, while the oxygen content of the sulphuric acid was determined using a modification of this procedure. The Winkler method and the modification used in this work are common commercial practice.  

V RESULTS AND DISCUSSION

A. The Sorption of Oxygen Upon Stainless Steel at Room Temperature.

During the initial experimental trials, made using stainless steel as a sorbent for oxygen, it became evident that the process was highly time dependent. First, let it be said, that since the word "adsorption" implies a mechanism which may not be true in each case, the author prefers to use the word "sorption" and to denote by this word any take-up of oxygen upon the surface, whatever its mechanism. The time element in the sorption of oxygen upon stainless steel was manifested, as shown in Figure 5, by a very slow attainment of equilibrium. The time for sorption to cease became longer as the pressures were increased until, as shown in Figure 6, the time-sorption curve showed no leveling off in 14-1/3 hours at 15.1 u. This type of behavior made it impossible
to determine an isotherm, which is a plot of pressure versus the equilibrium amount of gas sorbed at that pressure. Attempts to plot isotherms at low pressures, where a leveling off could be observed, yielded a curve such as that in Figure 7. The points show quite a degree of scatter although a fairly suitable curve may be drawn.

B. The Rate of Oxygen Sorption Upon Stainless Steel at Higher Pressures Over Longer Periods.

Many tests were made using a variety of pressures from 1 u, to 300 u. In general they yielded time-sorption curves of the sort shown in Figure 8. As shown there, the low pressure sorption reached equilibrium, while at higher pressures, the time-sorption relationship became nearly linear. As the pressure was further raised, the rapid initial sorption, evident at low pressures, apparently vanished.

This is shown more graphically in Figure 9 in which the differential adsorption at each pressure level was plotted against time. As is seen there the rapid initial rate was more evident upon the first gas addition to the freshly etched sample, than for any subsequent addition. Later work showed this observation to be partly fortuitous and it was found that this type of graph could only be obtained if the pressure increases were relatively small. If, instead, the pressure increase was relatively large
the rapid sorption phenomenon reappeared. This was shown in Figure 10 which indicated a disappearance of rapid sorption in the middle pressure regions, but the phenomenon reappeared at high pressures. Upon more careful examination it is seen that the criterion for whether rapid sorption takes place is not the absolute pressure, but is, instead, the magnitude of the pressure increase when a new oxygen addition is made.

This is more clearly shown in Figure 11 where the differential adsorption rates are plotted. As is seen, curve 3 shows a large amount of rapid sorption because the pressure has been nearly doubled over the prior curve, while curve 5 shows practically no rapid sorption because the pressure was increased only .2 u over that in curve 4.

The character of these curves indicated that a two stage mechanism was in operation. There was first a mechanism whereby oxygen was rapidly taken up on the surface of the stainless steel. It was followed in turn by a slow process, possibly oxidation or chemisorption which could involve a decay of the previously sorbed material. This initial sorption is explainable using the theory of Speiser, et al, who believe that oxygen, because of unbonded electrons in the valance shell possesses some of the properties of a free radical. As such, it may be chemisorbed with only a low activation energy and also with a low energy of formation.
This is in accordance with recent ideas that the sorption of gases such as oxygen upon the plane surface of a metal is a chemisorption process of low activation energy. This idea will be further developed in a later section.

In any case the occurrence of this two stage phenomenon made it impossible to actually find isotherms with values at high pressures. Attempts to do this, using sorption values obtained after long periods, resulted typically in plots such as Figure 12, through whose points it was not possible to draw a curve. The inability to do this made it impossible to find an adsorption isostere and thus no heat of adsorption could be estimated by use of the Clausius-Clapyron equation.

This higher pressure work was completed by exposing a freshly activated specimen to a pressure of oxygen as high as could be measured upon the guage. The results are shown in Figure 13. Exposing the specimen to an oxygen pressure of 307 u resulted in a tremendous increase in the magnitude of the rapid sorption. Approximately $150 \times 10^{-8}$ moles of oxygen were sorbed during the first fifteen minute period and approximately twenty-four hours were necessary for establishment of the linear part of the curve. It would appear then that if it were possible to perform this experiment at the partial pressure of oxygen in the atmosphere that the rapid sorption would be very large and could cover
the surface. The number of moles of oxygen necessary to form a monolayer upon \( \text{SiO}_2 \) is \( 613 \times 10^{-8} \).

