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The effect of allotropic changes in iron and cobalt on their initial reaction with oxygen

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Abstract

Isothermal kinetic studies of the initial oxidation of pure iron and cobalt have been made, using the volumetric and the manometric methods respectively. Results have been obtained for iron at two different pressures of oxygen, \( p_{O_2} = 7.6 \) and \( 29 \) cm. Hg. absolute), with the oxide-thickness ranging between 10 and 70\( \mu \)m for the period during which the studies have been made. The oxidation of both body centred - and face centred - cubic iron at \( p_{O_2} = 7.6 \) cm. and body centred-cubic iron at \( p_{O_2} = 29 \) cm. follows a modified parabolic rate law. A true parabolic rate law applies only to the oxidation of face centred - cubic iron at \( p_{O_2} = 29 \) cm. The rate of oxidation of iron, however, decreases with increasing \( p_{O_2} \) - values, though in the case of cobalt the rate is independent of \( p_{O_2} \) values. A direct-logarithmic rate law is obeyed in the oxidation of both hexagonal close-packed and face centred-cubic structure of cobalt and the oxide-thickness varies from 400 to 5000 \( \AA \).

The Arrhenius plots show, in all cases, an anomaly at the transformation temperature (namely, \( \sim 911^\circ \text{C} \) and \( 386^\circ \text{C} \) for the oxidation of iron and cobalt respectively). Such an anomaly is believed to be due to the effect of phase-boundary reactions on the oxidation kinetics. In the case of iron, it has been shown from the concept of vacancy distribution that, for a modified parabolic rate law, of the two phase-boundary reactions that at the metal/oxide interface is rate
controlling in face centred-cubic whilst in body centred cubic iron it is the oxide/gas interfacial reaction. In the case of cobalt, the mechanism of oxidation has been proposed to be controlled by the combined processes of electron emission at the metal/oxide interface and its availability at the oxide/gas interface.
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INTRODUCTION
Section 1. Introduction

Interest in the study of the oxidation reactions of metallic materials in gaseous media has grown considerably during the last decade. This is partly due to the significant increase in the range and availability of suitable instrumental techniques, and also to a better understanding of the physics and chemistry of the solid state.

Fifty years ago the metal industry started to become concerned with the problems of poor dry corrosion resistance of metallic materials. Neither complete thermodynamic data on the oxidation reactions at various temperatures nor the necessary kinetic data, or even useful working hypotheses were available to serve as a basis for a programme to develop scaling-resistant materials. In view of the scarcity of data at that time, it is not surprising that earlier experiments were carried out to solve these problems in a purely empirical manner; such methods are inadequate to solve the new problems constantly being imposed by the younger industries. This state of affairs presents a challenge both to research workers and to engineers to reassess the scientific origins of the current interpretation of the oxidation mechanism, so that such reactions may be controlled and the difficulties as far as possible surmounted.
The primary factor that affects the oxidation process is the structure of the metallic substrate which undergoes oxidation. Other factors will be the temperature of oxidation, oxidising atmosphere, the thickness and type of oxide formed, etc. A study of the effect of metallic structure on the oxidation process can be considered to provide information for a better understanding of the oxidation behaviour of metallic materials. In case of an alloy system, because of the presence of more than one metal, the effect of the crystal structure of the individual constituents on the oxidation process will not become as evident as it would have been if the oxidation of pure metal is studied. In the present case, investigations on the oxidation behaviour of pure metals such as iron and cobalt have been carried out in the range of their respective allotropie transformation temperatures. Allotropie transformations involve a change in the crystal structure of the metal, and thus while using the same metal, the structural dependence of the oxidation process can be studied. However such a study can only be made if the oxide formed is not too thick, otherwise diffusion across the oxide is the rate-controlling reaction, which means the oxide structure rather than the metal influences the kinetics of subsequent oxidation. Thus a study on the kinetics of the initial oxidation of metal, so as to form thin films, can be considered useful for the understanding of the effect of crystal structure on oxidation processes, because in such cases the oxidation kinetics may be controlled by the metal/oxide
interface and hence would be directly influenced by the crystal structure of the metal substrate. Hence in the present work a study has been made on the kinetics of the initial oxidation of pure metals, such as iron and cobalt, which have well defined crystallographic transformations. Also not much work has been carried out in the past to study the initial oxidation of these metals in the region of their respective crystallographic transformation temperatures. Before dealing with the relevant literature reviews for these metals, it will be worthwhile to first discuss the oxidation processes in general.

2. General Introduction to Oxidation Processes

2.1. Thermodynamics of Oxidation

The reaction between a solid metal and oxygen may be represented simply as,

Metal + Oxygen = Metal Oxide \( (1) \)

The possibility of the reaction occurring can be predicted from knowledge of the thermodynamic stability of the metallic oxide. If the activity of the components involved in the reaction be expressed in terms of pressure, then from van't Hoff's reaction isotherm it is known that for a non-equilibrium condition,

\[
-\Delta G = -\Delta G^0 + RT \log \left[ \frac{P_{O2}}{(P_{O2})_{Eq}} \right]
\]  

where \( \Delta G \) = change in the free-energy of formation of the oxide from its elements,

\( \Delta G^0 \) = the standard free-energy of formation of the oxide and is related to the equilibrium constant \( K_{Eq} \) and
temperature $T$, as

$$\Delta G^\circ = -RT \log_e K_{eq} \quad -(3)$$

$p'_o$ = the partial pressure of oxygen in gaseous phase
and $(p_{o2})_{eq}$ = the equilibrium pressure of oxygen during
dissociation i.e. the decomposition pressure of the oxide.

If $\Delta G$ is positive for a given chemical reaction, then the
reaction does not occur; if $\Delta G$ is negative, the reaction
proceeds to the right hand side of the equation (1). This
statement is equivalent to saying that, since $(p_{o2})_{eq}$
is constant
at a given temperature, the metal will be oxidised when
$p'_o > (p_{o2})_{eq}$ and, conversely, the oxide will dissociate
when $p'_o < (p_{o2})_{eq}$.

An oxide in equilibrium with its metal at constant activity
has a fixed decomposition pressure $(p_{o2})_{eq}$, which can be
calculated at any temperature from the eqn. (3), which can
be rewritten as $\Delta G^\circ = -RT \log_e \frac{1}{(p_{o2})_{eq}^{eq}}$, assuming
activity of solid as unity and substituting $\frac{1}{(p_{o2})_{eq}^{eq}}$ for $K_{eq}$.

By using fig. 1, as has been described by Gleiser (1),
Ellingham (2) and Richardson et al. (3), one can obtain the
relationship between $\Delta G^\circ$, $T$ and $p_{o2}$ – values. Figure 1
shows that the change in the free energy of the oxide-formation
Fig. 1

Oxygen potentials in oxide systems
is negative. This means that the process of interaction with oxygen are spontaneous at these temperatures and pressures. Thus most metals (with the exception of the noble metals) are thermodynamically unstable in an oxygen atmosphere and are transformed into oxides. The lower the $p_{O_2}$ equilibrium values, the lower the $p_{O_2}$ values at which the metal can be oxidised. The differences in the dissociation pressures of oxides of different metals are due to the differences in the strength of the bonds between the oxygen and the metal atoms.

As regards the entropy of formation $\Delta S^0$ (the difference between the entropy of solid products and the reactants) of the reaction (1), this must always be negative since the disorder, and hence the entropy of a gas, is much greater than that of a solid or liquid. Since $\Delta G^0$ is related to $\Delta S^0$ and the heat of formation $\Delta H^0$ by equation:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

and since $\Delta H^0$ may be taken as being approximately independent of temperature for reaction (1), $\Delta G^0$ will increase with rising temperature (fig.1.).

In the case where the product is a gaseous oxide, the entropy of the product is also large. If the number of gaseous molecules of the product exceed those of the reactant gases then $\Delta S^0$ becomes positive. This leads to decreasing values of $\Delta G^0$ with rising temperatures, so that the formation
of gaseous oxide is favoured. Such gaseous oxides therefore become increasingly predominant and hence more important at higher temperatures.

Available thermodynamic data thus serves as the basis for a working hypothesis, in terms of a classical model. However, since the kinetics remained rather vague owing to the ignorance of the true reaction mechanism, clearly the working hypotheses could not possibly explain the true state of affairs. This becomes obvious when practical cases of oxidation are considered.

2.2. Oxidation in practice

Experiments show that the mechanism of oxidation may be rather complex when, as happens in many cases, the reaction product appears as a compact phase with the reacting substances spatially separated from each other. In such cases adhesion between the oxide and the underlying metal will entirely depend on the crystal structures of the product and the metal. When a compact oxide layer is formed, further reaction is then possible only if at least one of the reactants diffuses through the layer of oxide to the other reaction partner. In such cases, the course of the reaction is no longer determined by the overall chemical process described by equation (1), but by diffusion processes and phase boundary reactions, for which the mechanism, as will be
described in some detail later, can be quite complex. Generally, the following partial processes are considered while studying the oxidation reaction. Of these processes the one, which is the slowest, would therefore be the rate determining step:

1) Phase boundary reactions, nucleation and crystal growth. Phase boundary reactions involve the following possibilities,

(a) Chemisorption of the non-metal molecules with simultaneous electron exchange

(b) Splitting of the molecules at the gas/oxide interface

(c) Transfer of the metal from the metallic phase in the form of ions and electrons, to the oxide at the metal/oxide interface with further reaction of the individual reactants and formation of the reaction products.

2) Diffusion or transport of cations, anions and electrons through the scale complicated by a special migration mechanism because of the appearance of chemical and electrical potential gradients in the thin or thick oxide layer.

3) Predominant transport processes in space-charge boundary layers in the case of thin oxide film.

The distinction between thin films and thick oxide scales is of necessity arbitrary. It is not, however, completely without basis since the processes governing the kinetics are
not the same in the two cases. Thin films are here defined as having a thickness of the order of 1000Å.

During the 1930's, various independent attempts were made to formulate, in terms of the then new concepts of the physics of solids, a general coherent theory of the oxidation of metals. Two of these commanded a very large following - the Cabrera-Mott theory and the Wagner theory. The first sought to explain the formation of thin oxide films on the surface of metals at moderate temperatures in terms of the effect of an electric field caused by the absorption of oxygen atoms at the outside of the oxide layer. The second, valid for rather higher temperatures, accounted for the growth of thick oxide layers by the thermal diffusion of metal ions in association with lattice defects. These two concepts, which are in themselves not incompatible, since they apply to different stages of the process and to different physical conditions, have formed the basis of a whole series of developments and continue to inspire some of the current work. Without questioning the truth of the fundamental physical mechanisms, it must be recognised that they have proved inadequate to account for all the factors operative in the control of the kinetics of oxidation reactions. On bases of qualitative considerations, it is not surprising that rate laws observed in the oxidation of metallic materials may take various forms.
To ascertain the rate law and hence the mechanism of oxidation reactions involving diffusion in oxides, the first essential requirement is a knowledge of the oxide structure in association with its lattice defects. Such information can be obtained from the electrical properties of the oxides.

2.3. Lattice defect phenomena in Ionic crystals

2.3.1. Inside the bulk crystal

Chemists have known for a long time that many inorganic chemical compounds e.g. the oxides, sulphides and nitrides do not have a stoichiometric composition, but may exhibit a considerable excess or deficit of one or another of the constituent components of the crystal. But in purely ionic compounds e.g. the alkali and silver halides, the composition must be stoichiometric, since the numbers of cations and anions must be in a simple ratio, otherwise the crystal would not be electrically neutral. However, even these compounds have been found to exhibit considerable disorder in their lattice site occupation, as will be shown later. It can be said, in general, these lattice building blocks (atoms and ions) leave their lattice sites with increasing frequency as the temperature increases and go either to an interstitial lattice site or, if this is not possible for spatial energetic reasons, break out to the surface. Thus there is left behind an unoccupied lattice site, which can be occupied, in turn, by particles lying deeper in the interior. Thus, the unoccupied lattice site (vacancy) moves
toward the interior, while the ions migrate to the surface. A condition of equilibrium is obtained when the particle and vacancy currents, which are in opposite directions, are of equal magnitude.

An ionic defect in stoichiometric ionic crystals may appear in such a manner as to affect predominantly only the cation or anion sublattice, or it may affect both the anion and cation sublattices to the same extent. Schottky (4) has distinguished four types of lattice defects in stoichiometric crystals:

Type I: Cations in interstitial lattice sites and vacancies in the cation sublattice (Frenkel type - fig.2) (vacant sites indicated by squares)

Type II: Anions in interstitial lattice sites and vacancies in the anion sublattice (anti-Frenkel type)

Type III: Cations and anions in interstitial lattice sites (anti-Schottky type)

Type IV: Vacancies in cation and anion sublattice sites (Schottky type - fig.3) (Vacant sites indicated by squares)

Thus a Frenkel defect essentially consists of an interstitial ion together with a vacancy, while a Schottky defect consists of anion and cation vacancies present in equal numbers.
In principle, all types of lattice defects can occur in a stoichiometric crystal, but a single type is usually preferred or predominant. Investigations have also shown that lattice defects corresponding to types I and IV are energetically preferred. Frenkel defects are predominant in the silver halides. The cations can perform movements either by shifting into the vacant sites or by drifting along the interstitial spaces. This model is supported by measurements of transference numbers. The transference numbers of the cations $t_c$ and anion $t_a$ are defined by the quotients

$$t_c = \frac{l_c}{l_c + l_a}, \quad t_a = \frac{l_a}{l_c + l_a}$$

where $l_a$ and $l_c$ represent the portions of the conductivity or the respective mobilities of the anion and cation. On the other hand, simultaneous migration of anions and cations giving rise to Schottky defects are found in alkali halides.
In contrast to the above mentioned stoichiometric ionic crystals, most of the oxides are non-stoichiometric ionic crystals. Such compounds are also not purely ionic compounds, most of them exhibit electronic as well as ionic conductivity and are generally defined as semi-conductors. A further factor, the portion of the conductivity that is electronic $I_e$ must be taken into account for the evaluation of transference numbers:

$$\begin{align*}
t_a &= \frac{l_a}{l_a + l_c + l_e} \\
t_c &= \frac{l_c}{l_c + l_a + l_e} \\
t_e &= \frac{l_e}{l_e + l_c + l_a}
\end{align*}$$

In general, these semi-conducting compounds can be divided into three groups:

1. $i$-type or intrinsic semi-conductors, or metal deficit
2. $p$-type or electron deficit, or metal deficit semi-conductors in which the current is carried by electron holes,
3. $n$-type or electron-excess, or metal excess, semiconductors in which the current is carried by electrons.

Thus an ionic crystal of non-stoichiometric composition in thermal equilibrium with oxygen always contains a certain number of vacant sites. If the number of vacant sites in which negative ions are missing exceeds the number of vacant sites in which positive ions are missing, the crystal contains an excess of metal. For electrical neutrality of an ionic crystal to be preserved...
it is necessary that the lattice sites in which negative ions are missing contain an extra electron. In a similar manner, a crystal may contain an excess of the electrically negative component if it has vacant sites in the cation sublattice and if one of the negative ions adjacent to these sites lack an electron. For example, \( \text{Cu}_2\text{O} \) contains somewhat more oxygen than copper, therefore is a metal-deficit p-type semiconductor. Whereas in \( \text{ZnO} \) there is usually an excess of metal and hence is an n-type semiconductor. Statistical thermodynamic study of equilibrium accounting for defects such as present in e.g. non-stoichiometric \( \text{Fe}_x\text{O} \), has been made by Chufarov et al. (5).

Nowadays p-type and n-type semiconductors are of interest in problems of metal oxidation, because only for these cases does one know the ionic as well as the electronic defect characteristics, and knowledge of both is requisite for treatment of the diffusion and transport phenomena in thin and thick oxide layer formation.

Wagner and co-workers (6) have developed the basic principles of ionic crystals possessing deviations from the ideal, integral, stoichiometric composition. In solids like \( \text{Cu}_2\text{O} \) there are cation vacancies \( \text{Cu}^2_\square \) and electron holes\( \Theta \). From the electro-neutrality view point, therefore an electron hole is represented by a \( \text{Cu}^{+2} \) ion (fig.4). In the presence
of oxygen, cuprous ions diffuse from the interior to the surface, there combining with chemisorbed oxygen which, on account of its electron affinity, has captured electrons, forming more \( \text{Cu}_2\text{O} \) molecules at the surface. It is, therefore, evident that the number of \( \text{Cu}^+ \) vacancies and electron holes increases with increasing oxygen pressure. Under these assumptions one can write

\[
\frac{1}{2} \text{O}_2 \text{(gas)} \rightleftharpoons \text{Cu}_2\text{O} + 2 \text{Cu}^{+} + 2\text{e}^-
\]

Oxides of Iron (FeO) and Cobalt (CoO and Co\(_3\)O\(_4\)) which are of chief interest here, are p-type semi-conductors i.e. metal-deficit type.

Solids containing an excess of metal are in distinct contrast to the above group of oxides. A representative of this group is zinc oxide (ZnO). An excess of metal may
Lattice defects in zinc oxide, be present in the form of zinc ions in interstitial positions and an equivalent number of quasi-free electrons (-) as shown in fig (5).

Summarising the various mechanisms of conductivity and their characteristics, the following classification is obtained with regard to the semi-conductors.

1. p-type semi-conductors
   1a. Metal-deficit: Excess of anion = cation vacancies + electron holes,
       Transference numbers: \( t_c \ll 1, \ t_a \text{ nil} \).
       Example, \( \text{Cu}_2\text{O}, \ \text{CoO}, \ \text{Fe}_2\text{O}, \ \text{Co}_3\text{O}_4 \) etc.

   1b. Anion-excess: Excess of anion = interstitial anions + electron holes,
       Transference numbers: \( t_c \text{ nil}, \ t_a \ll 1 \). Example, unknown (reason is probably because of large anion size, it may not fit into the interstitial site).

2. n-type semi-conductors
   2a. Metal excess: Excess of cation = interstitial cations + electrons,
       Transference numbers: \( t_c \ll 1, \ t_a \text{ nil} \). Example, \( \text{Zn}_2\text{O} \).
2b. **Anion deficit**: Excess of cation = anion vacancies + electrons.

Transference number: \( t_c \) nil, \( t_a \ll 1 \), Example, \( \text{ZrO}_2 \).

3. **Intrinsic semi-conductors**

Equivalent concentrations of holes and electrons.

Transference numbers of ions very small. Example, \( \text{CuO} \).

**2.3.2. Sub-Surface Defects in non-stoichiometric ionic crystals**

The above treatment of lattice defect phenomena in non-stoichiometric ionic crystals is based on the assumption that the ion lattice (i.e., ion-vacancies) and the free electrons and holes appearing in the whole crystal are uniformly distributed and are in thermodynamic equilibrium with the surrounding gas atmosphere. However, at lower temperature, migration rate of vacancies and electrons, electron holes is not high enough to attain the equilibrium in the entire crystal in a finite time. As a consequence, complicated phenomena appear. A large change in the electron and hole concentrations occurs because of a preferred chemisorption of the oxygen on the oxide surface. Thus the large electron affinity of the chemisorbed gas e.g. oxygen here, makes it possible to withdraw electrons from the oxide with a simultaneous formation of ions (e.g. \( \text{O}^- \)). While the concentration of free electrons \( n_\theta \) in an n-type conducting oxide is reduced in this way relative to the concentrations of interstitial cations \( (n_0) \), so that

\[ n_\theta < n_0 \]
additional holes are created in a p-type conducting oxide by chemisorption, which results in

\[ n_\Theta > n_\Theta' \]

The excess charges in either case become localised either in the chemisorption layer where they form a plane-phase or they group as a space-charge in the region close to the surface of the semi-conductor, the space-charge boundary layer. The depth of such a layer is a few hundred Å approximately, depending on the conditions of temperature and gas pressure. In the neutral bulk of the semi-conductor this inequality in the concentration of charges obviously disappears, fig. (6).

As shown in the figure, the positive space charge is compensated by the negative surface charge of the chemisorbed oxygen. A space charge layer can also be built up on the other side of the oxide i.e. at the metal/oxide interface. Volta potential measurements on the initial oxidation of copper and zinc by Uhlig (7) have confirmed the presence of a space charge extending several thousand angstroms into the
oxide. When a metal is first oxidised, because of the rapid escape of positive metal ions, an initial positive space charge is formed. As the oxide grows, a decrease of positive space charge occurs because a portion of the electrons escaping into the oxide become trapped at oxide lattice imperfections. Eventually, the oxide may acquire an overall negative charge, depending on the final equilibrium state of electric charge. A schematic representation of the concentration of metal ion vacancies \( n_0^- \) and electron holes \( n_0^+ \) in the oxide layer e.g. a p-type is taken, is shown in fig. (7). While a positive or negative space charge layer appears in the boundary layers, the bulk is however electrically neutral. The gradient across the oxide indicates that oxidation proceeds through the movement of holes and cation vacancies from the oxide/gas interface to the metal/oxide interface, which is the actual case for p-type of oxide. To discuss the mechanism of
oxidation it is worthwhile to mention first the laws which
govern the mechanism.

2.4. Oxidation Laws

Methods of investigating the growth of oxidation layers include
determination of the changes in thickness of the oxide, in weight (strictly, mass) of the metal sample, or in volume of the surrounding gas. Quantitative data has mostly been obtained as changes in weight (ΔW) per unit surface area. Reaction Kinetics are concerned primarily with a progress of a reaction with time; thus the first task is to find a relationship between oxidation and time. In fact, a number of relationships have been suggested. In most oxidation processes, however, any given rate law lasts for only a limited time. At the end of that time, the reaction rate ceases to be described by this rate law and either is immediately describable by another or passes through a transition period before another rate law is established. Sometimes this transition is not associated with a change in mechanism, for the overall rate of a process consisting of a number of consecutive steps is determined by the rate of the slowest step. If the hitherto slowest step eventually becomes more rapid than another or becomes equal to another process in the chain, this latter step alone or in
conjunction with the former step (as the case may be) will now control the overall rate. However, whatever may be the situation, all the laws of oxidation that have been observed empirically can be classified into three general groups. The following classification expresses the laws in terms of weight increases, $W$, and time, $t$.

1) Exponential laws:
   a) inverse logarithmic type, $(i/W) = A_1 - K_1 \log_e t$
   b) direct logarithmic type, $W = K_2 \cdot \log_e \left( \frac{t}{T} + 1 \right)$
   c) asymptotic type, $W = K^*_3 \left\{ 1 - \exp. (-K^*_4 \cdot t) \right\}$
   
   where $K^*_1, K^*_2, K^*_3, K^*_4, T$ and $A_1$ are constants

2) Empirical power laws:
   
   $$(W)^n = K_5 t + C$$
   
   where $n, K_5$ and $C$ are constants.
   
   Linear, parabolic, cubic, etc. laws are obtained by putting $n = 1, 2, 3$ etc. respectively.

3) Modified parabolic law:

   $$(W^2/K_6) + (W/K_7) = t$$
   
   where $K_6$ and $K_7$ are constants

2.5.1 Mechanism of Oxidation

2.5.1. Introduction

An understanding of the oxidation behaviour of metals (and alloys) involves an assessment of the relevant mechanisms; an appreciation of these enables the effects of working conditions (and alloying elements) to be predicted.
Oxide layers, thin or thick, formed on metals during oxidation are generally compact, adherent and pore-free. This is also observed if the reaction product layers have a smaller molar volume than the atomic volume of the metallic phase, contrary to the rule of Pilling and Bedworth (8) which states that compact surface layers can only be expected if the ratio of molar volumes of the surface layer and the metal is greater than one. Detailed examination indicates that the volume quotient does indeed play a role in the case of surface layers with greater thickness but not a decisive one. Schottky (9) was able to show recently that the essential prerequisite for the formation of a compact, adherent surface layer is the readiness of both the metal and the oxide to undergo plastic flow and perhaps some elastic deformability of the lattice. The mechanisms of oxidation for thin film and thick scales will be discussed in the following two sections.

2.5.2. Thin Films

The first stage of a reaction between a metal surface and a gas is the formation of a chemisorbed monolayer at the surface. Chemisorption rates are very fast — much too fast to be studied at room temperature and high pressure of the gas. It may be mentioned, however, that measurements at very low temperatures have shown that chemisorption rates are
logarithmic and this fact has induced Landsberg (10) to
assume that the rate controlling step in logarithmic film
growth is chemisorption.

Mott (11) contributed an analysis of electronic and
ionic processes in thin insulating oxide films of stoichiometric
composition on metals which led to a logarithmic equation.
He basically assumed that the layers are so thin that the
space charges contained in them may be neglected to a first
approximation. He employed the tunnel effect of quantum
mechanics (by which electrons, of lower maximum energy than
that of a barrier, possess a finite probability of penetrating
the barrier) to express rate of electron flow from metal to
oxide, which he assumed controlled the oxidation process.
Thus at low temperatures according to him, the ions cannot
simply diffuse through the film due to a concentration gradient
of ions but the electrons are supposed to be able to pass from
the metal to the oxygen adsorbed on the surface of the film,
either by thermionic emission or, more probably by, the
so-called tunnel effect. This special model accounted,
however, for oxide films only in the order of 40 Å. Subsequently
Mott and Cabrera (12,13) proposed an alternative mechanism,
rate controlled by diffusion of metal ions rather than escape
of electrons. It is supposed by them that a chemisorbed film
exists on a metal and that ions and electrons move independently in the film. The assumption is made that negatively charged oxygen ions when adsorbed on the oxide surface create an electric field within the oxide which induces migration of positive ions to the oxide surface. Thus cations would be formed at the metal/oxide interface, and oxygen anions at the oxide/gas interface - resulting in a strong electric field across the oxide film which would be mainly responsible for pulling the ions through the film. An inverse logarithmic law was established by them for thin films where migration velocity is proportional to the exponential power of the field strength. Hauffe and Illschner (14) revived the original idea by Mott (11) agreeing with most of his basic assumptions. Figure (8) shows the local dependence of the ion/electron current in very thin films, and

![Graph](image)

**Fig. 8**

- $s_e =$ Electron current
- $s_{ion} =$ Ion current

According to Hauffe (16).
according to Hauffe & Schottky. The rate is determined by electron transport in region I (thickness < 40 Å) obeying a direct logarithmic law, and in region II by ion transport, obeying an inverse logarithmic law. The transition region is still unknown.

Grimley and Trapnell (15) considered the formation of thin oxide films in terms of chemisorption of oxygen at the oxide/oxygen interface. According to these workers, the adsorbed layer consists entirely of,

Case (1) field-creating ions in n- and p-type oxides, or
Case (2) neutral pairs and field-creating ions in equilibrium in p-type oxides.

With regard to case (1), they assumed a strong uniform electric field independent of the oxide thickness (thus contradicting Mott's idea of a constant potential difference across the oxide, so that the field is inversely proportional to the thickness). A direct logarithmic law for a p-type oxide could then be derived when transport of metal ions in the oxide is rate-determining, and the linear law when a surface reaction is rate-determining. For an n-type oxide, the linear equation only was obtained for either control by ion transport, or surface reaction.
For Case (2), if transport of cations is rate determining then a cubic law is obtained assuming the drift velocity of vacant cation sites is proportional to the electric field. Other theories of the formations of thin oxide films have been suggested separately by Cabrera-Mott (13) and Hauffe - Ilschner (16). It was assumed by Cabrera-Mott that for oxide layers not thicker than a few hundred Angstroms the space-charge effects could be neglected. Hauffe (16) pointed out that such an assumption may be true for n-type oxide but not for metal-deficit or p-type oxide. The space charge layers generally cause field transport of ionic defects in the formation of thin film. Cabrera-Mott and Hauffe - Ilschner both showed that under conditions where the migration velocity of positive ions is proportional to field strength, a parabolic oxidation equation results for n-type oxide. Cabrera and Mott used the same physically-based assumptions that led to the derivation of the field-transport directed parabolic rate law for thin layers of n-type oxide, for the development of the rate law for p-type oxides and they derived a cubic equation. On the assumption of the whole oxide layer behaving as a space charge layer, Engell and Hauffe (16,17) however, also arrived at the same cubic rate equation for p-type oxides.
All the above mechanisms for thin-film formation are based on similar models. They differ in the assumptions concerning the rate determining reaction, whether electron-tunnelling, ionic transport or chemisorption. A further possibility is that the electron transfer from the metal to the oxide film may be the rate-determining process. This has been pointed out by Uhlig (7). If the theoretical derivations including the assumption that a change in work function should affect the oxidation rate of a metal, could be confirmed then this suggested mechanism would explain the persistence of the logarithmic growth to film thickness of the order of $10^{14}$Å. The theory would also then be relevant to crystal orientation effects (in single crystals), allotropic and magnetic transformations of the metal, on the oxidation rate.

Finally, it should be pointed out that none of the suggested thin-film mechanisms is as yet firmly established. They are all more or less hypothetical, which can be appreciated when one considers the fact that in the initial stages of oxidation, a non-ideal ordering of the crystal lattice is a prerequisite for penetration of atoms into the lattice and transport of ions through the oxide layers.
2.5.3. Thick Films

As the films formed by the oxidation of metals thicken, the metal-oxide separates the two reactants (metal and oxygen) from one another. The overall process of oxidation is now made up of the two phase-boundary reactions at the metal/oxide and oxide/oxygen interfaces, and of the diffusion of ions and electrons through the layer of metal oxide. There is considerable experimental evidence that the rate-controlling process in the growth of compact, non-porous oxide films on the surfaces of many metals (and alloys) is diffusion through the oxide of one particular ionic species. Assuming that there is no diffusion through pores or along grain boundaries, Wagner (18) made the working hypothesis that only cations or anions migrate across the compact layer, and that the migration of electrically neutral atoms or molecules may be neglected. Since the film is composed of anions and cations, the process of diffusion across the film (assuming a concentration gradient across it) must be accompanied by a simultaneous diffusion of electrons in the same direction as the cations, or in the opposite direction to the anions. The theory is based on the models of semi-conductors. Since in most cases, the migration of ions controls the rate of oxidation, it may be therefore assumed that either the metal ions and electrons
migrate from the metal/oxide interface across the oxide to the outer surface, or that oxygen ions migrate in the opposite direction. Schematic representation of diffusion through a p-type of oxide, e.g. Cu$_2$O is shown in figure (9).

Thus here copper ion vacancies (Cu$^{+}\square$) and electron holes (Θ) are formed due to metal deficiency, outward migration of copper ions (Cu$^+$) and electrons (e$^-$) will take place through vacancies and holes. Thus cation vacancies and holes are accumulated at the metal/oxide interface.

A similar diagram can be drawn for an n-type oxide, e.g. ZnO, as shown in figure 10.
In this case migration of zinc ions \( (Zn^{+2}) \) through interstitial lattice sites \( (Zn^2) \) together with free electrons \( (\bar{e}) \) occurs towards the outer ZnO boundary. Unlike the first case, here the lattice-defect current and metal-ion current proceed in the same direction.

Several theoretical treatments of the diffusion process have been published and are reviewed by Hauffe (16). They generally suppose that:

a) Concentrations of mobile ions at both interfaces are essentially independent of time. This is because interfacial reactions necessary to establish local thermodynamic equilibrium are sufficiently rapid to compensate for addition or removal of ions by diffusion.

b) Ionic transport is predominantly by a volume diffusion mechanism. With the above main assumptions, the rate of increase of film thickness, \( X \) with time, \( t \), in the thick film region is found to be inversely proportional to \( X \).

i.e. \( \frac{dX}{dt} \propto \frac{1}{X} \) leading to a parabolic growth law

\[
X^2 = Kt + C
\]

where \( K \) and \( C \) are constants. The rational rate constant, \( K \), can be evaluated from Wagner's work. However, sometimes the reactions at the phase boundaries may be rate-determining factors, in which case a linear oxidation rate law is
observed. For example, in porous layers where diffusional processes would be fast, it can be said from experimental observations that the reaction at the oxide/oxygen interface is the rate-determining step in the majority of cases. However, in the case of a non-porous layer, diffusion, although expected, may not be always the sole rate-determining step; a phase boundary reaction at either interface might play an important part. Jost (19) has stated, "if both processes, viz., reaction at an interface and diffusion, proceed with comparable speed, the 'reaction resistivities' might be expected to be additive". The foregoing considerations yield an expression of the so-called modified parabolic law,

$$\frac{W^2}{(K_p)_M} + \frac{W}{(K_1)_M} = t,$$

where \((K_p)_M\) and \((K_1)_M\) are parabolic and linear rate constants of the modified parabolic law.

Finally it is worthwhile mentioning that the parabolic rate law or linear law-mechanisms are completely different for thin and thick films. Thus in thick scales of p-type oxides, the parabolic oxidation rate increases with increasing partial pressure of oxygen; whereas in the case of n-type oxides, the oxidation rate is independent of external pressure. On the other hand, parabolic oxidation in thin films due to field-transport process leads to a pressure
dependence of the formation of n-type oxides, which is a reflection of the effect of space charge layer on the kinetics of oxidation.

3. Literature Survey

3.1. Effect of metal purity

In the study of gas-metal reactions it is important to know the purity of the materials used. Kubaschewski and von Goldbeck (20) found a difference of one power of ten in the oxidation rates of nickel of different purities. It is difficult to predict how particular impurities may affect experimentally obtained rates of oxidation. From the available information it appears that, impurities behaving chemically similar to the basis metal have much less effect than those chemically different. It seems desirable that the amount of the latter type of impurity should be kept well below 0.01%, as even such small amounts may alter the oxidation rate considerably [Gebhardt (21)]. In the present study spectrographically pure metal sheets were used.

3.2. Oxidation of polycrystalline metal

In all the familiar simple models of metal oxidation kinetics in which a solid oxide is formed on the surface, the metal structure is ignored and the metal/oxide interface is regarded as an isotropic source of metal. Actual behaviour,
however, is affected by certain structural heterogeneities of the polycrystalline metal undergoing oxidation. Such heterogeneities include impurities, crystallographic orientation, dislocations, grain boundaries etc., which may affect the diffusion process across the oxide and hence the oxidation kinetics.

The possibility as suggested by Bénard (22), Hauffe (23) and Mehl (24) that the metal/oxide epitaxial relationships can influence the chemisorption reaction and hence the different oxidation kinetics of the allotropic forms of a metal, need only be briefly mentioned here, because in the present work oxidation kinetics of polycrystalline metal substrate have been studied.

Interaction of vacancies with dislocations may play a role in the reaction kinetics [Maldy (25)], but the magnitude of such interactions is unknown in oxidation processes. For a p-type oxide, cation vacancies diffuse through the oxide towards the metal (sec.2,5.3.). To maintain a concentration gradient for diffusion, the vacancies must be continually destroyed in some fashion at the metal/oxide interface. One way is to sink the vacancies at suitable sites. It is proposed [by Cohen, et.al. (26) and Ervin and Mackay (27)] that dislocations or lattice steps on the surface of the metal provide such sinks, so presence of dislocation at the metal/oxide interface provides easier sink for vacancies and this would
result in a steeper concentration gradient of vacancies for diffusion across the oxide and thus a higher oxidation rate can be expected. This phenomenon has been observed by Cohen, et al. (26) for the oxidation of iron below 600°C when wüstite formation is almost negligible. Thus cold-worked iron was found to oxidise at a higher rate than the annealed one because of higher dislocation density in the cold-worked iron. However at higher temperatures where wüstite is the main oxide, such an effect does not seem to occur. It is believed that this is due to a certain basic property of wüstite which is lacking in the other oxides that are formed below 600°C. One possibility is the greater plasticity of wüstite [Birchenall, et al. (28), (29)] which makes it possible to continually destroy the vacancies present at the metal/oxide interface. No vacancies are left for preferential sinking at dislocation sites. So the oxidation rate of iron above 600°C becomes independent of the presence of dislocations at the metal/oxide interface. Thus oxidation rate of abraded (i.e. cold-worked) or annealed iron above 600°C will remain identical, because the major oxide is wüstite which is very plastic.

In the present work, oxidation study of iron has been made in the temperature between 800° and 1000°C.
3.3. Formation of Polycrystalline Oxide

It is said (sec. 3.2.) that the presence of dislocation networks on the metal surface i.e. metal/oxide interface cannot affect the overall diffusion kinetics if the oxide formed is wüstite. Since the oxide formed is also polycrystalline, it is worthwhile to deal with the effect of polycrystalline oxide on the diffusion kinetics and hence on the oxidation process.

The diffusion-rate along dislocations and grain boundaries in polycrystals of oxide may be very different from the diffusion rate through the bulk lattice of the oxide. Apparently it is important that, in some systems, boundary-diffusion predominates over bulk-diffusion up to considerably higher temperatures than in a pure metallic system [Arkharov et.al. (30)]. In other cases, on the contrary, the role of boundary-diffusion is not as important [Klotsman et.al. (31)]. Parabolic oxidation for thick films deals with the bulk-or volume-diffusion across the oxide only (sec. 2.5.3.). The pre-parabolic diffusional process is thus believed to be due to diffusion across grain boundaries, dislocations, etc. of the oxide [Gulbranson (32), Smeltzer (33)]. According to Smeltzer (33), the dislocations, grain boundaries etc. of the oxide act as low-resistance i.e. short-circuit diffusion paths. Such paths are very effective for the
diffusion of reactive species and are of sufficient number to account for the deviations from the parabolic rate law at the initial stages of oxidation. As the oxide film thickens, the oxide crystallites grow until at some critical thickness the contribution of short-circuit diffusion to the oxidation process becomes small compared to the bulk diffusion. Gibbs (34) has suggested the necessary correction to be made to account for the grain boundary diffusivity in the parabolic oxidation of metal when bulk diffusion becomes the major rate-controlling process.

At the present time there is very little data on intercrystalline diffusion in chemical compounds, especially in oxides. The result of measuring the coefficients of self-diffusion of oxygen in single- and poly-crystalline aluminium oxide with a mass spectrometer [Oishi, (35)] showed that even at a temperature of 0.9 of the melting point $T_m$ the presence of grain boundaries increases the effective diffusion coefficient of oxygen by two orders. On the other hand, it has been shown by Lindner (36) that there is no intercrystalline diffusion of nickel oxide even at 0.4 $T_m$. It has been suggested by Klotsman, et al. (37) that aside from the dependence on the properties of the boundary itself, there must also be a dependence of intercrystalline diffusion on the type of diffusing element. In chemical compounds, it is necessary
first of all to consider the susceptibility of the cation or the anion to intercrystalline diffusion. It has been stated by Klotsman (37) that, in ionic compounds intercrystalline diffusion of metalloids is intensified, while that of metals is decelerated. A similar result was found by Laurent, et al. (38) in their experiments on measurements of the diffusion parameters of polycrystalline halides of alkali metals: there was practically no intercrystalline diffusion of metal, while the diffusion of the metalloid along the grain boundaries was quite prominent. In the case of wüstite— or cobaltous oxide—growth, it is the diffusion of the metal ion in the p-type oxide that controls the reaction mechanism, not the diffusion of metalloid. So the effect of intercrystalline diffusion in the oxide is considered to be negligible on the overall oxidation kinetics.
3.4 Methods of studying oxidation

Various methods are available for the measurement of reaction of oxygen with metals [Kubaschewski and Hopkins (39)]. The following methods are of general use,

1) Gravimetric,
2) Manometric,
3) Volumetric,
4) Electrometric,
5) Optical.

It is the usual practice to obtain the oxidation results from the determination of the weight increase of the metallic sample with time, caused by the quantity of oxygen taken up by the oxide formation. Detailed descriptions of the various methods have been given by Kubaschewski and Hopkins (39), so only a brief outline is given for the methods other than those selected for use in the present investigation. The selected methods are described in greater detail in Sections (4.3, 4.4 and 4.5).

In gravimetric methods, the following general arrangement is used:

a) The metal specimen is weighed, placed in the hot zone of the furnace for a certain time, removed and weighed again after cooling. This is repeated a number of times for suitable heating periods.
b) the metal specimen can be suspended in a hot vertical tube on a wire which is connected to a suitable balance, and continuous readings of the weight changes can be taken on the balance without the specimen having to be removed from the hot zone. Gulbransen\(^{(40)}\) developed a highly sensitive vacuum micro-balance. Thus in its simplest form the gravimetric method requires no more than a hot furnace and an accurate balance.

The apparatus in the manometric method consists essentially of a heated reaction tube, a manometer, and a gas supply. The consumption of oxygen by the specimen during oxidation is recorded on the manometer by a gradual drop in pressure. The conventional manometric method has been described in the works of Campbell and Thomas\(^{(41)}\), Nwoko and Uhlig\(^{(42)}\), Hinshelwood\(^{(43)}\), Wilkins and Rideal\(^{(44)}\), Kubaschewski and Schneider\(^{(45)}\) etc.

A volumetric method has been described by Jenkins\(^{(46)}\), where the volume of oxygen absorbed during oxidation is shown up by the movement of an indicator (such as, mobile dibutyl phthalate indicator) on a calibrated capillary tube. Such a capillary tube is fixed between the gas reservoir and the reaction tube. Applying the same principle, Measor\(^{(47)}\) was able to study the rate of oxidation with time.
using a rotameter. Measor's method of constant pressure differential-rate technique utilises a stainless steel float as an indicator.

The electrometric method consists of determining the quantity of electricity needed to reduce the oxidation product either to the metallic state or to a lower state of oxidation. Such a method is thus applicable to determine the thickness of oxide film, and in aqueous solution. It is therefore unsuitable for use in the study of the dry corrosion of metals and their oxidation rates.

In optical methods, the film-thickness is estimated from its colour. According to Evans (48), the interference band of the film is directly related to the thickness. Thus as the film-thickness is increased, the first band enters the blue-violet range of the visible spectrum and the complementary yellow colour is produced. This changes to red and then blue as the thickness of the film increases, until the band reaches the infra-red region of the spectrum. As the film-thickness increases, the second band from the ultra-violet region passes through the visible spectrum producing colours of the second order. Winterbottom (49) has explained the variation of film-thickness with interference orders on the basis of classical optical theory.

The remaining sections of the literature review are
devoted to a detailed account of the oxidation characteristics of the specific metals used in this investigation.

3.5 The Oxidation of iron

Iron has a stable body-centred cubic (B.C.C.) structure (α-phase) which is ferromagnetic at room temperature. The Curie temperature is 755°C. The B.C.C. structure undergoes crystallographic transformation to a face-centred cubic (F.C.C.) structure around 910°C. At higher temperatures (1425°C) the F.C.C. structure reverts to the B.C.C. phase.