C. Effect of Prior Sorption Upon Subsequent Low Pressure Isotherms.

During the period when the high pressure, long-time tests were being made, several attempts were made to test the reversibility of the sorption process. In no case was it found that any material that had once been sorbed could subsequently be reversibly removed. In fact, in many cases where the pressure was cut in half, the sorption kept on at about the same rate as before. It would appear that this is then a highly irreversible process.

To test if the type of structure that is formed when oxygen is sorbed at room temperature, can be completely broken down under high vacuum, a study was made of the effect of prior sorption upon subsequent low pressure isotherms. In doing this, a specimen of active stainless steel was used to determine a low pressure isotherm. It will be remembered that a smooth curve may be drawn if the pressures are kept low. In the process of this sorption about \( 50 \times 10^{-8} \) moles of oxygen were sorbed. The specimen chamber was then re-evacuated for a period of 34 hours after which time another isotherm determination was made. This process was repeated still a third time, with the result as shown in Figure 14.
Apparently the sorbed product is able to reduce the ability of the remainder of the surface to sorb additional oxygen and this product, formed upon the surface, cannot be destroyed, at least not totally, by the exposure to high vacuums for a period of 24 hours. The effect of prior sorption may also be indicated in a curve such as Figure 15. In this particular experiment, an active stainless steel specimen was subjected to a two stage time-sorption treatment. After this time the sorption bulb was reevacuated for 24 hours and then gas was admitted to a pressure of 1.6 u, just above that used in the original run. It is seen, that although the pressure is higher in the second case, the rate of initial adsorption is slower.

If, as in Figure 16, the specimen is subjected to a relatively high pressure, the sorptive power is greatly affected.

Carrying this idea to its logical conclusion, a specimen of active stainless steel was exposed to the atmosphere for a period of 24 hours, after which time it was placed in the evacuated bulb of the sorption apparatus for a period of 2 hours. Oxygen was then admitted to a pressure of 1.6 u, yielding the time sorption curve as shown in Figure 17. Following this, the specimen chamber was reevacuated for 24 hours and when gas was readmitted to the chamber a small but distinct increase in sorption was noted. However both of these curves show the virtual disappearance of the rapid
sorption and a very slow rate of linear sorption. This would seem to indicate that a treatment such as exposure to air remarkably decreases the activity of the stainless steel surface.

D. Adsorption Characteristics of Oxygen Upon Stainless Steel at Low Temperatures.

Studies were made upon the ability of stainless steel to sorb oxygen at low temperatures. At a temperature of -78.6 °C the amount of oxygen sorbed was below the sensitivity of the instruments.

Upon cooling the specimen to -196 °C, however, the characteristics of the sorption process changed. A typical sorption determination at this temperature yielded a graph as shown in Figure 18. There was no time dependent factor in the determination of these points. The equilibrium was attained instantaneously at all pressures, moreover, attempts at desorption yielded the results as shown. Although some hysteresis is evident, the sorption appeared to be practically reversible. This would tend to indicate that the mechanism of sorption is related to a van der Waals type of force. This is to be expected since the temperature of the test is below the condensation point of oxygen. In any case, it may be said that this type of sorption is quite different from that of the form observed at room temperature.
This transition in type of sorption as the temperature is decreased has been noted in many metals. In general they follow the path as shown in the schematic diagram, Figure 19. As the temperature is first lowered, there is a general increase of activated adsorption until at some critical point, it falls to a very low value preceding the onset of van der Waals adsorption. This closely follows the facts as found in this case.

E. Sorption of Oxygen Upon Iron at Room Temperature.

Since iron is a good example of a metal upon which oxygen does not confer any great degree of passivity, a study was made of the general characteristics of oxygen sorption upon "Armco iron" strip. Initial experiments showed that the mechanism by which oxygen attaches to iron is similar to that which occurs in stainless steel. Figure 20 shows the characteristic time-sorption curve for iron as compared with such a curve for stainless steel. Since the pressures are different, no quantitative conclusion may be drawn from the graph. It merely serves to show that the general shape of the time-sorption curves are the same.

In this same study, the iron was subjected to a long-time, higher-pressure sorption experiment. The results were as shown in Figure 21. In general, as is apparent in these curves, iron shows a higher initial sorption than does stain-
less steel. Moreover, the linear type of sorption does not appear so readily. As the sorption progresses in some cases, a rust color can be noted upon the surface of the iron. No color was noted in the case of stainless steel.