A considerable amount of work has been carried out in the past to ascertain the mechanism of oxidation in the range of the first allotrope change point. The relevant results are summarised in Table 1. Typical Arrhenius plots in the neighbourhood of 910°C are reproduced later (Section 6.3). Bénard's work (50) is the most relevant in the present case, because he studied the initial stages of oxidation using air as the oxidant. His technique was not isothermal, because a cold specimen was pushed into the hot oxidizing atmosphere and the weight increase with time then recorded which led to the observation of a linear law in the initial stage of oxidation of iron. The linear law occurs, e.g. up to 40 seconds at 950°C, before the onset of a diffusion-controlled parabolic oxidation. Davies, et al. (54) have studied the diffusion-controlled (parabolic) oxidation
<table>
<thead>
<tr>
<th>Metal phase</th>
<th>Atmosphere</th>
<th>Activation energy (Kcal/mole.)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.C.C. iron</td>
<td>Air</td>
<td>60 ± 7</td>
<td>Bénard (50)</td>
</tr>
<tr>
<td>&quot;</td>
<td>CO₂</td>
<td>27 ± 3</td>
<td>Fishbeck, et.al. (51)</td>
</tr>
<tr>
<td>&quot;</td>
<td>CO₂/CO</td>
<td>60 ± 7</td>
<td>Hauffe, et.al. (52)</td>
</tr>
<tr>
<td>F.C.C. iron</td>
<td>Air</td>
<td>17 ± 7</td>
<td>Bénard (50)</td>
</tr>
<tr>
<td>&quot;</td>
<td>CO₂</td>
<td>30 ± 10</td>
<td>Fishbeck, et.al. (51)</td>
</tr>
<tr>
<td>&quot;</td>
<td>CO₂/CO</td>
<td>33 ± 10</td>
<td>Smeltzer (53)</td>
</tr>
</tbody>
</table>
Table-1 (continued)

II. Activation energies for true parabolic law of oxidation of iron in different atmospheres

<table>
<thead>
<tr>
<th>Metal phase</th>
<th>Atmosphere</th>
<th>Activation energy (Kcal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.C.C. iron</td>
<td>$O_2$</td>
<td>29.7</td>
<td>Davies, et.al. (54)</td>
</tr>
<tr>
<td>&quot;</td>
<td>Air</td>
<td>29</td>
<td>Zhuk (55)</td>
</tr>
<tr>
<td>F.C.C. iron</td>
<td>$O_2$</td>
<td>29.7</td>
<td>Davies et.al. (54)</td>
</tr>
<tr>
<td>&quot;</td>
<td>Air</td>
<td>17</td>
<td>Zhuk (55)</td>
</tr>
</tbody>
</table>

III. Activation energies for modified parabolic law of oxidation of iron in steam

<table>
<thead>
<tr>
<th>Metal phase</th>
<th>Activation energy (Kcal/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.C.C. &amp; F.C.C. iron</td>
<td>$(Q_p)_M$ = 39.9, $(Q_l)_M = 22.1$</td>
<td>Ipat'ev (56)</td>
</tr>
</tbody>
</table>
of iron (thick scale) in the temperature range of interest, using pure oxygen. Fischbeck, et al.\textsuperscript{51} reduced the oxygen potential in the gas phase by using carbon dioxide (CO\textsubscript{2}) and other atmospheres. They have demonstrated that the high temperature oxidation of iron under less oxidizing atmospheres obeys a linear law. The experimental technique in all these cases is the same, namely, the gravimetric method. Without explaining the occurrence of various activation energies at this point, one thing is apparent from Table-1, a linear law of oxidation can be expected in the initial stages of oxidation [Bénard\textsuperscript{50}] or, when oxidation is carried out in less oxidizing atmospheres [Fischbeck, et al.\textsuperscript{51}, Hauffe, et al.\textsuperscript{52}, Smeltzer\textsuperscript{53}]. A parabolic law can be expected for thick scale formation under enriched oxygen atmosphere [Davies, et al.\textsuperscript{54}, Zhuk\textsuperscript{55}]. As regards to the mechanism, Hauffe, et al.\textsuperscript{52} have proposed that, the linear oxidation is determined by a chemisorption reaction while the parabolic oxidation is determined by diffusion. Smeltzer\textsuperscript{53} concludes from his work that the activation energy of oxidation under certain conditions is equivalent to either the dissociation energy of the gaseous reactant at the gas/oxide interface (a linear law of oxidation) or, the activation energy for the diffusion of cation vacancies in the oxide, wüstite, (a parabolic law of
oxidation). Zhuk\(^{(55)}\) has shown that passage through the allotropic transformation changes the oxidation rate in air and this is manifested by a fall in the activation energy of oxidation, \(Q\). Unlike Davies, et al.\(^{(54)}\) he obtained two \(Q\)-values and the ratio \(Q_{(B.C.C.)}:Q_{(F.C.C.)}\) i.e. the ratio of the activation energy of oxidation of B.C.C.- and F.C.C.-iron is found equal to 1.70. The work of Ipat'ev\(^{(56)}\) on the oxidation of iron in steam has shown that the modified parabolic rate-law is obeyed. Ipat'ev, unlike Zhuk, did not observe any difference in \(Q\)-values for the oxidation of the two structures of iron. The difference in the values of \((Q_p)_M\) and \((Q_l)_M\) was found to be 17.8 Kcal/mol. [where \((Q_p)_M\) and \((Q_l)_M\) are the activation energies of oxidation obtained from the slopes of the Arrhenius plots of \(\log_{10}(K_p)_M\) and \(\log_{10}(K_l)_M\) against the inverse of temperature respectively and \((K_p)_M\) and \((K_l)_M\) are parabolic and linear rate constants respectively of the modified parabolic law].

3.6 Structure and properties of iron oxide

In oxidation studies, examination of the oxidation products provide complementary information to the measurement of oxidation rates. The various methods for the examination of the oxides are,

1) Electron diffraction,
2) X-ray diffraction,
3) Metallography, which includes both optical and electron microscope examinations,
4) Film stripping and chemical analysis.

The electron diffraction method is a well recognized tool for the identification of oxide films particularly those which are thinner because the depth of penetration of the electrons is small. The reflection technique is applied to oxide layers on lump samples, the electron beam grazing the flat surface of the sample at a small angle, a record of the diffracted rays being obtained on a photographic plate. Such a method thus reveals the surface topography only. To know the bulk structure, transmission method is always preferred. The X-ray method can be used for examining thicker oxide scales. If the scales are removed from the metal, the ground powder can be used as the specimen for the Debye-Scherrer method of X-ray diffraction. Glancing angle and back reflection techniques can be used whilst the oxide is still attached to the metal. Metallography is useful for providing information on some of the characteristics of the oxides and the mechanism of growth. Chemical analysis is an orthodox method of determining the chemical composition of the oxide. — The method that is best suited in any particular case depends
not only on the information that it is intended to obtain from the examination, but also on the individual circumstances.

Thermodynamic calculations enable a choice to be made of one from several possible mechanisms. The reactions which occur are those that are feasible both thermodynamically and kinetically. Thermodynamic calculations show only minor free-energy changes for the various possible iron-oxygen reactions, due to the \( \alpha \rightarrow \gamma \) transitions in iron at 910°C. In his micrographic study, Bénard\(^{(57)}\) has shown that for the temperature range of 650°C to 910°C, non-stoichiometric ferrous oxide (Fe\(_{0.91}\)O) i.e. wüstite makes up 95% of the film in contact with the metal. Above the \( \alpha \) to \( \gamma \)-iron transition at 910°C, the composition of the film changes and ferriferrous oxide (Fe\(_{3}\)O\(_{4}\)) becomes the more important component. In contrast, Jackson and Quarrell\(^{(58)}\), Gulbransen with Hickman\(^{(59)}\) and with Ruka\(^{(60)}\) have found, using a high temperature electron diffraction camera, that above 570°C up to 1050°C ferrous oxide is the main oxide formed. Confirmation of this was obtained by Davies, et. al.\(^{(54)}\), who have shown in their study on the mechanism and kinetics of the scaling of iron that, between 800°C and 1000°C the main oxide (\( \sim 96\% \)) is wüstite.

It is therefore reasonable to assume the formation of a single oxide, wüstite (of a non-stoichiometric formula) in the temperature range of the present study. Stability
of wustite is also supported from a recent work by Vallet and Raccah (61), which has shown that the dissociation pressure of oxygen over wustite, given by the following equation, is very low,

\[
\log(p_{O_2}) = -27330T^{-1} + 6.668
\]

where \(p_{O_2}\) is the equilibrium partial pressure of oxygen for the iron \(\rightarrow\) wustite reaction and \(T\) is the temperature.

3.7 The oxidation of cobalt

By using X-ray analysis Hull (62) was the first to detect the allotropie transformation of cobalt near 400°C from the close-packed hexagonal to the face-centred cubic structure. This transformation is now well established [Bolgov (63)]. Both modifications of cobalt are ferromagnetic; the Curie point for the F.C.C. phase is 1115°C. The reverse transformation, i.e. F.C.C. \(\rightarrow\) H.C.P. phase on cooling is a diffusionless martensitic reaction [Edwards and Lipson (64), Seeger (65), Houska et al. (66), Votava (67), Bollman (68) etc.]. According to Troiano and Tokich (69), and Owen and Jones (70), the F.C.C. structure can be fully retained at room temperature, depending on the deformation strains, grain sizes, etc., of cobalt.

The kinetics of oxidation of cobalt at low temperatures has received little attention. Between 400°C and 1400°C, a
parabolic relationship is obeyed [Moore, et. al. (71, 72), Phalnikar, et. al. (73), Johns and Baldwin (74), Gulbransen and Andrew (75), Bridges, et. al. (76), Carter and Richardson (77)], with some deviation from the parabolic law at the initial stages of oxidation [Gulbransen, et. al. (75) and Phalnikar, et. al. (73)]. In all these cases, the oxide formed is thick enough to make the oxidation process controlled by the diffusion of ions through the oxide. Gulbransen, et. al. (75) studied the oxidation behaviour of both H.C.P.- (cold-worked) and F.C.C.- (annealed) cobalt (in the form of strips) in oxygen (at a pressure of 76 mm. Hg. abs.) from 200°C to 700°C for 2 hours. The hexagonal was found to oxidize more rapidly than the cubic form. Although a number of empirical equations may be found to fit the data, they proposed that the rate law was parabolic for both forms of cobalt after an initial deviation from the true parabolic rate-law. Phalnikar, et. al. (73) indicated that, between 500-800°C the oxidation rate is faster in the time range of 1-2 hours than the parabolic rate-law would predict. Uhlig (78) replotted Gulbransen's results of the initial deviation from the parabolic law and found the deviation to be due to a different mechanism, such as a direct-logarithmic law of oxidation controlling the rate at the initial stages of oxidation. Zettlemoyer (79, 80) however, studied the initial oxidation of cobalt powder but at very low temperatures, namely between -195°C to 25°C. A direct-logarithmic
law was observed which can be explained by utilising the concept of Cabrera and Mott\(^{(13)}\) or of Grimley and Trapnell\(^{(15)}\). Unlike the previous Section (3.5), no Tables or Arrhenius plots are given, because not much work has been done in the temperature range of interest for thin films.

3.8 Structure and properties of cobalt oxide

Cobalt forms several compounds with oxygen. The existence of the oxides \(\text{CoO}\) and \(\text{Co}_2\text{O}_4\) has been established beyond doubt, but that of \(\text{Co}_3\text{O}_4\) is less certain. The \(\text{CoO}\) and \(\text{Co}_3\text{O}_4\) lattices are characterised by the occurrence of defects, which are more numerous in the former oxide. Both the oxides are p-type, metal-deficit semiconductors which grow by outward diffusion of cations [Kubaschewski\(^{(81)}\)]. According to Valensi\(^{(82)}\), the oxidation of cobalt in air above 700°C proceeds predominantly by \(\text{CoO}\) formation, and below 700°C with the formation of \(\text{Co}_3\text{O}_4\). An X-ray study of cobalt oxidized in air \((385^\circ - 800^\circ \text{C})\) by Arkharov et al\(^{(83)}\) shows that the main part of the oxide layer consists of \(\text{CoO}\) in contact with the metal and a small amount of \(\text{Co}_3\text{O}_4\) on the surface. At low temperatures, the relative amount of \(\text{Co}_3\text{O}_4\) increases. Arkharov with Lomakin\(^{(84)}\) has shown that the critical temperature of the \(\text{Co}_3\text{O}_4\) formation in air is 890°C. Phalnikar, et al.\(^{(73)}\) identified the scale products, formed in air during high temperature oxidation
of cobalt, by X-ray analysis at room temperature. The outer layer of Co$_2$O$_4$ occupied about 50% of the total scale thickness at low temperatures (600°C) but became relatively thinner when the temperature was increased and ~900°C it disappeared.

3.9 Object of the research

The literature review enables the objectives of the present work to be defined more precisely. It has been established quite definitely that, when oxidation of a metal obeys the conventional parabolic rate-law, it implies a diffusion controlled reaction across the oxide. This fact is supported by Davies et al.\(^{(54)}\) from their work on the oxidation of iron between 400°C and 1200°C, and by Gulbransen et al.\(^{(75)}\) from their work on cobalt between 200°C and 700°C. The Arrhenius plots of the logarithm of the parabolic rate constant against the inverse of temperature show no change at the allotropic transformation temperature in either case. This means that the oxidation kinetics obeying parabolic rate-law do not have any change in the activation energy of oxidation (which is obtained from the slope of the Arrhenius plot) around the allotropic change point of the metal. This is theoretically expected, since parabolic oxidation is controlled within the oxide film, and should not show any dependence on changes, electronic or crystallographic,
occurring in the metallic substrate during allotropic transformation. However, if the process of oxidation is controlled at either of the interfaces namely, metal/oxide or gas/oxide, then changes in the property of the metal substrate can affect the kinetics of oxidation because of the following reason. Oxidation in an interface controlled process depends on the number of ions or electrons present at (1) the metal/oxide or (2) gas/oxide interfaces.

Case (1): It is obvious that a change in the structure of the metal substrate will control the number of electrons or ions produced at the metal/oxide interface.

Case (2): These ions or electrons, produced at the metal/oxide interface, will diffuse through the oxide to reach the gas/oxide interface. Such diffusion across the oxide will be definitely affected by the property of the oxide. But diffusivity of ions or electrons across the same oxide remains constant, so the phase-boundary reaction at the gas/oxide interface, which depends on the number of electrons or ions available at this interface, will be directly dependent on the concentrations of ions or electrons that are produced at the metal/oxide interface and will be independent of the properties of the oxide, because the diffusivity of ions or electrons across the oxide remains unchanged.

Since thick oxide scales mostly obey a parabolic rate-law, the initial stages of oxidation which provide thin films are more likely to provide conditions for a non-parabolic
rate-law which could lead to the information about the effect of structural change of the metal on its corresponding oxidation behaviour.

Bénard\(^{(50)}\) has studied the initial stages of oxidation of iron between 850\(^{\circ}\) and 1050\(^{\circ}\)C in air at one atmosphere. However, in his work the metal specimens were pushed into the hot, oxidizing reaction zone from room temperature and the subsequent oxidation was recorded in terms of the weight increase of the specimen with time. Thus the metal-specimen gets oxidised to some extent on its way up to the experimental temperature and as a result of this technique, the recorded results do not represent the true values that can be expected at that particular experimental temperature. In the present investigation, arrangements were made to allow a study on the initial stages of oxidation for iron between 810\(^{\circ}\) and 1005\(^{\circ}\)C (and from 320\(^{\circ}\) to 520\(^{\circ}\)C in the case of cobalt) by having the metal specimen already in the reaction zone heated up to the particular experimental temperature before the introduction of oxygen. Results were obtained as soon as possible after oxygen was admitted into the reaction tube. In order to prevent the formation of any pre-formed film prior to the oxidation test, hydrogen annealing followed by argon annealing of the metal specimen were carried out in all cases before the test was done. In the case of iron, the present
work is based on the study of the kinetics of oxidation around the first transformation temperature (of $\sim 910^\circ C$). It is believed that valid results are difficult to obtain at the second higher change point of $1425^\circ C$, since the oxidation rate will be so fast that the very small specimen size, required by the particular method adopted, will be difficult to handle and also difficult to prepare.

Thus, the basic object of the present research is to study the kinetics of the initial stages of isothermal oxidation of metals, namely, iron and cobalt, and thereby to try to correlate the observed oxidation kinetics with the properties of the relevant structural changes in the substrate. Besides the kinetics other observations are also made on the reactivity of a metal with oxygen in the temperature range of the allotropic transformation.
EXPERIMENTAL
Section 4. Experimental
4.1. Metallic Materials

4.1.1. Purity of the Specimen

Because of the complexities in the oxidation process that could arise from the presence of impurities in the metal specimen, it is always desirable to have a pure specimen as the starting material. In the present study, spectrographically pure metals were used in the form of sheets, provided by Johnson Matthey & Co. Ltd., who also supplied the following typical analysis (Table-2).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Chemical analysis (quantities are expressed in parts per million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Manganese</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Cobalt</td>
<td>-</td>
</tr>
</tbody>
</table>

Sheets were 1 or 2 mm. thick in case of iron and of 0.5 mm. thick in case of cobalt with a length of 20 mm. in either case. Cobalt specimens were reduced by 15% in between anneals, (which is the maximum possible) and iron specimen by 85%.
4.1.2. Surface area used

To obtain accurately measurable rates when oxidation was rapid, specimens were cut with a wide range of surface areas. This is related to the theory of the rotameter and discussed in Section 4.4.2. The oxidation rate of iron in the present work was observed to decrease with increasing pressure of oxygen, which necessitates the use of specimens of larger surface areas at the higher pressure. The areas varied from about 8.5 cm$^2$ at 838°C to 3.7 cm$^2$ at 965°C when the pressure of oxygen, $p_{O_2} = 29$ cm Hg absolute and from about 1.7 cm$^2$ at 810°C to 0.55 cm$^2$ at 1000°C were used when $p_{O_2} = 7.6$ cm Hg absolute.

In the case of cobalt, since the temperatures in the range of study are relatively low, the oxidation rate therefore does not undergo appreciable change with temperature. Furthermore, the oxidation rate is found here to be independent of $p_{O_2}$ values. Thus the surface areas of cobalt specimens were not varied at all, remaining at about 20 cm$^2$ from 320°C to 520°C at any pressure of oxygen. For both iron and cobalt the measured surface area is uncorrected for roughness, but surface preparation was rigorously standardised.

4.1.3. Surface conditions

Since oxidation is essentially a surface phenomenon,
great care is necessary in the preparation of specimens for oxidation tests. A large number of specimens was required and therefore it was decided that the method of preparation chosen should be relatively easy to carry out and give reproducible results. Ideally the preparation should not result in a film being produced on the surface, because of the effect this might have on the course of the oxidation experiments. Although it was not possible to achieve this condition before the actual oxidation test, all the specimens were annealed in hydrogen to reduce any films present.

After being cut and ground to the desired size, areas were measured accurately by means of a travelling microscope or in some cases, by using a micrometer. Each specimen was then given a surface polish as uniformly as possible by means of a fine polishing emery paper (4 grade). It was next washed in acetone and degreased by washing first with sodium carbonate and then in carbon tetrachloride or benzene. Once the degreasing operation was complete, the specimen was handled by means of a small pair of tongs. After the specimen was dry, it was weighed. It was then ready for the subsequent reduction annealing prior to the oxidation test.
4.2. Properties of the gas used

4.2.1. Purity of the gas

Pure gases namely, oxygen, argon and hydrogen were used here. These were supplied by the British Oxygen Company, who also kindly provided the following typical analyses:

A) Oxygen gas: - 99.5 ±% oxygen,
   less than 0.5% argon,
   less than 0.1% hydrogen and
   less than 5 v.p.m. of carbon dioxide.

B) Argon gas: - 99.99 ±% argon,
   less than 10 v.p.m. of oxygen,
   usually less than 25 v.p.m. of nitrogen and
   less than 5 v.p.m. of hydrogen, carbon dioxide and water vapour.

C) Hydrogen gas: - The supplied physical properties of the gas shows it to be of 99.9% purity.

The oxygen gas was purified and dried by passing through soda asbestos and then through magnesium perchlorate in the drying tower assembled in the apparatus.
4.3. Methods of studying the oxidation process

In all the various methods, except the constant pressure differential-rate technique, the approach towards the study of an oxidation isotherm is in the conventional fashion. The value of $\Delta W$ (increase in weight of the oxide) or $\Delta \gamma$ (increase in film thickness) are determined over sufficiently large time intervals and hence, can be classified as integral rate methods. For the study of the kinetics of reaction, a more direct approach would be the differential rate method or the determination of instantaneous reaction rates, $(dW/dt)$. In the present investigation, this technique was achieved by adopting the method devised by Measor (47,85). In such a method, the measurements being purely concerned with gas flow rates, unlike gravimetric, electrometric and optical, there appears to be a natural advantage to apply it to an accurate and continuous study of the early stages of oxidation at high temperatures where there is a rapid onset of oxidation. Thus the oxidation of iron in the range of 800 to 1000°C has been studied by using this differential-rate technique. At lower temperature, where the oxidation rate itself is slow, the amount of oxygen consumed will be low - as a result, this could make it extremely difficult to obtain accurate measurement and hence consistent reliable results. Such a situation arises in the present work during the study on the oxidation of cobalt in the temperature
range of 320° to 520°C. It was found convenient to adopt a manometric method here by making some limited modifications of the differential-rate gas apparatus. The modifications were made in such a way that the apparatus may be used for either methods of measurement namely, manometric or differential-rate method.
4.4. Constant pressure-differential gas apparatus

According to Measor (47), this type of apparatus is very useful to obtain direct measurements of the kinetics of gas-solid reactions, especially when rates are high. Recent work (85) has supported the above statement. Thus, instead of W-values, which represent weight increase per unit area of the specimen, dW/dt, which is the weight increase (or weight of oxygen consumed) per unit area of the specimen in unit time, can be obtained. Experimentally this is achieved by measuring the rate of efflux of unused oxygen from the apparatus, in which the reaction takes place at constant pressure. At the end of oxidation, the supply flow rate (called the reference flow rate) is noted. The difference between the reference flow rate and the rate of efflux, both of which are obtained from readings of the same Rotameter, represent dW/dt (on conversion). The apparatus essentially includes a Rotameter which is the heart of the whole system of measurement.

4.4.1. Theory of the Rotameter

The Rotameter consists of a stainless-steel float which, by means of grooves cut in the flange, is caused to rotate freely in a precision-tapered bore of clear borosilicate glass tube supported vertically with the smaller end in the lower position. For general use, the tapered glass tube is moulded
to a tolerance within 0.0001" (in.). The instrument operates on the principle that different positions of the float in the graduated tube correspond to different sizes of the constriction for flow of fluid (fig. 11 & 12). The size of the constriction varies to accommodate the flow, whilst the differential head is held constant. The instrument gives consistent flow indication and is frictionless.

The theory of the performance of a Rotameter is based on the principles of dimensional analysis. The analysis involves the following quantities, \( F \) the rate of flow in \( \text{cm}^3 \text{sec}^{-1} \), \( m \) mass of float in \( \text{gm.} \), \( d \) and \( D \) diameters of the float and bore of tube respectively in \( \text{cm.} \), \( \rho \) and \( \sigma \) densities of fluid and float respectively in \( \text{gm. cm}^{-3} \), and \( \eta \) the viscosity of fluid in poises. This number can be reduced by writing \( W_1 = mg (\sigma - \rho) / \sigma \) for the gravitational force on the float. For a Rotameter of the conventional type, with a freely rotating float, which uses a specific fluid the main interest is in the relation between the flow and the height of the float in the equilibrium position. At high values of the \( D/d \) ratio, the following relationship holds good, where \( C^* \) is a constant,

\[
\log \left( \frac{W_1 \rho^{1/2}}{\eta} \right) = \log \frac{F \rho}{d \eta} + C^*
\]

or, \( F \propto \frac{d^{1/2} W_1^{1/2}}{\rho^{1/2}} \)

This indicates that in this region, the calibration of the instrument tends to become independent of the viscosity of
Details of Rotameter

Part of the rotameter, showing the position of the float while rotating.

Springs are used in order
a) to provide a smooth seat for the float,
b) to prevent the float coming off the rotameter accidentally from sudden flow of gas through the rotameter. (This may happen from incorrect opening of the valves.)
the fluid and that the force acting on the float is almost entirely due to impact head. At low values of the D/d ratio, the relationship becomes as follows,

\[
\log \left( \frac{W \cdot \rho}{\eta} \right)^{\frac{1}{2}} = \frac{1}{2} \log F \cdot \rho / d \cdot \eta + C
\]

or, \( F \propto d \cdot W / \eta \)

This expression shows that the force on the float is then almost entirely due to the viscosity of the fluid or, in other words, the viscous drag makes some considerable contribution to the force exerted by oxygen on the float.

The diameter of the float, \( d \), is approximately 1.6 mm and \( W_1 \) is about 0.02 gm. A scale range 0 to 14 cm. graduated in millimeter was used when the kinetics at \( p_{o2} = 7.6 \) cm. Hg. absolute were studied, while for \( p_{o2} = 29 \) cm. the scale range was 0 to 12 cm. Since the D/d ratio is lower in the bottom half of the instrument, the viscous drag of the fluid may be expected to make a significant contribution to the total force on the float. In the upper half of the instrument, where D/d ratio is higher, the impact force may be more predominating than the viscous drag. This was reflected in the calibration curves. To demonstrate the sensitivity of the lower and upper half part of the instrument, some calibration results will be considered.—Since the instrument is tapered, the mass rate of flow of oxygen (in \( \mu g \cdot m i n.^{-1} \)) would be different at different levels of the float. In such a case, to get a rough
idea of the sensitivity, the whole length of the instrument is to imagined as consisting of two halves, the lower half representing lower D/d ratios, although the length over which the condition for a low D/d ratio would be valid, is not strictly defined. On the basis of these assumptions the following table-3 is obtained.

<p>| Table - 3 |
|-----------------|-----------------|-----------------|
| Variation of mass rate of oxygen flow through the Rotameter at various pressures of oxygen |</p>
<table>
<thead>
<tr>
<th>$p_{O_2}$ value in cm.Hg.abs</th>
<th>Equivalent value (in $\mu$gm.min$^{-1}$) of each measurable division on the scale</th>
<th>Lower-half section</th>
<th>Upper-half section</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>15</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>50</td>
<td>110</td>
<td></td>
</tr>
</tbody>
</table>

From this table, it is evident that the sensitivity of such an apparatus increases as the pressure of the gas, namely oxygen, decreases. Instantaneous response of the apparatus to oxidation is verified by carrying out several athermal tests. A practical difficulty in applying the theoretical calculations, to instruments of similar size, arises because of the lack of exact similarity of surface finish and rotation flutes on the float. In practice, actual calibration with the fluid under the conditions of the experiment is necessary.
4.4.2. The apparatus and the method

A Schematic representation of the apparatus and its auxiliary equipment is shown in figure 13. Oxygen from the cylinder passes through the tower T which contains a filter made of a stainless-steel disc of porosity 4. The gas is purified and dried in the tower by soda asbestos and magnesium perchlorate. The purified dry gas next enters the gas reservoir $B_1$, through a needle valve $N_1$, which is opened at a predetermined figure. $B_1$ and $B_2$ are two gas reservoirs made of brass and each of capacity about 12.5 litres. Such a large capacity is necessary in order to ensure that the rate of gas consumption during the oxidation of the metal will not cause any sudden and appreciable change of pressure. The gas stream as it comes out of $B_1$, has three possible routes. It can pass through $R$ (the Rotameter), or $D_1$, a diaphragm valve, into the reservoir $B_2$, or alternatively, it can enter the furnace tube $C$ through the diaphragm valve $D_3$. During filling of the reservoirs $B_1$ and $B_2$ only, the valve $D_1$ is kept opened while $D_3$ is closed. Opening of $D_1$ not only saves time, but at the same time the gas-flow through the instrument would be kept at a minimum which reduces the chance of damage to the instrument. The needle valve $N_2$ is used to regulate the rate of efflux of gas from the apparatus and is set to maintain a pre-determined pressure. A mercury manometer, range 0-30 cm.Hg, is used to measure the pressure. $D_2$ is a diaphragm
Constant pressure-differential gas apparatus

Notations: -

B₁, B₂ : Gas reservoirs
C : Reaction tube
D₁, D₂, D₃, D₄, D₅ : Diaphragm valves
F : Furnace
N₁, N₂ : Needle valves
P : Brass rod
R : Rotameter
T : Tower

Fig. 13.
valve which serves the same purpose as \( N_2 \) and is used only for evacuating the apparatus. In normal working of the apparatus both \( D_1 \) and \( D_2 \) are closed. The diaphragm valve \( D_4 \) is connected to the outlet of the apparatus which is joined to the suction pipe of a high vacuum pump of ISC-50 series as supplied by Edwards High Vacuum Ltd. It is a single stage, rotary model and is capable of attaining ultimate vacuum of 0.005 mm.Hg, and with a displacement at normal speed of 48 litres/min. Any required gas such as hydrogen or argon (and which were used in the present work for pre-oxidation annealing of the specimen) can be admitted in the furnace tube C through the diaphragm valve \( D_5 \) and taken out through \( D_4 \) when required.

The furnace \( F \) is a Wild-Barfield horizontal high temperature laboratory tube furnace. It is capable of accommodating two standard combustion tubes 1\( \frac{1}{4} \)" outside diameter, and has an effective heating length of 6" (in). The chamber is centrally positioned in the case between two end vestibules of insulating brick, through which there are two 1\( \frac{3}{8} \)" diameter holes to accommodate the tubes. The space between the refractory chamber and the furnace case is filled with high grade insulating powder. Within the chambers are four equally spaced heating elements of silicon carbide. These run horizontally through the chamber, one being
situated in each corner. An entry into the chamber is provided for the insertion of a thermocouple for temperature measurement. A platinum-platinum/rhodium thermocouple was used which has a temperature range of 0 - 1400°C. The temperature in the heated zone was controlled by a saturable reactor unit to within ± 1°C.

The furnace tube was aluminous porcelain ("Pythagoras") of nominal bore 1" and 30" long. The valve D3, which as stated before, isolates the upstream of the apparatus from the reaction tube C, is connected into the tube through a flanged end of a brass cylinder which fits closely round the tube for a length of about an inch. The open end of the cylinder is shaped to retain an O-ring which fits tightly round the tube. A brass mating ring, designed to make metal-to-metal contact with the open end of the cylinder, is bolted to the flanged end of the fitting, thus ensuring a vacuum-tight sealing arrangement. At the other end of the furnace tube, exactly the same design of fitting is used, except that provision is made for entry into the flanged end of a freely movable brass rod P, which is ½" diameter and about 15" long. Such a provision was made in case some athermal studies became necessary. The whole system is vacuum tight and capable of retaining a vacuum of the order of 0.4 mm. of mercury for more than 72 hours. Brass tubing
was used to connect all parts of the apparatus and was rigidly supported wherever possible to minimise the vibrations of the pump reaching the Rotameter. Minimum vibration is an essential requirement for accurate and reliable measurement. The Rotameter was sealed at the ends with the brass holders by means of a special wax which ensures tight sealing to a glass-metal contact.

Initially with the pump running, \( D_1, D_2, D_3, D_4 \) and \( N_2 \) open, and \( N_1, D_5 \) closed, the reservoirs and the reaction tube are evacuated. \( D_2, D_3, D_4 \) and \( N_2 \) are then closed and \( N_1 \) is opened until sufficient purified oxygen has been admitted to give the required pressure with \( N_1 \) and \( D_1 \) closed. The brass fitting carrying the rod is then removed. The prepared specimen is pushed into the cold reaction zone. The fitting is then replaced, \( D_4 \) is opened and when the tube has been evacuated \( D_4 \) is closed. The gas used for annealing is admitted to the tube \( C \) through the valve \( D_5 \); with \( D_3, D_4, D_5 \) closed, the furnace is switched on. When the required furnace temperature has been reached, the tube is evacuated by pumping out the annealing gas by opening \( D_4 \). With the empty tube the metal specimen at the hot zone is ready for the oxidation test. \( D_4 \) is now closed and \( D_3 \) is opened to admit oxygen into the reaction tube \( C \) to react with the metal. Before starting the test, the reference flow rate (i.e. R.F.R.) of the
apparatus has to be set. For any setting \( D_1, D_2, D_3, D_4 \) are closed while \( N_1, N_2 \) are opened at suitable (predetermined) figures to avoid any pressure variation during the oxidation experiment. With this adjustment having been made at a particular pressure of oxygen in the apparatus, the total amount of gas coming out off \( B_1 \) will pass through the instrument i.e. the Rotameter and this is taken as the reference flow rate. This R.F.R. value is obtained at any time during the test whenever the valve \( D_3 \) is closed. At constant pressure the value of this flow rate remains practically constant as long as the settings of \( N_1, N_2 \) are not altered. With \( D_3 \) opened during the oxidation experiment, the gas stream would divide itself into two possible routes instead of three as mentioned earlier, because \( D_1 \) is closed now. The two routes are through \( D_3 \) and through the instrument \( R \). The instrument reading (i.e. I.R.) is taken at the shortest possible interval of time. The difference in the mass rate of flow (i.e. R.F.R.-I.R.) may be found by reference to the calibration curve obtained under the same experimental conditions. This value divided by the area of the specimen gives the instantaneous reaction rate which is expressed in \( \mu g m.m i n^{-1}.c m^{-2} \). The area of the specimen at a particular temperature and \( p_{O_2} \)-value, is a critical one in order to keep the float running within the Rotameter scale.
The critical area is found in every case by trial and error.

4.4.3. Calibration of the apparatus

The apparatus was calibrated for oxygen at 7.6 cm.
and 29 cm.Hg.absolute. If the viscosity of the gas may be
considered to be independent of pressure, the scale range in
$\text{cm}^3 \text{sec}^{-1}$ would be independent of pressure and the range of
mass rate of flow would be directly proportional to the
absolute pressure. The calibration procedure is the same
at both pressures of oxygen, and here the procedure to
calibrate the instrument at 76 mm.Hg.absolute is described.

First the apparatus is evacuated completely and then charged
with oxygen as described in the previous section. All the
valves namely $D_2$, $D_3$, $D_4$ and $N_2$ are closed. With $N_1$ and $D_1$
closed, the final pressure should be a little in excess of
76.25 mm. $N_2$ is then opened to give a predetermined
instrument reading. The time is taken for the pressure to
fall from 76.25 to 75.75 mm. and, during this time, instrument
readings are taken at fixed intervals of time, e.g. one
minute or, half a minute. Readings are obtained accurately
by using a cathetometer and to ensure the accuracy of
calibration, only clean mercury is used and care is taken to
make sure that sticking does not occur. The mass rate of
flow, in micrograms per minute, is calculated for the mean
instrument reading by using the following expression,
\[
\frac{0.5 \times \nu \times 288 \times 1429}{760 \times t \times T}
\]

where 0.5 is the change of pressure (i.e. 76.25 - 75.75) (in mm.),
\( \nu \) is the volume (in cm\(^3\)) of upstream of the gas of the apparatus,
288 is the standard temperature (in \( ^{0}\text{K} \)),
1429 is the standard density of oxygen (in \( \mu \text{gm/cm}^3 \)),
760 is the standard pressure (in mm.),
t is the time taken (in minutes) and
T is the temperature of the gas (in \( ^{0}\text{K} \)).

By closing \( N_2 \) and opening \( N_1 \) again, the procedure is repeated a sufficient number of times at different mean instrument readings to enable an accurate calibration curve to be drawn.

Figure 15 and 16 show the calibration curves drawn for the instrument specified using purified oxygen at 76 mm. and 290 mm. Hg. absolute respectively.
4.5. Manometric method

4.5.1. Principle

The manometric method for the determination of oxidation rates is very simple in principle. The apparatus consists essentially of a closed system of a heated reaction tube and a manometer. The rate of consumption of oxygen by the metal specimen is measured by following the decrease in pressure of oxygen over the metal in the closed system. If absolute values of the gas consumption are required, the volume of the apparatus must be determined. By proper conversion, the decrease in pressure of oxygen can be expressed in terms of $W$ (weight of oxygen consumed by the unit area of the specimen) and thus a $W$ against $t$ (the time) plot can be obtained. This method would not be recommended for experiments involving mixed gases. The reason is simply that the effect of thermal diffusion introduces certain errors which are difficult to estimate [Dunn (86)]. Further, since the oxidation process in such a method is followed by a decrease in oxygen pressure, it is desirable to choose a metal whose oxidation rate is independent of pressure.

4.5.2. The apparatus and the method

The apparatus used in this investigation however, differs from the standard practice in that, both manometric and
differential rate methods are incorporated in the same apparatus. A schematic diagram is shown in figure 14. Notations in the figure carry the same meaning as in the previous section - 4.4.2. Here $D_6$ and $D_7$ are extra diaphragm valves added to the system. A vacustat with a range of 0 - 10 mm. is also connected to the system. The same type of vacuum tight brass fittings are used at both ends of the reaction tube, C. Unlike the previous case, (Section 4.4.2) the brass fitting does not carry a brass rod. Thus the gas coming through $D_3$ with $D_4$, $D_5$ closed, enters the tube from both ends. This ensures not only a quick uniform distribution of temperature in the gaseous phase but also permits oxidation to proceed from both ends of the metal specimen uniformly. This is a particular advantage during the study of oxidation at a lower temperature when a larger surface area of the specimen is required.

The furnace is a Wild-Barfield tube furnace and the pump used is a single-stage, rotary type. Details of the furnace and the pump are given in the section 4.4.2.

With the pump running, the apparatus is completely evacuated by opening $D_1$, $D_2$, $D_3$, $D_4$, $D_6$, $D_7$ and $N_2$ with $N_1$ and $D_5$ closed. Next $D_2$, $D_3$, $D_4$ and $N_2$ are closed and $N_1$ is opened to admit purified dry oxygen from the drying Tower T into the reservoirs $B_1$ and $B_2$. When the required pressure of oxygen,
Fig. 14.

Manometric apparatus, coupled with the constant pressure-differential gas set up.

Notations:

- $B_1, B_2$: Gas reservoirs
- $C$: Reaction tube
- $D_1$ to $D_7$: Diaphragm valves
- $F$: Furnace
- $L$: Connecting brass tube
- $N_1, N_2$: Needle valves
- $R$: Rotameter
- $T$: Tower

To vacuum

To manometer

To pump
as registered on the manometer or vacustat, was reached the valve \( N_4 \) was closed but \( D_1, D_6 \) were still kept opened. Since the present study involves the oxidation at pressures higher than 10 mm Hg absolute, the vacustat was not used and therefore was isolated from the rest of the system by closing \( D_7 \). The end of the reaction tube, which is opposite to the diaphragm valves \( D_5, D_4 \), contains a removable connecting brass tube \( L \). This detachable tube was removed and the prepared specimen was pushed into the reaction zone of the tube at room temperature. The bend \( L \) was replaced. With \( D_5 \) closed, \( D_4 \) was opened to evacuate the tube. The annealing gas was admitted to the tube by opening \( D_5 \) and closing \( D_4 \). Next the valves \( D_3, D_4 \) and \( D_5 \) were closed and the furnace was switched on. When the required temperature was reached, the tube \( C \) was emptied by pumping out the annealing gas through \( D_4 \). The metal specimen in the empty tube was thus ready for the subsequent oxidation experiment (with \( D_4 \) closed) with oxygen gas at a predetermined pressure in the reservoirs and the brass tubing up to the valve \( D_3 \). The total volume of oxygen that is present on this side of the apparatus is much too great as compared to the volume of oxygen to be consumed by the specimen during oxidation and thus it is difficult to obtain an accurately measurable drop in oxygen pressure during oxidation with \( D_3 \) opened. This difficulty can be overcome by having \( D_6 \) closed when oxidation is proceeding.
The procedure adopted, when the metal specimen in the reaction tube C is ready for oxidation, is to open valve D$_3$ and at the same time D$_6$ is closed. The opening of D$_3$ and closing of D$_6$ should be completed as quickly as possible, for example, in a few seconds. In the present work, oxidation data were found to be independent of $p_{O_2}$-value and the results were obtained at $p_{O_2}$-value around 7.6 cm. Thus the manometer was used and not the vacustat and D$_7$ was closed always. Readings were then taken by observing the drop in pressure in the manometer at definite intervals of time. Accurate readings were obtained by using a cathetometer. This was done by aligning one of the horizontal cross-wires with the top of the mercury meniscus. Knowing the total volume of oxygen available to the reaction, amount of oxygen consumed by the unit area of the specimen, W at different time intervals, t may be calculated.
4.6. Oxidation of Iron

4.6.1. General procedure

Both Oxidation Kinetics of iron and cobalt have been studied in the present investigation. The difficulties experienced in the study of iron, which was studied first, were helpful to plan a smooth programme for the subsequent work on the oxidation of cobalt. Thus most of the difficulties in the present study were encountered during the work on the oxidation of iron.

The preparation of the specimen and the description of the apparatus are given in sections 4.1.3. and 4.4.2. respectively. A schematic diagram of the apparatus with its auxiliary equipment is shown in figure 13.

After complete evacuation of the apparatus, oxygen was admitted to the required pressure with $D_1$, $N_1$ opened, while $D_2$, $D_3$, $N_2$ being kept closed; $D_4$ and $D_5$ were also closed but it was not essential because by closing $D_2$, $D_3$ and $N_2$ the reaction side was already isolated from the gas supplying side. After the required amount of oxygen was admitted as registered by the manometer $M$, the valves $N_1$, $D_1$, were closed. The brass fitting, carrying the rod $P$, was next removed. The prepared specimen of iron was placed on silica beads and put into a refractory (alumina silicate) boat which was finally pushed into the cold reaction zone of the tube $C$. The fitting was
then replaced. The diaphragm valve $D_4$ was opened to evacuate the tube. With $D_4$ closed, hydrogen was next introduced through $D_5$ and the tube was purged several times. Hydrogen was used to reduce any air-formed film which may be present on the specimen. With this gas inside the tube and $D_5$ closed, the furnace was switched on and the temperature was raised slowly to about $600^\circ C$. At this stage fresh hydrogen was introduced again. The temperature of the furnace was next raised slowly to about $800^\circ C$ and the specimen was given a reducing treatment for about two hours. In the mean time, the needle valves $N_1$ and $N_2$ were next opened and adjusted so that the pressure variation for the duration of the oxidation experiment would be negligible. The extent to which $N_1$ and $N_2$ were required to be opened under particular set of oxidation conditions was found by trial and error. After this adjustment was made, the float was rotating steadily at some level in the instrument. The equivalent flow rate in $\mu g/m$ was the reference flow rate of the apparatus, which may alter if $N_1$, $N_2$ were not opened to the same extent everytime. After the reduction anneal, Hydrogen was pumped out of the tube. Argon gas was now admitted to the tube to remove any last trace of hydrogen (although the hydrogen solubility in iron at $800^\circ C$ is very low e.g. 1 p.p.m.).
The temperature was adjusted to the required figure and an argon-anneal of about half-an-hour was carried out with fresh argon introduced at frequent intervals. After the argon treatment, the tube was evacuated completely. Prior to admitting oxygen to the reaction tube i.e. prior to the oxidation test, more oxygen was admitted through \( N_1 \) to the reservoir to compensate for the reduction in pressure due to the volume that would be taken up by the tube \( C \). The exact amount of excess oxygen was determined beforehand by trial and error by running blank tests at the experimental temperatures. After admitting the correct amount of excess oxygen the valve \( N_1 \) was returned to the original setting figure. Next the oxidation test was carried out by opening \( D_3 \) after making sure that \( D_1, D_2, D_4, D_5 \) were all closed. As soon as conditions were steady, which may be after 30 seconds or less, instrument readings were taken at the shortest possible intervals of time. At any instant the instrument reading (I.R.) gives the amount of gas passing from \( B_4 \) to \( B_2 \). Hence the reference flow rate (R.F.R.) less the instantaneous instrument reading (I.R.) (values of both these readings being obtained from the calibration curve in \( \mu \text{g/m}\text{m/min} \)) would give the instantaneous reaction rate for the specimen. On dividing this by the surface area of the specimen, the instantaneous oxidation rate is obtained in
μgm/cm². min. — The solubility of oxygen in iron is very low (less than 0.003 wt. % in F.C.C. and less than 0.022 wt % in B.C.C iron). So the amount of oxygen dissolved in the metal is assumed to be negligible and results are interpreted (sec. 6) purely in terms of oxidation reaction. Also the working pressures of oxygen 7.6 and 29 cm. are high enough to prevent any dissociation of wüstite already formed, so wüstite is taken to be the main oxide produced.

The same procedure was adopted to study the kinetics of oxidation at both pressures of oxygen namely, 7.6 cm. and 29 cm. Hg. absolute. The following points are worth mentioning.

I) The first comment is with regard to the setting of the needle valve N₁. Just before the oxidation test, N₁ was operated to a specific degree in order to admit the correct amount of excess oxygen which would account for the volume of oxygen taken up by the reaction tube only. This setting of N₁ was determined from blank tests as mentioned earlier. It was found that the setting of N₁ not only depends upon the volume of the particular tube but also on the pressure of oxygen and to a certain extent on the experimental temperature. Thus a wider opening of N₁ was required in the following cases,
Case 1.) for the tube of higher capacity;

Case 2.) when the apparatus is at a higher pressure; this is because with higher pressure inside the apparatus, the greater will be the resistance to the flow of oxygen which is coming from the tower into the reservoir. As a result of this, \( N_1 \) has to be opened more in order to overcome the resistance from inside;

Case 3.) for high temperatures; but the extent to which the valve-opening varies with temperature, is not so marked as it is for the two above cases.

II. The first instrument reading was obtained at an earlier time while working at lower pressure of oxygen i.e. at \( p_0^2 = 7.6 \text{ cm.} \) than \( p^2 = 29 \text{ cm. Hg. absolute} \); the reason is probably connected with the greater capacity time-lag at the higher pressures.

III. Proper de-gassing of a new tube at a high temperature was found to be an essential part of the procedure to remove any trace of absorbed moisture, as otherwise unusually low oxidation results were obtained. Lower oxidation rates can also result if the brass rod \( P \) is pushed too far inside the tube \( C \).
4.6.2. Procedure to study velvet oxide formation

In this section, certain experimental procedures will be described which were followed to study the interesting phenomenon of velvet-oxide formation. Such oxides are mostly produced in the B.C.C. temperature range, while the usual metallic grey oxides are found in the F.C.C. range on cooling down. Various possible combinations of the following experimental procedures were carried out in order to elucidate the mechanism of formation of such oxides. The procedures included:

1) cooling down the specimen after the oxidation test, either quickly by drawing in air, or slowly in the furnace;
2) varying the extent of oxidation from a very short time to a longer period;
3) changing the cooling atmosphere in the furnace from air, argon, oxygen to pure vacuum;
4) carrying out the cooling either continuously or intermittently;
5) applying different pressures of oxygen in the apparatus.

Certain conclusions were reached after careful observations during these various experiments. These will be given in section (8.1.1.)

4.6.3. Calculation of $dW/dt$

The method of calculating $dW/dt$ will be shown first and this will be followed by the method showing how the oxide
thickness is estimated graphically. A typical data-sheet at a particular temperature and pressure is given below, where the equivalent values of reference flow rate (R.F.R.) and instrument reading (I.R.) (in μgm/min.) are obtained from the calibration-curve. The values obtained by subtracting I.R. from R.F.R. (in μgm/min) represent the rate of flow of oxygen into the tube to oxidize the specimen or, in other words, it represents the rate of oxygen consumption by the specimen. This value when divided by the surface area of the specimen, will give \( \frac{dW}{dt} \) in μgm/cm^2.min. A typical set of calculation is shown in Table-4.