F. Sorption of Oxygen Upon Armco Iron at Low Temperatures.

As in the case of stainless steel, iron showed no appreciable sorption of oxygen at a temperature of -78.6 C. At -196 C, the oxygen showed a reversible type of sorption as exemplified by Figure 23. Sorption of this type showed practically the same characteristics as that exhibited in the case of stainless steel.

G. Sorption of Nitrogen and Argon Upon Iron and Stainless Steel.

The sorption properties of stainless steel and "Armco iron" were studied at temperatures of 27, -78.6 and -196 C, using nitrogen and argon. Neither of these gases was measurably sorbed at room temperature. This observed fact is in agreement with the work of many other investigators. Likewise at -78.6 C neither gas was sorbed within the limit of accuracy of the apparatus.

At -196 C, both gases exhibited a reversible type of sorption comparable with that observed for oxygen at this temperature. The characteristic sorption isotherms are
shown in Figure 33 and 34. Although desorption curves are not shown whenever adsorption runs were made they in general were similar to the results obtained using oxygen. That is, the desorption showed only a slight hysteresis. In Figure 23 the typical plots for argon and nitrogen sorption upon stainless steel at -196 °C are shown. The curves are very similar. Figure 24 shows the same gases upon "Armco iron". There is a distinct difference between their magnitude of sorption, which does not seem to have any logical explanation. The effect was reproducible however.

F. Comparison of the Sorption Properties of Iron and Stainless Steel.

As has been pointed out in the foregoing sections, the general manner of sorption of oxygen upon stainless steel and "Armco iron" were similar. They both appear to show the initial rapid sorption followed by a sorption at a much slower rate. The behavior of the materials toward oxygen, nitrogen and argon also appeared to be similar. There were, however, certain differences in behavior which might prove to be the key to the different behaviors in corroding solutions.

One significant observation was the effect of prior sorption upon subsequent low pressure isotherms. As is illustrated in Figure 14 the effect of prior sorption upon
"Armco iron" was substantially different as witness in Figure 25. The experimental work leading to the facts reproduced upon this graph, was similar to that used in the experimental work to derive Figure 14. After one low pressure isotherm had been determined, the system was re-evacuated for a period of 24 hours and another isotherm determination made. This was repeated still a third time. The graph indicated that the sorptive power of the iron was actually increased by prior sorption. It is hard to imagine a basic reason for this, and it is quite possible that the actual increase in sorptive power is caused by the continuous evacuation of contaminants from the surface of the iron. In any case, it can certainly be said that sorbed oxygen had no great affect on the ability of iron to take-up additional oxygen. This fact was substantiated by an experiment in which iron and stainless steel were exposed to air for 24 hours and then were subjected to a low pressure time-sorption study. The results are indicated in Figure 36. As is noted, iron retained its rapid sorption characteristics, while stainless steel had practically none.

I. Vacuum Breakdown of Passivity.

The work of this dissertation was initiated because of the work of Fontana and Beck who found that under high vacua the passive film, present upon stainless steel, is either
removed or is made to lose its protective qualities. As a basis for the present work, certain parts of the work of Beck were reproduced. A verification has made of the fact that passivity could indeed be destroyed under high vacua.

In view of the results obtained in the sorption studies, a check was made to see if the passivity could be destroyed no matter how long the sample was exposed to the atmosphere before subjecting to high vacuum. In the work of Beck, the activated specimens usually remained in contact with air only a matter of minutes before being subjected to vacuum breakdown. In this connection then, a series of samples of activated stainless steel were exposed to air for varying time periods and then were placed in an evacuated chamber to test their susceptibility to vacuum breakdown. The results indicated that after approximately 6 hours of exposure to air, the passivity of the stainless steel could not be broken down under high vacuum. This would indicate that some secondary product not decomposed by vacuum has, after a period of hours, been able to form a protective layer over the sample.

J. Investigation of the Active-Passive Transition Point for Stainless Steel.

The pressure factor seemed to be the controlling point in the rapid sorption phenomenon. Therefore, it was reasoned that a reduction of oxygen pressure above an active stainless
steel specimen could delay the onset of passivity. Accordingly, several bottles of distilled water were treated in such a manner that each contained a different amount of oxygen in solution. The oxygen contents varied from 35 to 0.8 parts per million. A series of stainless steel specimens were activated in boiling 10% sulphuric acid and rinsed in distilled water as their corrosion products were wiped off. The specimens were then immersed in one of the vials and at intervals, the specimens were checked to ascertain if the transition to the passive state had occurred. The results are shown in Figure 37. As is indicated there, the time for passivation is sharply dependent upon the oxygen partial pressure in the distilled water. It might be mentioned here that at any time if the specimens became dry while exposed to air they would become instantaneously passive.