Table-4

Calculation of \( \frac{dW}{dt} \) at \( p_{O_2} = 7.6 \) cm. for the oxidation of

F.C.C - iron ( at 965°C)

Surface area of the specimen : - 0.6016 cm^2

R.F.R : - 13.0 which is equivalent to 3,700 μgm/min.

<table>
<thead>
<tr>
<th>Time (secs)</th>
<th>I.R. (number)</th>
<th>Equivalent values of I.R. (μgm/min.)</th>
<th>R.F.R-I.R. (μgm/min.)</th>
<th>( \frac{dW}{dt} ) (μgm/cm^2.min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23( \frac{1}{2} )</td>
<td>3</td>
<td>650</td>
<td>3050</td>
<td>5070</td>
</tr>
<tr>
<td>26</td>
<td>3.6</td>
<td>745</td>
<td>2955</td>
<td>4911</td>
</tr>
<tr>
<td>28</td>
<td>4.0</td>
<td>800</td>
<td>2900</td>
<td>4820</td>
</tr>
<tr>
<td>31</td>
<td>4.5</td>
<td>875</td>
<td>2825</td>
<td>4696</td>
</tr>
</tbody>
</table>
4.6.4. Estimation of oxide thickness

The graphical estimation of oxide thickness from a plot of rate, \( \frac{dW}{dt} \) against time, \( t \) is not a very accurate one; but one can get an approximate idea about the thickness range. Calculation is based on the following assumptions, namely

I) The graph is a straight line when extrapolated to zero time, e.g. fig. 17, although the first reading was obtained at a later stage but not before 20 seconds in any case;

II) the non-stoichiometric oxide is assumed to be \( \text{Fe}_0.907^0 \) whose density is 5.62 g/cm\(^3\).

Since the oxide groups on top of the specimen, the length and breadth of the oxide and not the width or thickness are therefore assumed to be the same as that of the specimen. A typical calculation is shown below. The experimental temperature was 965°C with \( p_{O_2} = 7.6 \) cm. The oxide thickness is estimated for a time up to 36\( \frac{1}{2} \) seconds.

A general sketch, showing the variation of \( \frac{dW}{dt} \) with time.
Step - (1)

\[ (dW/dt) = 6150 \mu g m. of oxygen/min. cm^2 \] of the specimen at \( t=0 \)

and \[ (dW/dt) = 4446 \mu g m. of oxygen/min. cm^2 \] of the specimen at \( t=36\frac{1}{2} \)

Total amount of oxygen consumed by the specimen is equal to the area, \( A B C D \). Since \( A.B.C.D \) is a trapezium, the area = \( \frac{1}{2} (6150 + 4446) \times \frac{36.5}{60} = 3222 \)

So the total amount of oxygen consumed by the specimen = 3222 \( \mu g m \) of oxygen/cm^2 of the specimen.

Step -(2)

For wüstite, \( (Fe_0.907^0) \) of molecular weight 66.65 it can be written that,

1 part by weight of oxygen = \( \frac{66.65}{16} \) i.e. 4.1656 parts by weight of wüstite.

\[ 3222 \mu g m. of oxygen/cm^2 \] of the specimen = \( 3222 \times 4.1656 = 1.342 \times 10^4 \) \( \mu g m \) of wüstite/cm^2 of the specimen.

Step -(3)

Total weight of oxide = volume of oxide \times \text{density of oxide}

\[ = (l \times b \times t_h)_{\text{oxide}} \times 5.62 \times 10^6 \mu g m. \]

where, \( l = \) length of the oxide = length of the specimen = 0.478 cm.

\( b = \) breadth of the oxide = breadth of the specimen = 0.449 cm.

\( t_h = \) thickness of the oxide.
Therefore, $1.342 \times 10^{11} \mu \text{gm} \text{ of wüstite/cm}^2 \text{ of the specimen}$

$= \text{total weight of the oxide/cm}^2 \text{ of the specimen}$

$= \frac{0.478 \times 0.449 \times t_h \times 5.62 \times 10^6}{(\text{area of the specimen})}$

Area of the specimen is $0.6016 \text{ cm}^2$.

$\therefore t_h = \frac{1.342 \times 10^{11} \times 0.6016}{0.478 \times 0.449 \times 5.62 \times 10^6} \text{ cm}$

$= 6.694 \times 10^3 \text{ cm}$

$= 6.694 \times 10^5 \text{ Å}$

$= \text{thickness of the oxide}$.
4.7. Oxidation of cobalt

4.7.1. General procedure

The description of the apparatus has been given in detail in section 4.5.2. Preparation of the specimen has been already described in section 4.1.3. A Schematic diagram of the apparatus is shown in figure (14).

Unlike the case of iron, the experimental procedure is quite straightforward here. The prepared specimen was pushed into the cold reaction zone of the tube without placing it on a refractory boat. To prevent any inflow of air into the empty apparatus the valves \( D_2, D_3, N_2 \) were closed when the specimen was pushed inside the tube. The tube was next evacuated through \( D_4 \) with \( D_5 \) closed. Hydrogen was introduced into the tube by opening \( D_5 \) and closing down \( D_4 \).

Hydrogen and argon were used in the same sequence as in the case of iron. The purpose was the same in both cases. The furnace was switched on as soon as the hydrogen was admitted. Reduction annealing of one hour followed by an argon annealing of half-an-hour were given at the particular experimental temperature. On the gas inlet side of the apparatus, dry oxygen was introduced to the required pressure. After the annealing treatments, the tube was evacuated completely with the cobalt specimen in the hot reaction zone of the tube, ready for the oxidation test. The test was
carried out, as described before, by simultaneous opening and closing of \( D_3 \) and \( D_6 \) respectively. Readings were taken every minute or half-a-minute when there was any change in pressure of the manometer as observed through a cathetometer. The cathetometer can be used to read a pressure change of as low as 0.001 cm on the manometer quite accurately and it is estimated that it is possible to read to 0.0005 cm Hg.

The same procedures were followed for different pressures of oxygen, namely 2 cm., 7.6 cm., 29 cm. Hg. absolute.

In Cubicciotti's work (87) the gas volume in the temperature gradient between the furnace and the room temperature of the manometer was filled as completely as possible with glass rods to minimise fluctuations from changes in the temperature gradient. In the present investigation, it is assumed that the experimental temperature is low enough to avoid such fluctuations, thus the glass rods were not used. Calculation of the results and the sensitivity of the procedure will be given in the next section. Some striking differences in the colour and structures of the oxides were noticed on cooling down after the tests (sec. 8.2).

4.7.2. Calculation of W-values

The oxidation process of the metal is measured by following the decrease in the pressure of oxygen over the metal in the close system. Suppose the volume of oxygen,
hence the weight of oxygen, available per unit area of the
specimen at the onset of oxidation is $M$ and that during
subsequent oxidation be given by different values of $N$
as the $pO_2$-value decreased with time. Then $(M-N)$-values will
give the various weights, $W$ of oxygen consumed by unit area of the
specimen at different periods. In order to evaluate the
absolute values of oxygen consumption, the volume of the
apparatus i.e. the space enclosed between $D_4$, $D_5$ and $D_6$, $D_7$
must be known. From dimensional measurements, this volume
including the volume of the reaction tube is found to be
435 cm$^3$ at atmospheric pressure. Blank tests at various
temperatures showed that with the present procedure, the low
experimental temperatures tried and the design of the apparatus
(where the heating zone covers only about 20 cm. inside the
tube), there is negligible change in the volume of oxygen with
temperature; thus using the volume-correction for temperature,
the $W$-values alter with time by 1 to 3 $\mu$gm/cm$^2$ only from the
figures accepted here, at the maximum temperature tried. So the
volume of oxygen in the enclosed space is always taken to be
435 c.c. at one atmospheric pressure. The available data on the
density of oxygen at one atmospheric pressure is $7.7 \times 10^{-4}$
gm/cm$^3$ at an arbitrary temperature of 500$^\circ$K. One typical
set of calculation is shown in Table-5 below,
Table 5

Calculation of the weight gain, W on the oxidation of F.C.C. cobalt (at 470°C).

Surface area of the specimen: $20.5432 \text{ cm}^2$

Density of oxygen: $7.7 \times 10^{-4} \text{ gm/cm}^3$

Conversion factor, $x^* = \frac{7.7 \times 10^{-4}}{20.5432 \times \frac{435}{76}} \text{ gm of oxygen/cm}^2$

At the onset of oxidation, $p_{o2} = 7.617 \text{ cm}$, which is equivalent to,

$$M = 7.617 \times x^*$$

$$= 16.34113 \times 10^{-4} \text{ gm of oxygen/cm}^2$$

of the specimen

<table>
<thead>
<tr>
<th>Time (minute)</th>
<th>Cathetometer value (cm), $B$</th>
<th>$B' x^* (\text{gm/cm}^2)$, $N$</th>
<th>$(M-N)_W (\mu\text{gm/cm}^2)$, $W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1\frac{1}{2}$</td>
<td>3.7965x2=7.593</td>
<td>16.28965x10^{-4}</td>
<td>5.148</td>
</tr>
<tr>
<td>2</td>
<td>3.7885x2=7.577</td>
<td>16.25532x10^{-4}</td>
<td>8.581</td>
</tr>
<tr>
<td>$2\frac{1}{2}$</td>
<td>3.7830x2=7.566</td>
<td>16.23172x10^{-4}</td>
<td>10.941</td>
</tr>
<tr>
<td>3</td>
<td>3.7785x2=7.557</td>
<td>16.21241x10^{-4}</td>
<td>12.872</td>
</tr>
</tbody>
</table>

The cathetometer reading gives the value on one limb of the manometer, so the reading is to be multiplied by two.

The $(M-N)_W$ values are required $W$ values, where $W$ is the weight of oxygen, consumed by the unit area of the specimen. The sensitivity of the apparatus can be estimated from the above data. For the first two results a cathetometer reading of
3.7965 - 3.7885 = 0.008 cm. gives a weight change by 
8.581 - 5.148 = 3.433 \mu gm/cm^2. Therefore for each measurable 
division on the cathetometer, which can be taken as 0.001 cm, 
the weight change is \frac{3.433}{0.008} \times 0.001 = 0.4 \mu gm/cm^2. Thus the 
apparatus is sensitive to the extent that a change in weight 
of oxygen consumption by 0.4 \mu gm/cm^2 of the specimen, can be 
detected.

4.7.3. Estimation of oxide thickness

The thickness of the oxide scale can be calculated on the 
basis of certain approximations. At 470°C the oxide is assumed 
to be only CoO (cobaltous oxide) of molecular weight 74.94 and 
density 6.437 gm/cm^3. The thickness is calculated for time up 
to 10 minutes when \( W \) becomes equal to 26.388 \mu gm/cm^2.

Thus:

**Step: 1**

1 part by weight of oxygen = \frac{74.94}{16} parts by weight of the 
oxide

\[ \therefore 26.38 \mu gm \text{ of oxygen/cm}^2 \text{ of the specimen} = \frac{74.94 \times 26.388}{16} \mu gm. \]

of oxide/cm^2 of the specimen,

\[ = 123.6 \times \mu gm \text{ of oxide/cm}^2 \text{ of the specimen} \]

**Step: 2**

Total weight of the oxide = volume of oxide \times density of 
oxide

\[ = (1 \times b \times t_{\text{oxide}}) \times 6.437 \times 10^{-6} \mu gm. \]
where,

\[ l = \text{length of the oxide} = \text{length of the specimen} = 4.955 \text{ cm}. \]

\[ b = \text{breadth of the oxide} = \text{breadth of the specimen} = 2.0 \text{ cm}. \]

\[ t_h = \text{thickness of the oxide}, \]

\[ \therefore 123.6 \mu \text{gm of oxide/cm}^2 \text{ of the specimen} = \text{Total weight of the oxide/cm}^2 \text{ of the specimen} \]

\[ = \frac{4.955 \times 2 \times t_h \times 6.437 \times 10^6}{\text{area of the specimen}} \]

and surface area of the specimen = 20.5432 cm\(^2\).

\[ \text{thickness } t_h = \frac{123.6 \times 20.5432}{4.955 \times 2 \times 6.437 \times 10^6} \]

\[ \approx 4 \times 10^3 \text{ Å} \]

The oxide thickness thus obtained is approximate, because the basic assumption of the presence of a single oxide, CoO at 470°C may not be totally correct. The oxide may be a mixture of two, namely CoO and \( \text{Co}_3\text{O}_4 \). Electron and x-ray diffraction of the oxide could only reveal the actual structure of the oxide. However, at a given temperature the \( t_h \) values, either for a mixed, or a single oxide, are found very much similar. This is mainly because of the uniform changes in the oxygen equivalence of the oxide with the changes in the oxide composition, which keep the relevant ratio very much the same. On the basis of the above results it can be said that,

\[ 26.388 \mu \text{gm of oxygen/cm}^2 \text{ of the specimen} \approx 4 \times 10^3 \text{ Å of the oxide film}, \]

\[ \therefore 1 \mu \text{gm of oxygen/cm}^2 \text{ of the specimen} \approx 150 \text{ Å of the oxide film}. \]
4.8. Structural Examination of oxides

4.8.1. Cobalt-oxide

The highest temperature that was used to study the oxidation kinetics was 520°C. From the phase diagram of the cobalt-oxygen system, there is not eutectoid decomposition or any other solid phase reactions when oxides are cooled down from this temperature. This is supported by the work of Phalnikar, et.al. (73). Thus it can be assumed that CoO/ or Co$_3$O$_4$ formed at the experimental temperature can be retained when cooled to room temperature inside the tube. The film thickness here ranges from about 400 Å at 324°C to 5,000 Å at 520°C for the time during which the oxidation process was studied. Such a thin film makes it possible to use the transmission electron diffraction method. Besides this method, X-ray techniques were also used to study the structure. The as-received metal was studied in addition to the oxides. In the case of cobalt, and unlike iron, the effect of grain size on the crystal structure [Owen, et.al (70)] makes it possible for either of the allotropic modifications of cobalt namely F.C.C. and H.C.P. structures or a mixture of both to be stable at room temperature. So X-ray diffraction was carried out to determine the crystal structure of the as-received sample. Some metallography of the oxide was also carried out.
4.8.2. Electron diffraction and micrography of cobalt-oxide

A transmission method can be used directly on a thin metal film with superimposed oxide film, [White, (88)], but in the present case, the metal was quite thick. Therefore the alternative procedure of stripping off the oxide layer from the metal was followed. This may be done electrolytically or chemically, the oxide film being lifted off after attack of the metal at the metal/oxide interface. The chemical method was found to be a success. A saturated solution of iodine in 10% potassium iodide in water was found to be the right reagent to attack the metal/oxide interface and thereby lifting the oxide film from the metal. Evans (89) adopted the same solution in his work. A freshly prepared reagent was found to be not very active. Reagent which was prepared some two or three weeks earlier, was found to be quite effective. First of all, the metal specimen with the oxide on it, was scratched on one side with a sharp knife-edge to ease the attack on the metal/oxide interface. Then it was dipped into the reagent solution for four to five minutes, washed in methanol, dried and then slowly pushed along the edge of water contained in a beaker. The oxide stripped off gradually. Such stripping was noticed to be predominantly occurring from the side which was not scratched.

The Electrolytic method used by Gulbransen, et al. (90), with some modifications, was not found to be very successful.
Consequently, an electrolytic solution of boiled, saturated potassium chloride was used. Along with the stripping of the oxide films, the metal itself was corroded to some extent, making it impossible to identify and collect the oxide film from the solution with any surety. Unlike Gulbransen's work, a hydrogen atmosphere was not used during electrolysis because of the difficulties in designing the apparatus and this could be the reason for failure of this method.

Once the oxide is stripped off, it is next washed and after washing in water the oxide was removed with a copper grid (100 to 200 μm), dried, and examined at 100 KV in an AEI EM6G microscope equipped with an electron diffraction unit. The oxides formed below 400°C were quite coherent, but those formed at high temperatures were non-coherent, light and mechanically unstable and a certain amount of difficulties were faced while working with the latter type. Along with the electron diffraction, electron micrographs were also taken for the same area.

4.8.3. X-ray diffraction of cobalt oxide

A Phillips X-ray diffraction camera was used of 5.73 cm diameter in which the specimen rotates horizontally. A Straumanis-mounting was applied using Cobalt $\gamma$-radiation ($2 \times 10^{-14} \mu A$). In the case of the as-received metal sheet, it was cut into a thin strip ($\sim 1/8$ in. wide), and then immersed in hydrochloric acid for the purpose of both
removing any strained edges which may be produced during cutting, and for subsequently thinning the strip down into a wire which was then used directly in the diffraction camera as the specimen.

While studying the oxide, the stripped off oxide films were fine enough to stick them directly onto a fine glass fibre by means of glue and then put into the camera. An exposure of about four hours was given in both cases.

4.8.4. Iron oxide

In the studies on the oxidation of iron, the oxide thickness varies with temperature and pressure of oxygen, its magnitude ranges from 10 to 70 μ for the period during which the oxidation process was studied. Knowledge about the bulk structure of the oxide is a more fundamental study than the knowledge about the surface topography; but the transmission electron diffraction method is not suitable here, because the oxide is too thick. X-ray diffraction method appears to be a more suitable method but the oxide formed, namely, Wüstitite, reverts to higher oxides when cooled from the experimental temperature. The eutectoid decomposition of Wüstitite at 570°C has been the subject of investigation by several workers, namely Davies, et al. (54). Therefore in the present case, examination of the oxide at room temperature by any method would be futile. Use of a high temperature X-ray camera or a very rapid cooling to retain Wüstitite at room
temperature may be a useful technique to study the oxide structure that was present at the experimental temperature, but was considered to be outside the scope of the present research. Hence in the present investigation emphasis has been placed on the measurement of reaction rate kinetics only and some optical microscopic studies.
RESULTS
5. Results

In this chapter results of the kinetic measurements are given only. In the three sub-sections, results of the calibration for the oxidation of iron and of cobalt are dealt with. Results of the examination of the oxide by different techniques are given later.

5.1. Calibration

Calibrations were carried out at two different pressures of oxygen, namely $p_{O_2} = 7.6$ and 29 cm.Hg.absolute. The change in the mass rate of flow of oxygen through the rotameter can be expected to be greater at higher pressure of oxygen. The calibration results are given in Table-6 and 7, and curves are shown in figs. 15 and 16.

5.2. Oxidation of iron

To obtain consistent results at each temperature, a large number of kinetic measurements were necessary and in all amounted to nearly three hundred. Instead of showing all the results, three typical temperatures are chosen, for which the data are given in tabulated forms. These three temperatures include one in B.C.C.-iron, one in F.C.C.-iron and one at or nearest to the allotropic transformation temperature. Thus, Tables 8,9,10 show results that were obtained at $p_{O_2} = 7.6$ cm.Hg. absolute and Tables-11,12,13 at $p_{O_2} = 29$ cm.Hg. absolute.
In all these six tables, the sixth column gives the inverse values of \((\frac{dW}{dt})\) and squares of the inverse values are given in the seventh column. Units of the sixth and seventh column are not shown because they are obvious from the units of \((\frac{dW}{dt})\) values. The \((\frac{dW}{dt})^{-1}\) and \((\frac{dW}{dt})^{-2}\) values are calculated for the first few readings, the main object being to illustrate the sequence with which these values change at the initial stages of oxidation. The following abbreviations are used in tables 8 to 17. 

- **R.F.R.** means reference flow rate 
- **I.R.** signifies instrument reading 
- \(T_c\) is the temperature of allotropic transformation 
- \((K_p)_M\) and \((K_l)_M\) are the parabolic - and linear - rate constants respectively of the modified parabolic rate law.

Equivalent values of I.R. and R.F.R. are obtained from the calibration curve. Plots of \(\frac{dW}{dt}\) against \(t\) at \(p_{o2} = 7.6\) cm. are shown at \(965^\circ C\) and \(834^\circ C\) in figs. 17 and 18 respectively. Similar type of plots were obtained at \(p_{o2} = 29\) cm. In order to get an idea of the order of the oxide thickness formed during the initial stages of oxidation, the \(W\)-values were qualitatively estimated from the plot of \(\frac{dW}{dt}\) against \(t\). The film thickness is thus estimated to vary between 10 and 70\(\mu\) depending on the temperature and \(p_{o2}\) -value.
Figure 19 is a plot of \( \log_{10} (dW/dt) \) against \( \log_{10} t \). Two curves are shown here at \( p_{O_2} = 29 \) cm, one at 965\(^\circ\)C (curve-1) and the other at 838\(^\circ\)C (curve-2). Slope of curve (1) is constant throughout and is equal to 2 \( \pm \) 0.1. On the other hand, two slopes were obtained for curve (2) where an initial slope of 1.5 \( \pm \) 0.1 is followed by a slope equals to 2 \( \pm \) 0.1. Except for the results on the oxidation of F.C.C. iron at \( p_{O_2} = 29 \) cm, when curve (1) type was obtained, in all other cases graphs of curve (2) type were obtained. Figures 20 and 21 show the plot of \( (dW/dt)^{-2} \) against \( t \) for the oxidation of F.C.C. iron at \( p_{O_2} = 7.6 \) and 29 cm. respectively. Values of the parabolic rate constant, \( (K_P)_M \), and linear rate constant, \( (K_L)_M \), were calculated by using the method of least squares from which the Arrhenius plots with \( \log_{10} (K_P)_M \) and \( \log_{10} (K_L)_M \) both obtained from results at \( p_{O_2} = 7.6 \) cm and 29 cm plotted as ordinates were drawn as shown in figs 22, 23, 24, and 25. The notations \( (K_P)_M \) and \( (K_L)_M \) are used to denote the rate constants as derived from the modified parabolic rate-law and are thus distinguished from the rate constants \( K_P \) or \( K_L \) derived from only true parabolic or true linear law.
5.3. Oxidation of cobalt

In view of decreasing pressure during a single run, it was necessary to estimate the effect, if any, of oxygen pressure on the oxidation rate. Three runs were carried out at different temperatures, e.g. 350, 400 and 420°C, one at 2 cm. of oxygen pressure, the second one at 7.6 cm. and the third at 29 cm. The results showed that the rate remains almost the same i.e. within the experimental error despite a fourteen fold change in oxygen pressure. To save repetition, these results at different \( p_{O_2} \) values are not given, only results at \( p_{O_2} \sim 7.6 \text{ cm.Hg.} \) The normal decrease of pressure during a single run, reaching a maximum of 0.2% of the initial pressure when the temperature was 320°C and 2% at 520°C, did not therefore influence the oxidation rates. Temperatures 320°C and 520°C are the lowest and highest temperatures tried in this investigation. X-ray diffraction work revealed that at higher temperatures of oxidation i.e. above 400°C in the F.C.C. range of cobalt about 60% of cobalt oxide, \( \text{(Co}_2\text{O}_4) \) and 40% \( \text{(Co}_0 \) are formed, while below 400°C i.e. in the H.C.P. region of cobalt about 90% \( \text{Co}_3\text{O}_4 \) is formed. On the basis of this and assuming \( \text{Co}_3\text{O}_4 \) of density 6.054 and Co 0 of density 6.437 gm/cm³, each microgram of oxygen consumed by unit area of the metal specimen was found equivalent to a film of oxide 150 Å thick, uncorrected for metal roughness factor. The oxide-thickness thus estimated
varied from 5000 Å at 520°C to 400 Å at 320°C. As in the case of iron, typical results are given at three different temperatures. These temperatures include one in H.C.P.-cobalt, one in F.C.C.-cobalt and one at or near the transformation temperature, which was found to be 386°C. Oxidation rates appear to vary quite markedly. Thus two sets of results are given at 386°C.—Tables 18 & 22 illustrate these results. The cathetometer readings represent the values of Hg. - meniscus on one limb of the manometer and to obtain the total pressure these have to be multiplied by two. The following abbreviations are used for Table-22.

T represents temperature in degrees Kelvin, and

$K_0$ is the oxidation rate constant of the direct-logarithmic law.

Oxidation data at various temperatures are plotted in figure-26. The data fall on smooth curves in figure-26 but when plotted semilogarithmically as in figure-27, they are all on straight lines. Arrhenius plot is shown in figure-28 where $\log_{10} K_0$ against $1/T$ is drawn. The solid line represents the line that was obtained from experimental results.
Table-6

Calibration result:

Pressure of oxygen: 7.6 \text{Hg absolute}

<table>
<thead>
<tr>
<th>Instrument reading (number)</th>
<th>Mass rate of flow of oxygen (\text{ugm/min.})</th>
<th>Instrument reading (number)</th>
<th>Mass rate of flow of oxygen (\text{ugm/min.})</th>
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<tbody>
<tr>
<td>1.0</td>
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<td></td>
<td></td>
<td>14.0</td>
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</tbody>
</table>
Table-7

Calibration results :-

Pressure of oxygen :- 29 cm. Hg. absolute

<table>
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<tr>
<th>Instrument reading (number)</th>
<th>Mass rate of oxygen flow (µg/m/min.)</th>
<th>Instrument reading (number)</th>
<th>Mass rate of oxygen flow (µg/m/min.)</th>
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</thead>
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</table>
Calibration curves

At $p_{O_2} = 7.6$ cm.

Fig. 15

At $p_{O_2} = 29$ cm.

Fig. 16
Table 8

Oxidation of B.C.C. iron (at 834°C) at $p_{O_2} = 7.6$ cm.

Weight of the specimen : $0.4840$ gm.
Surface area of the specimen : $1.6250$ cm$^2$
R.F.R. : $13.35$ which is equivalent to $3,985$ $\mu$gm/min.

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<th>Equivalent value of I.R. (µgm/min)</th>
<th>R.F.R-I.R (dW/dt) (µgm/min)</th>
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<th>$(dW/\text{dt})^{-2} \times 10^{-8}$</th>
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Table 9
Oxidation of iron at 911°C (nearest to Tc), and pO₂ = 7.6 cm.
Weight of the specimen: 0.1442 gm.
Surface area of the specimen: 0.5680 cm².
R.F.R.: 13.9 which is equivalent to 4,550 µgm/min.

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<th>Equivalent value of I.R. (µgm/min)</th>
<th>R.F.R - I.R. (µgm/min)</th>
<th>(dW/dt) (µgm/min cm²)</th>
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<th>(dW/dt) x 10⁻⁸</th>
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</table>
Oxidation of F.C.C. - iron (at 965°C) at \( p_{O_2} = 7.6 \text{ cm} \).

Weight of the specimen: 0.1577 gm.
Surface area of the specimen: 0.6016 cm.²
R.F.R.: 13.0 which is equivalent to 3,700 µgm/min.

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<th>R.F.R. (µgm/min)</th>
<th>Equivalent value of I.R. (µgm/min.cm.)</th>
<th>( \frac{dW}{dt} \times 10^{-6} )</th>
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Table 11

Oxidation of B.C.C - iron (at 838°C) at $p_{O_2} = 29$ cm.

Weight of the specimen: 5.601 gm.
Surface area of the specimen: 8.4744 cm²
R.F.R. = 10.0 which is equivalent to 6.010 μgm/min.

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<th>R.F.R. - I.R. (μgm/min)</th>
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Table-12

Oxidation of iron at 914°C (nearest to T_c) and p_o2 = 29 cm.

Weight of the specimen : - 3.351 gm.
Surface area of the specimen : - 5.4982 cm²
R.F.R. : - 11.9 which is equivalent to 8,500 μgm/min.

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<th>Equivalent value of I.R. (μgm/min)</th>
<th>R.F.R-I.R. (μgm/min)</th>
<th>(dW/ąt) (μgm/min.cm²)</th>
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<th>(dW/ąt)^2 x 10^-6</th>
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Table 13
Oxidation of F.C.C. - iron (at 965°C) at $p_{O_2} = 29$ cm.

Weight of the specimen :- 1.182 gm.
Surface area of the specimen :- 3.739 cm².
R.F.R = 11.65 which is equivalent to 7600 µgm/min.

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<th>R.F.R-I.R. (µgm/min)</th>
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<td>( \log_{10}(K'_D) )</td>
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<td>( K'_D ) (gm^2/cm/sec) \times 10^{-6}</td>
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<td>Temperature (°C)</td>
<td>( \frac{(K_p)_M}{(K_p)_M} \text{ (mg/m(^2)/cm/min)} \times 10^6 )</td>
<td>Log(_{10}(K_p)_M )</td>
<td>Temperature (°C)</td>
<td>( \frac{(K_p)_M}{(K_p)_M} \text{ (mg/m(^2)/cm/min)} \times 10^6 )</td>
<td>Log(_{10}(K_p)_M )</td>
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### Table-17

Variation of \((K_1)_M\) with temperature

Pressure of oxygen = 29 cm. Hg. absolute

Metal - Iron

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<tr>
<th>Temperature (°C)</th>
<th>((K_1)_M) (µgm/cm².min)x10⁻³</th>
<th>(\log_{10}(K_1)_M)</th>
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<td>838</td>
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</table>
Curves of oxidation rate, \((dw/dt)\)
against time, \((t)\)

Oxidation of F.C.C.-iron \((T=965^\circ C)\)
at \(p_{O_2} = 7'6 \text{ cm.}\)

Fig. 17

Oxidation of B.C.C.-iron \((T=834^\circ C)\)
at \(p_{O_2} = 7'6 \text{ cm.}\)

Fig. 18
Logarithmic plots of (Oxidation rate) against (Time)

Curve: 1 Oxidation of F.C.C.-iron (T = 965°C) at $p_{O_2} = 29$ cm.

Curve: 2 Oxidation of B.C.C.-iron (T = 838°C) at $p_{O_2} = 29$ cm.
Curves of $(\text{Oxidation rate})^{-2}$ against (Time)

According to true parabolic-law

\[
\begin{align*}
\text{Oxidation of F.C.C.-iron (T=965°C)} \\
\text{at } p_{O_2} = 7.6 \text{ cm.}
\end{align*}
\]

Fig. 20

According to true parabolic-law

\[
\begin{align*}
\text{Oxidation of F.C.C.-iron (T=965°C)} \\
\text{at } p_{O_2} = 29 \text{ cm.}
\end{align*}
\]

Fig. 21
Arrhenius plots of $\log_{10}(K_p)_M$ against $1/T$

**Fig. 22**

Oxidation of iron at $p_{O_2} = 7.6$ cm.

\{Unit of $(K_p)_M$ is $\mu g m^2/cm^4 \cdot sec.$\}

**Fig. 23**

Oxidation of iron at $p_{O_2} = 29$ cm.

\{Unit of $(K_p)_M$ is $\mu g m^2/cm^4 \cdot min.$\}
Fig. 24

Oxidation of iron at $p_{O_2} = 7.6$ cm.

\[ \text{Unit of } (K_1)_{M} \text{ is } \mu g/m^2 \cdot min. \]

Fig. 25

Oxidation of B.C.C.-iron at $p_{O_2} = 29$ cm.

\[ \text{Unit of } (K_1)_{M} \text{ is } \mu g/m^2 \cdot min. \]
Table-18

Oxidation of H.C.P. - cobalt (at 335°C)

Weight of the specimen : - 4.4745 gm.
Surface area of the specimen : - 20.5038 cm².

Conversion factor, \( x^* \) : \( 7.7 \times 10^{-4} \times 435 \) gm. of oxygen/cm² of the specimen

(per unit pressure \( \frac{20.5038 \times 76}{\text{gm. of oxygen/cm}} \) of the specimen

= \( 21.494731 \times 10^{-5} \) gm. of oxygen/cm² of the specimen

At the onset of oxidation, \( p_{O_2} = 7.627 \) cm.,

which is equivalent to, \( M = 7.627 \times x^* \) gm. of oxygen/cm² of the specimen

= \( 16.38328 \times 10^{-4} \) gm. of oxygen/cm² of the specimen
<table>
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<th>Time (minute)</th>
<th>Cathetometer value (cm.), B'</th>
<th>$B' x \times$ (gm/cm$^2$), N</th>
<th>$M - N$ (µgm/cm$^2$), W</th>
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<td>16.33598 x 10$^{-4}$</td>
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<td>16.32955 x 10$^{-4}$</td>
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Table-19

Oxidation of Cobalt at 386°C (nearest to transition).

Weight of the specimen: 4.6017 gm.

Surface area of the specimen: 26.0078 cm².

Conversion factor, \( x^* \): \( \frac{7.7 \times 10^{-4} \times 4135}{26.0078 \times 76} \) gm. of oxygen/cm² of the specimen

= 16.945827 \times 10^{-5} \text{ gm. of oxygen/cm}² \text{ of the specimen}

At the onset of oxidation, \( p_{O_2} = 7.545 \text{ cm} \),

which is equivalent to \( M = 7.545 \times x^* \text{ gm. of oxygen/cm}² \text{ of the specimen} \)

= 12.78562 \times 10^{-4} \text{ gm. of oxygen/cm}² \text{ of the specimen}

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<th>Cathetometer value (Cm.), B'</th>
<th>( B' x^* ) (gm/cm²), N</th>
<th>( M - N ) (µgm/cm²), W</th>
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<td>2</td>
<td>3.7655x2 = 7.531</td>
<td>12.76190 \times 10^{-4}</td>
<td>2.372</td>
</tr>
<tr>
<td>5</td>
<td>3.7645x2 = 7.529</td>
<td>12.75851 \times 10^{-4}</td>
<td>2.711</td>
</tr>
<tr>
<td>10</td>
<td>3.7635x2 = 7.527</td>
<td>12.75512 \times 10^{-4}</td>
<td>3.050</td>
</tr>
<tr>
<td>13</td>
<td>3.7625x2 = 7.525</td>
<td>12.75173 \times 10^{-4}</td>
<td>3.389</td>
</tr>
<tr>
<td>16</td>
<td>3.7615x2 = 7.523</td>
<td>12.74834 \times 10^{-4}</td>
<td>3.728</td>
</tr>
</tbody>
</table>
Table-20

Oxidation of cobalt at 386°C (nearest to transition)

Weight of the specimen : - 4.4656

Surface area of the specimen : - 20.4684 cm²

Conversion factor, \( x^* \) : - \( \frac{7.7 \times 10^{-4} \times 1.35}{20.4684 \times 76} \) gm. of oxygen/cm² of the specimen

\[ \text{Conversion factor, } x^* = \frac{7.7 \times 10^{-4} \times 1.35}{20.4684 \times 76} \] gm. of oxygen/cm² of the specimen

\[ \text{At the onset of oxidation, } p_{o_2} = 7.645 \text{ cm.} \]

which is equivalent to, \( M = 7.645 \times x^* \) gm. of oxygen/cm² of the specimen

\[ M = 16.46114 \times 10^{-4} \text{ gm. of oxygen/cm² of the specimen} \]

<table>
<thead>
<tr>
<th>Time (minute)</th>
<th>Cathetometer value (Cm.), B</th>
<th>( Bx \times x^* ) (gm/cm²), N</th>
<th>( M - N ) (µgm/cm²), W</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.806x2 = 7.612</td>
<td>16.39009x10^{-4}</td>
<td>7.105</td>
</tr>
<tr>
<td>3</td>
<td>3.7945x2 = 7.589</td>
<td>16.34056x10^{-4}</td>
<td>12.058</td>
</tr>
<tr>
<td>4</td>
<td>3.7885x2 = 7.577</td>
<td>16.31472x10^{-4}</td>
<td>14.642</td>
</tr>
<tr>
<td>5</td>
<td>3.783x2 = 7.566</td>
<td>16.29319x10^{-4}</td>
<td>16.795</td>
</tr>
<tr>
<td>6</td>
<td>3.7805x2 = 7.561</td>
<td>15.28027x10^{-4}</td>
<td>18.087</td>
</tr>
<tr>
<td>7</td>
<td>3.7765x2 = 7.553</td>
<td>16.26305x10^{-4}</td>
<td>19.809</td>
</tr>
<tr>
<td>8</td>
<td>3.7735x2 = 7.547</td>
<td>16.25013x10^{-4}</td>
<td>21.101</td>
</tr>
<tr>
<td>9</td>
<td>3.771x2 = 7.542</td>
<td>16.24152x10^{-4}</td>
<td>21.962</td>
</tr>
<tr>
<td>10</td>
<td>3.770x2 = 7.540</td>
<td>16.23506x10^{-4}</td>
<td>22.608</td>
</tr>
<tr>
<td>11</td>
<td>3.7675x2 = 7.535</td>
<td>16.22429x10^{-4}</td>
<td>23.685</td>
</tr>
<tr>
<td>12</td>
<td>3.7645x2 = 7.529</td>
<td>16.21137x10^{-4}</td>
<td>24.977</td>
</tr>
</tbody>
</table>
Table-21

Oxidation of F.C.C. - cobalt (at 4700°C)
Weight of the specimen : 4.4822 gm.
Surface area of the specimen : 20.5432 cm².

Conversion factor, $x^* := \frac{7.7 \times 10^{-4} \times 435}{20.5432 \times 76}$ gm. of oxygen/cm² of the specimen

= $21.453506 \times 10^{-5}$ gm. of oxygen/cm² of the specimen

At the onset of oxidation, $p_0^2 = 7.617$ cm,

which is equivalent to, $M = 7.617 \times x^*$

= $16.54413 \times 10^{-4}$ gm. of oxygen/cm² of the specimen

<table>
<thead>
<tr>
<th>Time (minute)</th>
<th>Cathetometer value (cm), $B^*$</th>
<th>$B^* x^* \left( \frac{gm}{cm^2} \right)$, $N$</th>
<th>$\frac{M - N}{\mu gm/cm^2}$, $W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1½</td>
<td>$3.7965x2 = 7.593$</td>
<td>$16.28965 \times 10^{-4}$</td>
<td>5.148</td>
</tr>
<tr>
<td>2</td>
<td>$3.7885x2 = 7.577$</td>
<td>$16.25532 \times 10^{-4}$</td>
<td>8.581</td>
</tr>
<tr>
<td>2½</td>
<td>$3.783x2 = 7.566$</td>
<td>$16.23172 \times 10^{-4}$</td>
<td>10.941</td>
</tr>
<tr>
<td>3</td>
<td>$3.7785x2 = 7.557$</td>
<td>$16.21241 \times 10^{-4}$</td>
<td>12.872</td>
</tr>
<tr>
<td>3½</td>
<td>$3.774x2 = 7.548$</td>
<td>$16.19310 \times 10^{-4}$</td>
<td>14.803</td>
</tr>
<tr>
<td>4</td>
<td>$3.7705x2 = 7.541$</td>
<td>$16.17870 \times 10^{-4}$</td>
<td>16.243</td>
</tr>
<tr>
<td>5</td>
<td>$3.765x2 = 7.530$</td>
<td>$16.15449 \times 10^{-4}$</td>
<td>18.664</td>
</tr>
<tr>
<td>6</td>
<td>$3.7605x2 = 7.521$</td>
<td>$16.13518 \times 10^{-4}$</td>
<td>20.595</td>
</tr>
<tr>
<td>7</td>
<td>$3.7565x2 = 7.513$</td>
<td>$16.11802 \times 10^{-4}$</td>
<td>22.311</td>
</tr>
<tr>
<td>8</td>
<td>$3.753x2 = 7.506$</td>
<td>$16.10515 \times 10^{-4}$</td>
<td>23.598</td>
</tr>
<tr>
<td>9</td>
<td>$3.7485x2 = 7.497$</td>
<td>$16.08370 \times 10^{-4}$</td>
<td>25.743</td>
</tr>
<tr>
<td>10</td>
<td>$3.747x2 = 7.494$</td>
<td>$16.07725 \times 10^{-4}$</td>
<td>26.388</td>
</tr>
</tbody>
</table>
Table-22
Variation of $K_o$ with temperature

<table>
<thead>
<tr>
<th>Temperature, $T$ (°C)</th>
<th>$1/T \times 10^3 (o_K)$</th>
<th>$K_o$ (μgm/cm$^2$)</th>
<th>$\log_{10} K_o$</th>
<th>$\log_{10} (K_o/T)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>1.261</td>
<td>57.36</td>
<td>1.7586</td>
<td>2.8594</td>
</tr>
<tr>
<td>514</td>
<td>1.271</td>
<td>56.01</td>
<td>1.7482</td>
<td>2.8523</td>
</tr>
<tr>
<td>505</td>
<td>1.285</td>
<td>42.80</td>
<td>1.6314</td>
<td>2.7403</td>
</tr>
<tr>
<td>505</td>
<td>1.285</td>
<td>44.99</td>
<td>1.6531</td>
<td>2.7620</td>
</tr>
<tr>
<td>476</td>
<td>1.335</td>
<td>26.99</td>
<td>1.4312</td>
<td>2.5567</td>
</tr>
<tr>
<td>474</td>
<td>1.339</td>
<td>26.21</td>
<td>1.4185</td>
<td>2.5453</td>
</tr>
<tr>
<td>470</td>
<td>1.346</td>
<td>24.42</td>
<td>1.3878</td>
<td>2.5168</td>
</tr>
<tr>
<td>458</td>
<td>1.368</td>
<td>19.42</td>
<td>1.2883</td>
<td>2.4244</td>
</tr>
<tr>
<td>453</td>
<td>1.377</td>
<td>18.40</td>
<td>1.2648</td>
<td>2.4038</td>
</tr>
<tr>
<td>449</td>
<td>1.385</td>
<td>15.85</td>
<td>1.2001</td>
<td>2.3416</td>
</tr>
<tr>
<td>443</td>
<td>1.397</td>
<td>14.89</td>
<td>1.1731</td>
<td>2.3184</td>
</tr>
<tr>
<td>436</td>
<td>1.410</td>
<td>12.70</td>
<td>1.1036</td>
<td>2.2528</td>
</tr>
<tr>
<td>434</td>
<td>1.414</td>
<td>10.76</td>
<td>1.0319</td>
<td>2.1823</td>
</tr>
<tr>
<td>427</td>
<td>1.429</td>
<td>11.11</td>
<td>1.0458</td>
<td>2.2008</td>
</tr>
<tr>
<td>427</td>
<td>1.429</td>
<td>14.08</td>
<td>1.1485</td>
<td>2.3035</td>
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<tr>
<td>420</td>
<td>1.443</td>
<td>9.629</td>
<td>0.9836</td>
<td>2.1429</td>
</tr>
<tr>
<td>420</td>
<td>1.443</td>
<td>7.250</td>
<td>0.8603</td>
<td>2.0196</td>
</tr>
<tr>
<td>412</td>
<td>1.460</td>
<td>6.819</td>
<td>0.8337</td>
<td>3.9981</td>
</tr>
<tr>
<td>405</td>
<td>1.475</td>
<td>6.449</td>
<td>0.8095</td>
<td>3.9785</td>
</tr>
<tr>
<td>400</td>
<td>1.486</td>
<td>6.142</td>
<td>0.7883</td>
<td>3.9604</td>
</tr>
<tr>
<td>386</td>
<td>1.517</td>
<td>22.00</td>
<td>1.3424</td>
<td>3.5234</td>
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<tr>
<td>386</td>
<td>1.517</td>
<td>1.166</td>
<td>0.0668</td>
<td>3.2478</td>
</tr>
<tr>
<td>382</td>
<td>1.527</td>
<td>0.9835</td>
<td>1.9924</td>
<td>3.1762</td>
</tr>
<tr>
<td>375</td>
<td>1.543</td>
<td>5.218</td>
<td>0.7175</td>
<td>3.9058</td>
</tr>
<tr>
<td>362</td>
<td>1.575</td>
<td>4.397</td>
<td>0.6432</td>
<td>3.8405</td>
</tr>
<tr>
<td>353</td>
<td>1.597</td>
<td>4.057</td>
<td>0.6082</td>
<td>3.8116</td>
</tr>
</tbody>
</table>
Table 22 (continued)

<table>
<thead>
<tr>
<th>Temperature, T (°C)</th>
<th>1/T × 10^3 (°K)</th>
<th>K_0 (µgm/cm²)</th>
<th>log_{10} K_0</th>
<th>log_{10}(K_0/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>344</td>
<td>1.621</td>
<td>3.459</td>
<td>0.5390</td>
<td>3.7488</td>
</tr>
<tr>
<td>342</td>
<td>1.626</td>
<td>3.331</td>
<td>0.5225</td>
<td>3.7336</td>
</tr>
<tr>
<td>335</td>
<td>1.645</td>
<td>2.7270</td>
<td>0.4356</td>
<td>3.6517</td>
</tr>
<tr>
<td>334</td>
<td>1.647</td>
<td>2.6760</td>
<td>0.4275</td>
<td>3.6441</td>
</tr>
<tr>
<td>331</td>
<td>1.656</td>
<td>2.482</td>
<td>0.3949</td>
<td>3.6140</td>
</tr>
<tr>
<td>329</td>
<td>1.661</td>
<td>2.390</td>
<td>0.3783</td>
<td>3.5987</td>
</tr>
<tr>
<td>327</td>
<td>1.667</td>
<td>2.257</td>
<td>0.3535</td>
<td>3.5754</td>
</tr>
<tr>
<td>324</td>
<td>1.675</td>
<td>2.088</td>
<td>0.3198</td>
<td>3.5438</td>
</tr>
<tr>
<td>320</td>
<td>1.686</td>
<td>1.892</td>
<td>0.2769</td>
<td>3.5038</td>
</tr>
</tbody>
</table>
Plots on the oxidation of cobalt at various temperatures

**Fig. 26**
Direct plots of weight gain, (W) against time, (t);
Curves - Temperature
1 - 470°C
2 & 4 - 386°C
3 - 335°C

**Fig. 27**
Semi-logarithmic plots of weight gain, (W) against time, (t);
Curves - Temperature
1 - 470°C
2 & 4 - 386°C
3 - 335°C
Arrhenius plots of $\log_{10}(K_o)$ against $1/T$

(Unit of $K_o$ is $\mu$ gm./cm$^2$)
DISCUSSION
6. Discussion on the oxidation of iron

6.1. Identification of the oxidation law

In order to find the law of oxidation applicable to a particular set of results, the usual procedure is to try a graphical approach by plotting various co-ordinates in accordance with the different oxidation-law equations (Section 2.4). The relevant law can then be identified when the plot of the results according to that particular law-equation will give a straight line. In the present case, kinetic data was obtained experimentally in terms of the rate of oxidation, \( \frac{dW}{dt} \) and the time, \( t \). Since the results were obtained in terms of the differential rate, \( \frac{dW}{dt} \) and time, \( t \), all the different oxidation laws of section (2.4) must first be converted into the differential forms. Plots of the data in terms of these various differential forms of the oxidation equations can then lead to the identification of the correct law.