In the distilled water containing only 0.8 part per million of oxygen, nearly six hours was necessary for the specimen to become passive. In cases where every precaution was taken to avoid oxygen in the water, there were none where passivity failed to set in at all. This might be said to be in agreement with the work of Gulbransen who noted that even at pressures of $10^{-6}$ mm. of mercury, oxygen was still sorbed upon the surface of stainless steel.
K. General Discussion of Results as Applied to the Sorption of Oxygen Upon Iron and Stainless Steel.

The sum total of the results as discussed in this section has led this author to believe that a two stage phenomenon is the only means by which all of the data may be explained. This is not a new idea in gas-metal equilibria, since it has been proposed for several other systems, namely hydrogen on tungsten and oxygen upon tungsten.

The two steps might be visualized in a manner such as this. As oxygen approaches the surface of stainless steel or iron, it is first sorbed as the complete molecule. This follows the idea of Speiser, et al, who visualized the surface of a metal as having a "residual valence". This is a result of the existence of "surface states" as defined by quantum mechanical relationships. Molecules such as \( \text{N}_2 \) and \( \text{CO}_2 \) are polarized by the surface and are attracted by so called "van der Waals" forces. This type of attraction has no activation energy and a small heat of reaction.

On the other hand, gases with unpaired electrons in the valence shell, such as oxygen, may react in a somewhat different manner. A gas of this type may be considered to act somewhat as a free radical and as such it possesses residual valences. The interaction of this type of molecule with the surface of a metal will be stronger than would be the case with a saturated
molecule. The sorption would then probably involve a small activation energy and have a somewhat higher heat of reaction than in the case of physical adsorption. This type of adsorption, according to Speiser, would be more prevalent in transition metals because of the contribution of the partially filled "d" shells to the surface states. It will be noticed that this type of sorption does not involve the breaking of the bonds in the $S_2$ and it is supposed that the oxygen exists upon the surface of the metal as the whole molecule.

It would appear then, that this complex might break down to form an atomically sorbed product. Since this decay would involve the breaking of the oxygen bond, it would involve a large activation energy which would dictate a slow rate of reaction. This second step might even be termed an oxidation. Certainly no result in this thesis could disprove this view.

As support of this idea, this author considers the work upon vacuum-breakdown of passive films as carried out by Beck and supplemented by the present work to be very indicative. It has been pointed out by Taylor that chemisorbed systems may be broken down under the influence of high vacuums. It is then quite possible that the molecular chemisorption mentioned in this discussion could be, at least partially destroyed by such a treatment. It is quite doubtful, however,
if the secondary sorption product would be susceptible to such breakdown. Reasoning in this manner, it is seen that after a certain time passivity can no longer be destroyed by vacuum. This would result when enough time had elapsed to allow the secondary sorption product to completely cover the metal surface.

An interesting verification of this mechanism can be derived from the work of Berwick and Evans. According to their investigation, a stainless steel specimen which was actively corroding in a sulphuric acid solution could be made to "passivate" immediately by bubbling oxygen over the surface. This passivation could be destroyed by subsequently bubbling argon over the specimen. The period of the argon treatment necessary to initiate activity was dependent upon the length of time that oxygen was fed in, in the initial passivation. If, however, the oxygen treatment was continued longer than a certain critical time, no period of argon treatment could restore activity. The experimenters explained this on the theory of an oxide film which does not appear to take in all of the facts.

An explanation of these data is easily made by use of the hypothesis presented in this thesis. When oxygen is initially bubbled over the active specimen, rapid molecular
sorption takes place, inducing passivity very quickly. When argon is, in turn, bubbled over the surface, the oxygen gradient in an argon bubble impinging upon the surface is very high and the complex may be decomposed. The time of decomposition would be dependent upon the amount of complex formed, which accounts for the time interval which Berwick and Evans observed. In this concept of the mechanism, the molecular film is contently degenerating into the atomic film or oxide. Thus there would come some time when this more stable film would entirely cover the surface and no amount of argon treatment could then destroy passivity.