6.1.1. Differential form of the exponential laws

The exponential type of laws are considered first. An inverse logarithmic law has only been found by other workers to be valid for oxidation at low temperature regions, so such a law is not considered here. The direct-logarithmic rate law,

\[
W = K_2 \log_e \left( \frac{t}{T} + 1 \right)
\]

(5)

can be re-written on differentiation as,
\[
\frac{dW}{dt} = K_2 \cdot \frac{1}{\left( \frac{t}{T} + 1 \right)} = \frac{1}{T} = \frac{K_2}{(t + T)}
\]

or, \((dW/dt)^{-1} = \frac{t}{K_2} + \frac{T}{K_2} \) \(\cdots \cdots \cdots \cdot (6)\)

where, \(dW/dt\) = amount of oxygen consumed by unit area of the specimen in unit time i.e. the rate of oxidation, \((\mu g/m^2 \cdot \text{min.})\).

t = time, \((\text{min.})\).

\(T\) = constant, \((\text{min.})\).

\(K_2\) = direct-logarithmic rate constant, \((\mu g/m^2)\)

From eqn. (6) a plot of \((dW/dt)^{-1}\) against \(t\) can be expected to give a straight line if a direct-logarithmic law holds good.

The asymptotic law,

\[W = K_3^* \left\{ 1 - \exp. \left( -K_4 t \right) \right\} \] \(\cdots \cdots \cdots \cdot (7)\) where \(K_3^* = K_3\)

can be re-written on differentiation as,

\[\frac{dW}{dt} = K_3 \cdot \exp. (-K_4 t)\]

or, \(\log_{10}(dW/dt) = \log_{10} K_3 - \frac{K_4 t}{2.303}\)

where, \(K_3\) = asymptotic rate constant, \((\mu g/m^2 \cdot \text{min.})\)

\(K_4\) = constant, \((\text{min.}^{-1})\)

In this case, a plot of \(\log_{10}(dW/dt)\) against \(t\) will give a straight line if an asymptotic law holds good. In practice, linear plots were obtained when graphs were drawn according to both the eqns. (6) and (8). Such a phenomenon is not unusual, because according to Evans (91) the direct-logarithmic and asymptotic laws are indistinguishable at the
early stages of oxidation. Since the present data were obtained at the initial stages of oxidation, so linear-plots according to both laws can be expected.

If by such graphical method, linear plots were obtained for exponential laws then non-linear plots can be expected for non-exponential laws. This is next checked by deriving first the differential forms of the empirical power laws and the modified parabolic law, both of which are non-exponential type.

6.1.2. Differential form of the empirical power law

The empirical power law equation, becomes

\[ W^n = K_5 t + C \]

becomes

\[ W = K_5 t + C \] when \( n = 1 \)

Eqn (9) is a true linear equation and \( K_5 \) is replaced now by the conventional notation for linear rate-constant, \( K_1 \), thus

\[ W = K_1 t + C' \]

where \( C' \) is an integration constant. On differentiation, eqn (10) will become

\[ \frac{dW}{dt} = K_1 \]

Thus a constant \( \frac{dW}{dt} \) value is expected if a linear law holds good; this was not confirmed in the present study. With \( n = 2 \), the empirical equation becomes

\[ W^2 = K_5 t + C' \]

Eqn (11) is a true parabolic equation and \( K_5 \) is now replaced...
by the conventional notation for parabolic rate-constant, $K_p$, thus
\[ W^2 = K_p t + C \] 
where $C$ is an integration constant. Eqn. (12) on differentiation will become,
\[ 2W \frac{dW}{dt} = K_p \]
or,
\[ 2 \frac{dW}{dt} = K_p = \frac{K_p}{W} \left( K_p t + C \right)^{1/2} \]
On squaring both sides,
\[ 4 \left( \frac{dW}{dt} \right)^2 = \frac{(K_p)^2}{(K_p t + C)^{2}} \]
or,
\[ \left( \frac{dW}{dt} \right)^2 = \frac{1}{K_p} \left( t + \frac{C}{(K_p)^2} \right)^2 \] 
According to eqn. (13), if a parabolic law is obeyed then a plot of $(dW/dt)^2$ against $t$ yields a straight line. However, the same kind of linear plot is also expected if a modified parabolic law holds good.

6.1.3. Differential form of the modified parabolic law

The modified parabolic law,
\[ \frac{W^2}{K_6} + \frac{W}{K_7} = t \] 
can be written as
\[ \frac{W^2}{K_6} = t - \frac{W}{K_7} \]
or,
\[ \frac{1}{K_6} = \frac{t}{W^2} - \frac{1}{W.K_7} = \frac{t.K_7 - W}{W^2.K_7} \] 
Eqn. (14) can be expressed alternatively as,
\[ W^2 K_1 + W K_2 = t K_1 K_2 \]

On differentiation,
\[ \frac{dW}{dt} (2W K_1 + K_2) = K_1 K_2 \]

or,
\[ \frac{dW}{dt} = \frac{K_1 K_2}{(2W K_1 + K_2)} \]

\[ \therefore (\frac{dW}{dt})^{-1} = \frac{2W K_1 + K_2}{K_1 K_2} = \frac{2W}{K_2} + \frac{1}{K_1} \tag{16} \]

Replacing the value of \( \frac{1}{K_2} \) from eqn. (15), the eqn. (16) becomes

\[ (\frac{dW}{dt})^{-1} = 2W \left( \frac{t K_1 - W}{W^2 K_2} \right) + \frac{1}{K_1} \]

\[ = \frac{2tK_1 - 2W}{W K_2} + \frac{1}{K_1} = \frac{2tK_1 - W}{W K_2} = \frac{2t}{W} - \frac{1}{K_1} \tag{17} \]

Eqn (14) can be written as

\[ W^2 + \frac{K_2}{K_1} W - K_1 t = 0 \tag{18} \]

Eqn. (18) is a quadratic equation whose two roots are,

\[ W = \alpha = -\frac{K_2}{2K_1} + \sqrt{\left(\frac{K_2}{4K_1}\right)^2 + t K_1} \]

and

\[ W = \beta = -\frac{K_2}{2K_1} - \sqrt{\left(\frac{K_2}{4K_1}\right)^2 + t K_1} \]

Since \( \beta \) gives a negative value, \( \alpha \) is taken as the relevant value. It is known that multiplication of the two roots gives
gives a constant value which is equal to the third term of the quadratic equation, (18), i.e.

$$\alpha, \beta = \text{constant} = -t.K_6$$

$$\therefore \alpha = -\frac{t.K_6}{\beta}$$

substituting the value of $\beta$,

$$\alpha = \frac{-t.K_6}{-\frac{K_6}{2K_7} - \sqrt{\frac{(K_6)^2}{4(K_7)^2}} + t.K_6}$$

$$\therefore \frac{1}{W} = \frac{1}{\alpha} = \frac{K_6}{2K_7} + \sqrt{\frac{(K_6)^2}{4(K_7)^2} + t.K_6}$$

Hence by replacing this value of $\frac{1}{W}$, the eqn. (17) becomes

$$\left(\frac{dW}{dt}\right)^2 = 2t \left\{ \frac{K_6}{2K_7} + \sqrt{\frac{(K_6)^2}{4(K_7)^2} + t.K_6} \right\} - \frac{1}{K_7}$$

$$= \frac{2}{K_6} \left\{ \frac{K_6}{2K_7} + \sqrt{\frac{(K_6)^2}{4(K_7)^2} + t.K_6} \right\} - \frac{1}{K_7}$$

$$= \frac{2}{K_6} \left\{ \sqrt{\frac{(K_6)^2}{4(K_7)^2} + t.K_6} \right\}$$

$$\therefore \left(\frac{dW}{dt}\right)^2 = \left(\frac{K_6}{K_7}\right)^2 \left\{ \frac{\left(\frac{K_6}{K_7}\right)^2}{4(K_7)^2} + t.K_6 \right\} = \frac{1}{K_7^2} + \frac{4}{K_6} \cdot t$$

- - - - - - - - (19)
where \( K_6 \) and \( K_7 \) are parabolic and linear rate constants respectively as applied to a modified parabolic law. These two constants are represented by the notations \( (K_p)_M \) and \( (K_1)_M \) to identify them from the true rate-constants \( K_p \) and \( K_1 \) respectively. Thus eqn. (19) can be written now as,

\[
\left( \frac{dW}{dt} \right)^{-2} = \frac{\frac{4}{3} \cdot t}{(K_p)_M} + \frac{1}{(K_1)_M^2} \tag{20}
\]

According to eqn. (20), a linear plot of \( (dW/dt)^{-2} \) against \( t \) is therefore obtained from a modified parabolic law as well as for a true parabolic law. In fact, straight line plots were obtained from the present results when \( (dW/dt)^{-2} \) values were plotted against time, \( t \). Thus for the same set of results, linear plots are obtained which satisfy the exponential laws \( \text{i.e. eqns. (6) and (8)} \), parabolic law \( \text{i.e. eqn. (13)} \) and the modified parabolic law \( \text{i.e. eqn. (20)} \). The linearity in all these cases means that the graphical method of identifying the oxidation law cannot be used in the present case, therefore an alternative procedure was tried to ascertain the oxidation law.

6.1.4. Procedure. alternate to the graphical method

An empirical powers equation is taken as the basic starting point:

\[
W^n = K_5 t + C \tag{21}
\]

which on re-arrangement gives \( W = (K_5 t + C)^{1/n} \).
or, \( w^{n-1} = (K_5 \cdot t + C)^{n-1} \) \( - - - - - - (22) \)

Eqn. (21) on differentiation becomes

\[
\frac{n \cdot w^{n-1} \cdot \frac{dw}{dt}}{dt} = K_5 \cdot n \cdot \frac{1}{w^{n-1}} = K_5 \cdot \left( \frac{1}{(K_5 \cdot t + C)} \right)^{n-1} \]

\[
\therefore \frac{dw}{dt} = \frac{K_5}{n} \cdot \frac{1}{n} \cdot \left( \frac{n-1}{K_5 \cdot t + C} \right)^{n-1} \]

or, \( \log_{10} \frac{dw}{10 \cdot dt} = -\log_{10} \left( K_5 \cdot t + C \right)^{n-1} + \log_{10} \left\{ \frac{K_5}{n} \right\} \)

\[
= \log_{10} \left( \frac{K_5}{n} \right) - \frac{n-1}{n} \log_{10} \left( K_5 \cdot t + C \right) -2 - - - - (23) \]

Eqn. (21) can also be written as

\[
n \log_{10} w = \log_{10} \left( K_5 \cdot t + C \right) - - - - - - (24) \]

Use of either eqns. (23) or (24) gives \( n \) values of \( 1.5 \pm 0.1 \) for the initial oxidation period except for the results in the F.C.C. region at \( p_{O_2} = 29 \) cm. Hg. where \( n = 2 \pm 0.1 \).

Typical plots of \( \log_{10} \left( \frac{dw}{dt} \right) \) against \( \log_{10} t \) are shown in fig. (19). The curve (1) of fig. 19 is for the oxidation of F.C.C. iron (at 965°C) at \( p_{O_2} = 29 \) cm. where \( n = 2 \pm 0.1 \).

The curve (2) of fig. 19 is typical for F.C.C. iron at \( p_{O_2} = 7.6 \) cm. and B.C.C. iron at \( p_{O_2} = 29 \) cm., where \( n = 1.5 \pm 0.1 \) at the earlier part of the curve. This is then followed by \( n = 2 \pm 0.1 \). We are here only interested in the earlier part of oxidation i.e. where \( n = 1.5 \pm 0.1 \). A constant value of \( n \) equals to \( 2 \pm 0.1 \) is an indication that a
parabolic law holds good in that particular case. However, recalculation of the results of Baur, et. al. (92) gives \( n = 1.5 \pm 0.1 \) for both eqns. (23) and (24) and a modified parabolic law was shown to hold in their work. The assumption for which a modified parabolic law was shown to hold in their work. The assumption can now be made that a set of results \( n = 1.5 \pm 0.1 \), indicates a modified parabolic law. Additional justification of the latter statement is given (using certain assumptions) in the appendix-(I). Recalculation of Uhlig's work (42) on the logarithmic oxidation of zinc gives \( n = 2.45 \) from eqn. (18). This variation of \( n \) indicates that this constant \( n \) value is not a characteristic where a logarithmic rate law is obeyed. The constancy of \( n \)-value \( (1.5 \pm 0.1) \) in the present work leads to suggest a modified parabolic as the general rate law, except for results in the F.C.C. range at \( p_{O_2} = 29 \) cm. where a purely parabolic law is obeyed, \( n = 2 \pm 0.1 \). (fig. 19, curve 1).

6.1.5. Discontinuity in the \( [(dW/\Delta t)^{-2} \text{ against } t] \)-plot

A linear plot of \( (dW/\Delta t)^{-2} \text{ against } t \) is always found to exhibit a discontinuity (fig.20) except for those at \( p_{O_2} = 29 \) cm. in F.C.C. iron (fig.21). Davies, et.al. (54) and Bénard (50) have shown that, in the later stages of oxidation a parabolic law is always obeyed. One can therefore expect that a \( [(dW/\Delta t)^{-2} \text{ against } t] \)-plot would yield a
straight line in the later stages of oxidation with \( n = 2 \) i.e. a parabolic oxidation. However, if in the initial stages of oxidation a modified parabolic law is obeyed, then the earlier part will be also a straight line but with \( n = 1.5 \). This is confirmed from the work of Evans (93) where the slope in the modified parabolic region is found less steep than that in the parabolic stages of oxidation. Such a difference in the steepness of the slope will not be present if only one of the two laws applies over the whole range. The present work is therefore consistent with a modified parabolic law at the initial stages of oxidation where \( n = 1.5 \pm 0.1 \), followed by a true parabolic law at later stages of oxidation when \( n = 2 \pm 0.1 \). However, for the results that were obtained on the oxidation of F.C.C. iron at \( p_{O_2} = 29 \text{ cm.} \), a continuous plot of \( (\frac{dW}{dt})^{-2} \) against \( t \) (fig. 21) with \( n = 2 \pm 0.1 \) indicates a single rate controlling law, namely a parabolic law here, applies. The periods over which the non-parabolic oxidation applies are of the order of 40 and 55 sec. (max) at \( p_{O_2} = 7.6 \) and 29 cm. respectively. Such a short lived non-parabolic stage has been indicated by Bénard in his work on iron (50) and Krupnikova-Perlina (94) on copper.
6.1.6. Comparison of results

The parabolic rate constants as obtained by using the modified parabolic law are found to compare reasonably well with the figures given by Davies et al. (54), (Table-23), bearing in mind the fact that, the rate constants are much affected by the specimen purity, specimen preparation technique, $p_{O_2}$ - value, purity of gas etc.

<table>
<thead>
<tr>
<th>Temperature $^\circ C$</th>
<th>From the present work</th>
<th>From the work of Davies et al. (47)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$p_{O_2}$ = 7.6 cm.Hg</td>
<td>$p_{O_2}$ = 29 cm.Hg</td>
</tr>
<tr>
<td></td>
<td>$(K_P)^{\frac{1}{2}}_M$</td>
<td>$(K_P)^{\frac{1}{2}}_M$</td>
</tr>
<tr>
<td>800</td>
<td>$2.31 \times 10^{-3}$</td>
<td>$1.36 \times 10^{-3}$</td>
</tr>
<tr>
<td>850</td>
<td>$4.36 \times 10^{-3}$</td>
<td>$1.83 \times 10^{-3}$</td>
</tr>
<tr>
<td>900</td>
<td>$6.96 \times 10^{-3}$</td>
<td>$1.30 \times 10^{-3}$</td>
</tr>
<tr>
<td>930</td>
<td>$7.33 \times 10^{-3}$</td>
<td>$1.63 \times 10^{-3}$</td>
</tr>
<tr>
<td>965</td>
<td>$9.01 \times 10^{-3}$</td>
<td>$1.63 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table - 23 is given in order to compare the order of magnitude of different values, rather than to compare absolute values. Because the results of Davies et al. were obtained
only for a true parabolic law of oxidation.

A comparison will be shown now between the parabolic rate constant, \((K_p)^M\), obtained in the present case and a theoretical value as calculated by using Gulbransen's (95) transition state theory of reaction rate which however, gives a \(K_p\) value. According to Gulbransen (95),

\[
\frac{K_p'}{K_p} = \frac{2kT}{h} \cdot \lambda^2 \cdot \exp \left( \frac{S^*}{R} \right) \cdot \exp \left( -\frac{Q}{RT} \right) \tag{25}
\]

where \(K_p'\) = rational rate constant, (cm\(^2\)/sec)

\(k\) = Boltzman's constant, \(1.38 \times 10^{-16}\) erg/degree,

\(h\) = Planck's constant, \(6.62 \times 10^{-27}\) erg sec.,

\(\lambda\) = distance between diffusion sites i.e. normal interatomic distance, (cm),

\(S^*\) = Entropy of activation (cal/°C),

\(Q\) = energy of activation (cal/mole).

With wüstite of formula \(\text{Fe}_0.910\), having density of 5.613 gm/cm\(^3\) and lattice parameter 4.282 Å, the following result is obtained using \(T = 930\)°C (1203°K), and a value of \(Q\) or \(Q_p\) = 35,000 cal/mole taken from the present study and a value of \(S^* = 8.6\) cal/°C from the work of Moore (96),

\[
K_p' = 3.16 \times 10^{10} \text{ Å}^2 /\text{sec.}
\]

\[
= 3.16 \times 10^{-6} \text{ cm}^2 /\text{sec.}
\]

According to Wagner (6), the scaling constant, \(K_p\) is written as
\[ K_p = K_p' \times 2 \left( \frac{y_V \times \rho_{\text{oxide}}}{\rho_{\text{oxide}}} \right)^2, \text{ gm}^2/\text{cm}^4\text{.sec.} \]

where \( y_V \) = vacancies in the sublattice of iron

\[ \text{and } \rho_{\text{oxide}} = \text{density of oxide which is equal to 5.613 gm/cm}^3. \]

Since the wüstite is taken as Fe\(_{0.91}^0\),

Therefore \( 1 - y_V = 0.91 \)

\[ : y_V = 0.09 \]

\[ : K_p = K_p' \times 2 \left( 0.09 \times 5.613 \right)^2 \]

\[ = 1.613 \times 10^{-6} \text{ gm}^2/\text{cm}^4\text{ sec.} \]

Results from the present work at 930°C are

\[ (K_p)_M = 0.9 \times 10^{-6} \text{ gm}^2/\text{cm}^4\text{.sec. at } p_{O_2} = 7.6 \text{ cm. Hg.} \]

and \( (K_p)_M = 0.03 \times 10^{-6} \text{ gm}^2/\text{cm}^4\text{.sec. at } p_{O_2} = 29 \text{ cm. Hg.} \)

And from the work of Davies (54),

\[ K_p = 0.35 \times 10^{-6} \text{ gm}^2/\text{cm}^4\text{.sec. at } p_{O_2} = 76 \text{ cm.Hg.} \]

Gulbransen's theoretical approach is primarily based upon the parabolic oxidation only. Any comparison of the experimental values with the theoretical one is therefore restricted by the same limitations that are applicable to the comparisons in Table-23.

6.2. Character of the modified parabolic law

Since the modified parabolic law is established as the general law of oxidation in the present study, it is
worthwhile to consider the assumptions that have been made in the derivation of such a law. References can be made to works of Deal (97), Evans (93), Hedden (98), Ipat'ev (56) and Wagner (6).

Oxidation proceeds by inward movement of cation vacancies and outward movement of cations. The velocities of diffusion and interface or phase-boundary reactions are assumed to be linear functions of the concentration difference of the same variable (e.g., the vacancy concentration $C$ in mol/cm$^3$ in the lattice). The validity of the assumption of a steady-state approximation will be given later. The overall process of oxide growth is considered to be comprised of the following stages:
Stage 1. Chemical reaction at the metal/oxide interface, which is given by,

\[ F_1 = K_a \left( C_1 - C_{1e} \right) \]

where \( F_1 \) = flux of vacancies i.e. the number of vacancies crossing a unit surface area in unit time

\( K_a \) = velocity constant at the metal/oxide interface

\( C_1 \) = vacancy concentrations at the metal/oxide interface

\( C_{1e} \) = equilibrium vacancy concentration and is related to the oxygen potential in the wüstit/iron equilibrium system.

Stage 2. Chemical reaction at the oxide/oxygen interface, which is expressed as,

\[ F_2 = K_b \left( C_{2e} - C_2 \right) \]

where \( F_2 \) = flux of vacancies arriving per unit area of the oxide/gas interface in unit time

\( K_b \) = velocity constant at the oxide/gas interface

\( C_{2e} \) = equilibrium vacancy concentration at the oxide/gas interface and is related to the oxygen potential of the gas phase.

\( C_2 \) = vacancy concentration at the oxide/gas interface
Stage 3: A flux of vacancies, \( F_3 \) across the oxide layer, which is assumed to be given by Fick's law,
\[
F_3 = - \text{Deff} \left( \frac{\partial \phi}{\partial x} \right)
\]
at any point \( x \) within the oxide layer, where \( \text{Deff} \) = effective diffusion coefficient. Under steady-state conditions,
\[
\frac{dF_3}{dx} = 0, \quad \text{and flux} \quad F_3 = \text{Deff} \left( \frac{C_2 - C_1}{\Delta x} \right) \cdot M_o
\]
where \( \Delta x = \frac{W \cdot M_{ox}}{M_o \cdot \rho_{ox}} \)

and \( W = \) amount of oxygen adsorbed/cm².