Hackerman and Antes in studying the contact potentials of iron in air, found that as oxygen was admitted to an evacuated system containing iron that the contact potential, which is a function of sorbed films upon the surface, rose rapidly at first and then, after a period, more slowly. If at any time, the pressure was lowered by a considerable amount, the contact potential lowered somewhat indicating some desorption. If then, oxygen was admitted back to the original pressure, sorption would again proceed. And if again, the pressure were lowered, the same amount as previously, a certain desorption would take place but the amount of desorption would not be down to the level of that which was observed on the first trial. This would
indicate that at any given time a duplex film is present, part of which is subject to decomposition under vacuum, while the other is not. Let it be emphasized here that this author does not differentiate between the mechanism of oxygen sorption upon iron and upon stainless steel. It has been shown, however, that certain discernible differences exist. The sorption of oxygen upon the surface of iron does not appear to reduce the sorption ability of the surface as it does with stainless steel. It might possibly be that the molecularly sorbed oxygen upon the surface of iron is so rapidly broken down into iron oxide that it cannot form a protective film, while the oxide is not protective because of its physical characteristics. Gulbransen has shown that while the sorbed oxygen film upon iron may be reduced quantitatively by hydrogen at 600°C, the film formed upon stainless steel is not subject to such reduction.

VI RECOMMENDATIONS FOR FUTURE WORK

A review of the results of this investigation would indicate that pursuit of the following lines of investigation might be profitable.

A. Establishment of the heat of reaction of the two stage mechanism should be carried out. This is a complex problem since, if the proposed mechanism is true, the processes are going on simultaneously and a differentiation
of heat values would be involved.

B. The determination of the difference in the sorption processes occurring upon iron and stainless steel would pinpoint the reason for the formation of a protective film in one case and a non-protective barrier in the other.

C. A fruitful line of investigation would include the expansion of this type of study to other stainless steels. This might include the effect of molybdenum in the alloy upon its sorption characteristics.

D. The formation of the films upon stainless steel and iron under oxygen atmospheres has given a basic idea of the mechanism involved. However, a study should be made of the mode of formation of these films under electrochemical cell conditions, to find if they are similar.
VIII. LITERATURE CITED


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85. T. Rhodine, Unpublished Data.


Figure 1. Equipment for Determination of the Adsorption Characteristics of Metals

Photograph by the Department of Photography, Ohio State University
Adsorption Apparatus - Schematic Diagram

Figure 2
Figure 3. Equipment for the Destruction of Passivity under High Vacuum

Photograph by the Department of Photography, Ohio State University
Schematic Diagram of Vacuum Breakdown Apparatus

Figure 4
Typical Low Pressure Time-Sorption Curve

Figure 5
Typical High Pressure Time-Sorption Curve

Figure 6
Figure 1
Adsorption Isotherm - Oxygen on Type 304 Stainless Steel at 300°C

Pressure in millimeters of Hg

Amount Adsorbed in oxygen moles x 10^8

Area - 0.923 sq.in.
Stainless Steel Strips
Sorbent - Type 304

Time-Sorption Plot for an Extended Period

Figure 8
Figure 9

Time-Sorption Curves Showing Effect of Increasing Pressure on Sorption Rate.
Time-Sorption Plot for an Extended Period

Figure 10
Differential Sorption Curves Showing the Effect of Successive Increases in Pressure on the Rate of Sorption.

Figure 11
Figure 12

Plot of Pressure vs. Equilibrium Sorption Values

Sorbate - O₂
Sorbent - Type 304 Stainless Steel strips
Area - 0.483 m²

Moles O₂ Sorbed x 100
Figure 13

Time-Sorption Curve Showing Sorption on Freshly Etched Specimen at High-Pressure

Sorbate - O₂
Sorbent - Type 304 Stainless Steel strips
Area - 0.423 meters²

Time - Hours

Moles O₂ Sorbed X 10^8

Introduced O₂ to pressure 0.202 0.50 0.80 1.02 0.50 0.02 0.24 0.60 1.02 0.50 0.02
Low Pressure Isotherms Showing Reduction in Sorptive Power of Surface due to Successive Sorption and Desorption

Figure 14
© Sorption made on freshly etched specimen

② Sorption made on same specimen as ① after reevacuation

Introduced O₂ to pressure of 1.7 μ

Introduced O₂ to pressure of 1.8 μ

Sorbent - Type 304 Stainless Steel Strips
Area - 0.423 meters²

Time Sorption Curve Showing Effect of Prior Low Pressure Sorption on Subsequent Sorption

Figure 15
Oxygen Sorption on Type 304 Stainless Steel after Prior Exposure to Oxygen at 400 \mu Pressure

Figure 16
Time Sorption Curves Illustrating Effect of Exposure to Air on Low Pressure Sorption Properties of Stainless Steel.

Figure 17
Characteristic Isotherm for Oxygen on Stainless Steel at -196°C

Sorbate O$_2$
Sorbent Type 304
Stainless Steel Strips
Area - 0.423 meters$^2$

Figure 18
Schematic Diagram of Transition from Van der Walls Sorption to Activated Adsorption
Comparison of Time-Sorption Characteristic of Type 304 Stainless Steel and Armco Iron.

Figure 20
Moles Sorbed $\times 10^6$

Oxygen introduced to a Pressure of 10.5$\mu$

Oxygen introduced to a Pressure of 11.4$\mu$

Oxygen introduced to a Pressure of 11.2$\mu$

Oxygen introduced to a Pressure of 9.9$\mu$

Figure 21

Typical Time-Sorption Plot for Oxygen on Armco Iron
Sorption Isotherm for Oxygen upon Armco Iron at -196°C

Figure 22

Sorbent - Armco Iron Strip
Area - 0.423 m²
Sorbate - O₂
Figure 23

Sorption Isotherm upon Stainless Steel at -196°C

Sorbent - Type 304 Stainless Steel
Area - 0.423 m²

- ○ Argon
- ● Nitrogen
Sorption Isotherms upon Armco Iron at -196°C

- **Sorbent**: Type 304 Stainless Steel
- **Area**: 0.423 m²
- **Temp**: -196°C

- **Argon**
- **Nitrogen**

**Figure 24**
Low Pressure Isotherms Indicating Effect of Successive Sorption and Desorption on the Sorptive Power

Figure 25
Both specimens exposed to air for 24 hours and pumped on for 24 hours.

O₂ introduced to a pressure of 1.75 μ

O₂ introduced to a pressure of 1.59 μ

Time-Sorption Curves Comparing Effect of Exposure to Air on Low Pressure Sorption Properties Between Armco Iron and Stainless Steel.

Figure 26
Oxygen Content in parts per million

Time in Minutes

Time in Hours

Time for Passivation of Type 304 Stainless Steel in Distilled Water of Various Levels of Oxygen Content

Figure 27
APPENDIX II

SAMPLE CALCULATION
SAMPLE CALCULATION OF A SORPTION ISOTHERM

1. From calibration determination:

Measuring volume — — — — — — — — 758 cm³
Total volume — — — — — — — — — 2150 cm³
Temperature — — — — — — — — — 27 °C

2. Gas admitted to measuring volume and pressure reading made.

\[ P_1 = 11.9 \text{ u} \]

\[ n = \frac{PV}{RT} = \frac{11.9 \times 10^{-3} \times 758}{760} \times \frac{1}{1000} \times \frac{1}{0.083} \times \frac{1}{300} \]

48.3 \times 10^{-8} \text{ moles}

3. Gas expanded by lowering cutoff #2 and pressure reading made.

\[ P_2 = 3.54 \text{ u} \]

\[ n = \frac{PV}{RT} = \frac{3.54 \times 10^{-3} \times 2150}{760} \times \frac{1}{1000} \times \frac{1}{0.083} \times \frac{1}{300} \]

Amount sorbed \[ 48.3 \times 10^{-8} - 42.7 \times 10^{-8} \]

\[ 5.5 \times 10^{-8} \]

These sample calculations are typical of those performed for each point on a sorption curve.
AUTobiography

I, Roy Johnson, was born in Sioux Falls, South Dakota, June 5, 1926. I received my secondary school education in the public schools of that city. From 1944 to 1946, I spent two years in the United States Navy. I received my undergraduate training at the South Dakota School of Mines. I received the degree of Bachelor of Science in Metallurgy from the South Dakota School of Mines in 1949 and the degree of Master of Science in Metallurgy from the University of Utah in 1950. From 1950 until 1952, I spent in industrial research work with the Union Carbide and Carbon Corporation and Battelle Memorial Institute. In 1952, I was awarded the DuPont Fellowship in Metallurgy at The Ohio State University. I held this award for two years while completing the requirements for the degree of Doctor of Philosophy.