\( M_{ox} = \) molecular weight of wustite

\( M_o = \) atomic weight of oxygen

\( \rho_{ox} = \) density of oxide

Assuming a steady state equilibrium to be valid here,
\[
F_1 = F_2 = F_3 = F
\]

Hence,
\[
\frac{dW}{dt} = F = K_a (C_1 - C_{1e}) = K_b (C_2 - C_2) = M_o \cdot \text{Deff} \left( \frac{C_2 - C_1}{\Delta x} \right)
\]

Elimination of \( C_1 \) and \( C_2 \), followed by integration yields an equation (27) of the same form as equation (15):
\[
\frac{1}{(K_1)^M} + \frac{W}{(K_p)^M} = \frac{t}{W} \quad \text{--- (27)}
\]
where,
\[
(K_1)^M = \frac{K_a \cdot K_b}{(K_a + K_b)} \quad (C_{2e} - C_{1e}) \quad \text{--- (28)}
\]

and
\[
(K_p)^M = \left( \frac{M_o}{M_{ox}} \right)^2 \cdot 2 \cdot \text{Deff} \cdot \rho_{ox} \quad (C_{2e} - C_{1e}) \quad \text{--- (29)}
\]
Equation (27) is the modified parabolic equation. In the limiting case when \( \frac{1}{(K_1)_M} \ll \frac{W}{(K_p)_M} \), then eqn. (27) becomes \( W^2 = K_p t \) which is a parabolic equation. According to Hedden (98), application of the limiting condition (i.e., the equation \( W^2 = K_p t \)) is justifiable only for a ratio of

\[
\frac{(K_1)_M}{(K_p)_M} \geq 10^4 \text{ cm}^2/\text{gm}.
\]

In the present investigation the ratio

the ratio is equal to \(-10^2\) and \(2.5 \times 10^2 \text{ cm}^2/\text{gm. at 1005}^\circ\text{C and 820}^\circ\text{C respectively at } p_{o_2} = 7.6 \text{ cm. Hg. and is equal to 5} \times 10^2 \text{ at 850}^\circ\text{C when } p_{o_2} = 29 \text{ cm. Thus the values of } (K_p)_M \text{ and } (K_1)_M \text{ obtained in the present case are consistent with Hedden's hypothesis that the modified parabolic law must be used when } (K_1)_M \ll 10^4.

6.2.1. Validity of the steady-state approximation

According to Deal (97), if the distribution of vacancy concentration is disturbed, the return to equilibrium would take a period of time of the order of,

\[
t_{\text{transient}} = \frac{(\text{Total amount of vacancy needed to return to the transient steady-state equilibrium})}{(\text{Flux of vacancies})}
\]

Formation of vacancies is due to the incorporation of oxygen into the oxide lattice. The numerator is approximated by the total amount of vacancies present within the oxide layer in
excess of a uniform concentration i.e. $\frac{1}{2}(C_2-C_1)AxM_o$. The denominator can be approximated by the flux of vacancies across the oxide, i.e. $F_2 = \text{Deff.} \frac{C_2-C_1}{Ax}M_o$. Thus the relaxation time will be of the order of

$$t_{\text{transient}} \approx \frac{(Ax)^2}{2 \text{Deff.}}$$

From the relation $Ax = \frac{W}{M_o \rho_{ox}}$ it can be written as,

$$W^2 = \left(\frac{AxM_o}{\rho_{ox}}\right)^2 \left(\frac{M_o}{\rho_{ox}}\right)^2$$

For simplicity, the parabolic eqn. $W^2 = K_p t$ is taken here.

Hence $W^2 = \left(\frac{M_o}{\rho_{ox}}\right)^2 2 \text{Deff.} \frac{M_o}{\rho_{ox}} (C_{2e} - C_{1e}) \frac{M_o}{\rho_{ox}}$.

So,

$$t_{\text{transient}} \approx \frac{M_o}{\rho_{ox}} (C_{2e} - C_{1e})$$

For wüstite of formula Fe$_{0.910}$, the values of $M_{ox}$ and $\rho_{ox}$ are 66.82 gm of oxide/mol and 5,613 gm/cm$^3$ respectively. The value of $(C_{2e} - C_{1e})$ shown later (sec. 6.4.3) to be of the order of $10^{-3}$ mol/cm$^3$. Therefore the time ratio $\frac{t_{\text{transient}}}{t} \approx 10^{-2}$ in the parabolic range of oxide growth - surely a negligible time period. For the pre-parabolic stage i.e. the modified parabolic law of oxide growth the time ratio can thus be assumed to be negligible and hence in the validity of the steady-state approximation to derive the modified parabolic law.
6.3. Arrhenius plots

The Arrhenius plots show an anomaly in each of the three figs. 22, 23 and 24. Evidence of a similar type anomaly in oxidation studies has been reported by Gulbransen (99) for chromium and also by Köfstad (100) for niobium. In the first case a sudden change of vapour pressure at the quoted temperature is proposed to be the cause, while in the second case a nucleation-growth mechanism has been suggested. In the case of iron, a change of vapour pressure at the allotropic transformation temperature, 910°C is negligible. When oxidation is carried out at high \( p_{O_2} \) values the activation energy for nucleation becomes very small [Cabrera (101)] and pressures of 7.6 cm. and 29 cm. Hg. may be considered quite high. Thus the above suggested mechanisms are thought not to be applicable in the present case.

Vernon (102) has reported a change in the slope of Arrhenius plot at 200°C. This is attributed to a change in the crystal structure of the oxide from \( \gamma \text{Fe}_2\text{O}_3 \) (below 200°C) to \( \alpha \text{Fe}_2\text{O}_3 \) (above 200°C). At the B.C.C. \( \rightarrow \) F.C.C. transformation temperature of iron there is no reason to expect a crystallographic change of wüstite. The properties of wüstite should not markedly differ whether it is
formed from B.C.C.- or F.C.C. - iron. This implies that the crystallographic transformation will not influence the diffusion rate of the reactants across the wustite layer. Since a parabolic law operates for a diffusion-controlled process, the Arrhenius plot in such a case will therefore not show any change of slope at the transition point (~910°C) and the value of the activation energy for diffusion of reactants through the oxide is expected to remain constant, fig. 30. This was expected by Engell (103) and observed experimentally by Davies et.al. (54), Evans, et.al.(104), Schmahl (105) and Smeltzer (106).

However, the B.C.C.→F.C.C. transition can only affect the rate of transfer of iron from its lattice into the oxide lattice. This being so, the change in rate of the interfacial reactions may be so marked that it affects the nature of the overall oxidation process and a true parabolic law would no longer be expected. In such a case, the process of diffusion through the oxide is affected by the interfacial i.e. phase-boundary reactions. A linear law is obtained when the phase-boundary reactions totally control the oxidation process; this has in fact been observed in the works of Bénard (50), Fishbeck, et.al. (51), Hauffe, et.al. (52), Smeltzer (53) on the oxidation of iron. Their results are based purely on linear oxidation kinetics, and the Arrhenius plots are shown

(.....continued to page-174)
Arrhenius plots of $\log_{10} K_p$ against $1/T$

(Unit of $K_p$ is $\text{cm}^2/\text{cm}^4\text{min}$.)

Temperature, °C

<table>
<thead>
<tr>
<th>Curve</th>
<th>Ref. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>103</td>
</tr>
<tr>
<td>B</td>
<td>103</td>
</tr>
<tr>
<td>C</td>
<td>106</td>
</tr>
</tbody>
</table>
"Figure - 30"

Taken from, "The Kinetics of Wüstite formation on iron"

Arrhenius plots of parabolic rate constant, $K_p$ against inverse of temperature:

Curve, 1. Theoretical curve, with diffusion co-efficient of cation being evaluated from electrochemical measurements.

Curve, 2. Theoretical curve, with diffusion co-efficient of cation being determined from iron self-diffusion measurements.

Curve, 3. Experimental curve, for oxidation in carbon dioxide.

Red dotted curve - Experimental curve, for oxidation in oxygen.

Blue dotted curve - Experimental curve for oxidation in oxygen.

Curve (1) and (2) :- Engell, H.J., Acta Met. 6, 439, 1958

Curve (3) :- Smeltzer, W.W., Acta Met. 8, 382, 1960


Blue dotted curve :- Davies, M.H., Simnad, M.T., and Birchall, C.E.,
Arrhenius plots of $\log_{10} K_1$ against $I/T$

Temperature, °C

![Graph](image)

Fig. 31.

(Unit of $K_1$ is mgm./cm$^2$.min., except for Curve C, where the unit is $\mu$gm./cm$^2$.min.)

<table>
<thead>
<tr>
<th>Curve</th>
<th>Ref. no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50</td>
</tr>
<tr>
<td>B</td>
<td>51</td>
</tr>
<tr>
<td>C</td>
<td>52</td>
</tr>
<tr>
<td>D</td>
<td>53</td>
</tr>
</tbody>
</table>
"Figure 31"

Taken from an article by Smeltzer, W.W., Trans. A.I.M.E., 218, 674, 1960. (53)

Arrhenius plot of linear rate constant, $K$ for wüstite scale growth in following atmospheres:

**Curve-1:** Oxidation in an atmosphere of air at 760 mm pressure,

**Curve-2:** Oxidation in an atmosphere of CO$_2$ at 760 mm pressure,

**Curve-3:** Oxidation in an atmosphere of 50:50 mixture by volume of CO$_2$ and CO at 200 mm pressure,

**Curve-4:** Oxidation in an atmosphere of 70:30 mixture by volume of CO$_2$ and CO respectively at 760 mm pressure,
to have a change of slope with an indication of an anomaly at the B.C.C. → F.C.C. change point, fig. 31. It can be stated therefore, that a change of slope in the Arrhenius plot can be expected when the phase-boundary reaction becomes only one or one of the rate controlling factors in the oxidation process. In the present investigation, a change of slope with an anomaly at the B.C.C. → F.C.C. iron transformation point in the Arrhenius plot was observed (fig. 24). Recently, D'yachKov (107) found a modified parabolic rate-law to hold for the oxidation of titanium between 750º and 1050º C at p_o2 = 16.4 cm. The temperature dependence of both the linear and the parabolic rate constant exhibited an abrupt change at the allotropic transformation (≈ 900º C). The simultaneous occurrence of phase-boundary and diffusion-controlled reactions, as in the case of a modified parabolic oxidation, can be expected to affect the modified parabolic rate constants (K_p)_M, so that an anomaly may be observed in the Arrhenius plot of Log_{10}(K_p)_M, as has been observed in the present work (fig. 22, 23) and by D'yachKov (107) on his work on titanium. The Arrhenius plots of parabolic rate constants against temperature at p_o2 = 7.6 cm. and 29 cm. are shown in fig. 22 and 23 respectively. The Arrhenius plot at p_o2 = 7.6 cm. (fig. 22) is affected in both B.C.C.- and F.C.C. - iron by the phase-boundary reactions because n = 1.5 ± 0.1 always.
On the other hand, the plot at \( p_{O_2} = 29 \) cm. (fig. 23) is affected only in the B.C.C. by the phase-boundary reaction and not in the F.C.C region where \( n = 2 \pm 0.1 \). In these two figures, the drop in parabolic rate constants is higher (about twice) in fig. (23), just above the transformation point, than that in fig. (22). This seems to indicate that the phase-boundary reaction results in keeping the value of the diffusion controlled parabolic rate constants greater than that expected for a true diffusion-controlled process. Thus when a transition occurs between the parabolic rate constants of a modified parabolic law and of a true parabolic law (fig. 23), the drop in the values of the rate constants at the B.C.C. \( \rightarrow \) F.C.C. change point is greater than the drop occurring for the parabolic rate constants of the same modified parabolic law used throughout the oxidation (fig. 22).

6.4. Basic properties of iron

In order to evaluate the significance of the activation energy values from the Arrhenius plots it is necessary to consider certain properties of iron.

6.4.1. Vacancy diffusion in B.C.C. iron

According to Dunnington (108), the energy \( E \) required to form a vacant lattice site in iron is given by,

\[
E^* = \frac{1}{2} \left( \Delta H_{Vap} - \Delta H_{fus} - RT \right)
\]

where, \( \Delta H_{Vap} = \) heat of vapourisation
\( \Delta H_{fus} = \) heat of fusion
According to Kelley (109), the $H_{vap}$ for paramagnetic B.C.C.-iron is given by,

$$H_{vap} = 96,620 - 0.49T - 1.68 \times 10^{-3} T^2$$

:. At $T = 847^\circ C$, $H_{vap} = 94,005$ cal/mol

:. $E^* = 44,028$ cal/mol

The number of lattice vacancies, $n^*$ is related to the total number of sites, $N^*$ in the following way

$$n^* = N^* \exp \left( -\frac{E^*}{RT} \right)$$

With $E^* = 44,028$ Kcal/mol,

$$\frac{n^*}{N^*} = 2.535 \times 10^{-9} \text{ at } T = 847^\circ C$$

The vacancy diffusion co-efficient in iron, $D_{vac}$ is, related to the co-efficient of self diffusion of iron $D^*$ as follows,

$$D_{vac} = \frac{N^*}{n^*} \cdot D^*$$

$D^*$ can be expressed as,

$$D^* = D_0 \exp \left( \frac{-Q_D}{RT} \right)$$

where $D_0$ = pre-exponential term and is a constant,

$Q_D$ = Activation energy of diffusion.

Various $D_0$ - and $Q_D$ - values are quoted in the literature and lead to the $D^*$ and $D_{vac}$ values listed in Table(24).
Table 24

<table>
<thead>
<tr>
<th>Work of</th>
<th>( D^* ), (cm²/sec)</th>
<th>( D_{vac} ), (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Birchenall, (110)</td>
<td>1.18 x 10⁻¹¹</td>
<td>4.655 x 10⁻³</td>
</tr>
<tr>
<td>2) Borisov, (111)</td>
<td>1.094 x 10⁻¹¹</td>
<td>4.6 x 10⁻³</td>
</tr>
<tr>
<td>3) James, (112)</td>
<td>3.88 x 10⁻¹¹</td>
<td>12 x 10⁻³</td>
</tr>
<tr>
<td>4) Leymonie, (113)</td>
<td>5.825 x 10⁻¹²</td>
<td>2 x 10⁻³</td>
</tr>
</tbody>
</table>

6.4.2. Vacancy diffusion in F.C.C. - iron

According to Kelley (109) for F.C.C. - iron,

\[
H_{vap} = 96,610 - 2.77T
\]

Taking the temperature \( T = 945^\circ C \), the \( H_{vap} \) value becomes equal to 93,236 cal/mol,

\[
\therefore E^* = 43,546 \text{ cal/mol}
\]

\[
\therefore \frac{n^*}{N} = \exp. - \frac{E^*}{RT} = 1.521 \times 10^{-8}
\]

As in the case of B.C.C. - iron, the calculated \( D^* \) and \( D_{vac} \) values are given in Table (25)

Table 25

<table>
<thead>
<tr>
<th>Work of</th>
<th>( D^* ), (cm²/sec)</th>
<th>( D_{vac} ), (cm²/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Birchenall (110)</td>
<td>2.77 x 10⁻¹³</td>
<td>1.825 x 10⁻⁵</td>
</tr>
<tr>
<td>2) Borisov, (111)</td>
<td>6.4 x 10⁻¹³</td>
<td>4.0 x 10⁻⁵</td>
</tr>
<tr>
<td>3) Sparke, (114)</td>
<td>7.1 x 10⁻¹³</td>
<td>5.0 x 10⁻⁵</td>
</tr>
</tbody>
</table>
The following conclusions are therefore reached in this section:

a) The self-diffusion of vacancies in B.C.C. is about a hundred times faster than that in F.C.C. - iron [this was also shown qualitatively by Fishbeck (51)]. A greater $D_{\text{vac}}$ value means faster diffusion of vacancies from the metal/oxide phase interface to the interior of the metal.

b) The energy of vacancy formation is found to be nearly the same in both B.C.C. and F.C.C. - iron.

c) The equilibrium concentration of vacancies in F.C.C. is twice that in B.C.C. - iron.

6.4.3. Velocity constants at the interfaces

In this section, $K_a \cdot K_b$ values for both B.C.C. and F.C.C. - iron are calculated. This is achieved by using eqn. (28) in which the $(C_{2e} - C_{1e})$ value is the only unknown. This may be obtained from eqn. (29) by evaluating $D_{\text{eff}}$, which is achieved in the following way:

Since wüstite is a p-type oxide,

$$D_{\text{eff}} = 3 \cdot D_{\square}$$

where $D_{\square}$ = Diffusion co-efficient of vacancies through the oxide.

According to Wagner (6):

$$y_v \cdot D_{\square} = (1 - y_v) \cdot D_c$$

where $y_v$ = vacancies in the sublattice of iron

$D_c$ = self-diffusion co-efficient of cation through the oxide

Himmel, (115) derived the following expression,

$$D_c = 0.118 \exp \left( -\frac{Q}{RT} \right)$$

(30)
where, \( Q = 29.7 \text{ Kcal/gm.atm.} \) when the wustite is of composition \( \text{FeO}_{0.907} \), or in other words, when \( \gamma = 0.093 \) and the oxide with density, \( \rho_{\text{ox}} = 5.643 \text{ gm/cm}^3 \).

At a particular temperature, of say, \( 850^0°C \), the eqn. (30) may be written as

\[
\log_{10} D_c = 7.2879 \text{ which yields } D_c = 1.94 \times 10^{-7} \text{ cm}^2/\text{sec.}
\]

Hence, \( D_\square = \frac{1-n}{\gamma} \cdot D_c = 0.907 \times 1.94 \times 10^{-7} = 1.892 \times 10^{-6} \text{ cm}^2/\text{sec.} \)

and \( \text{Deff} = 3D_\square = 5.676 \times 10^{-6} \text{ cm}^2/\text{sec.} \)

Using eqn. (29)

\[
(C_{ze} - C_{1e}) = \frac{(K_p)_M \times 66.65}{(16)^2 \times 2 \times 5.676 \times 10^{-6} \times 5.613} \text{ mol/cm}^3.
\]

From the present study, \((K_p)_M = 0.317 \times 10^{-6} \text{ gm}^2/\text{cm}^4 \cdot \text{sec.} \)

at \( 850^0°C \) and \( p_{O_2} = 7.6 \text{ cm.Hg.} \)

\[
(C_{ze} - C_{1e}) = 1.295 \times 10^{-3} \text{ mol/cm}^3 \text{ at } 850^0°C.
\]

At \( 850^0°C, (K_M) = 0.783 \times 10^{-4} \text{ gm/cm}^2 \cdot \text{sec.} \), which will give from eqn. (28) \( K_a \cdot K_b \left( K_a + K_b \right) = 0.06 \text{ cm/sec. at } 850^0°C. \)

Nearly the same value is found at 870°C. Such equality at different temperatures is expected provided the metal substrate has the same crystal structure, because \( K_a \) and \( K_b \).
are the velocity constants at the interfaces. Recalculation of Engell's (103) figures also gives almost the same value of 0.07 cm/sec. In F.C.C. - iron the $\frac{K_a}{K_a + K_b}$ value is found to be of the order of 0.7 cm/sec. It can be therefore stated that for a constant $p_{O_2}$ - value of 7.6 cm.Hg, the $\frac{K_a - K_b}{K_a + K_b}$ value in F.C.C. is ten times greater than that in B.C.C. - iron, i.e.

$$\frac{10\{K_aK_b\}}{K_a + K_b} \approx \frac{K_aK_b}{(K_a + K_b)^2} \text{F.C.C.}$$

or

$$\left\{\frac{1}{K_a} + \frac{1}{K_b}\right\} \text{B.C.C.} \approx 10\left\{\frac{1}{K_a} + \frac{1}{K_b}\right\} \text{F.C.C.} \quad (31)$$

In the previous section (6.4.2) it has been established that a very high rate of self-diffusion of vacancies prevails in B.C.C. - iron, or in other words, metal supply from the interior to the metal/oxide interface is faster in B.C.C. - iron. This means a higher $K_a$ - value in B.C.C. than in F.C.C. - iron, i.e. $(K_a)^{\text{B.C.C.}} \gg (K_a)^{\text{F.C.C.}}$

So,

$$\left\{\frac{1}{K_a}\right\}^{\text{B.C.C.}} \ll 10\left\{\frac{1}{K_a}\right\}^{\text{F.C.C.}}$$
But it is shown in eqn. (31) that
\[
\left\{\frac{1}{K_a} + \frac{1}{K_b}\right\}_{\text{B.C.C.}} = 10 \left\{\frac{1}{K_a} + \frac{1}{K_b}\right\}_{\text{F.C.C.}}
\]
Therefore,
\[
\frac{1}{K_b}_{\text{B.C.C.}} \gg 10 \frac{1}{K_b}_{\text{F.C.C.}}
\]
or
\[
(K_b)_{\text{B.C.C.}} \ll (K_b)_{\text{F.C.C.}}
\]
Thus of the two values of \(K_a\) and \(K_b\), \(K_b\) is smaller in B.C.C., whilst \(K_a\) is smaller in F.C.C. - iron. Therefore for a modified parabolic law of oxidation, it appears that of the two phase-boundary reactions, that at the metal/oxide interface is the controlling step in F.C.C. - iron, whilst in B.C.C. - iron it is the gas/oxide interface reaction acting as the rate controlling reaction.

6.5. Lattice geometry and the activation energy of oxidation

The various activation energies obtained in the present work are given in Table-26. The result in column -3 for F.C.C.-iron (i.e. activation energy of oxidation of F.C.C.-iron at \(p_{O_2} = 29\) cm.) refers to the case where only a true parabolic law is obeyed. In all other cases, the modified parabolic law of oxidation holds good. It will now be shown that the parabolic rate constants are the results of diffusion of ionic species across the oxide, while the
linear rate constants are due to the phase-boundary reactions, occurring at either the metal/oxide or gas/oxide interface.

### Table-26

Comparison of activation energy of oxidation (Kcal/mol) of iron.

<table>
<thead>
<tr>
<th>Structure of iron</th>
<th>Present work</th>
<th>Bénard's work (50)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{O_2} = 7.6\text{cm}$</td>
<td>$P_{O_2} = 29\text{cm}$</td>
</tr>
<tr>
<td>B.C.C.</td>
<td>$Q(p)_M$ = 62 ± 0.5</td>
<td>$Q(1)_M$ = 64 ± 1</td>
</tr>
<tr>
<td>F.C.C.</td>
<td>$Q(p)_M$ = 35 ± 1</td>
<td>$Q(1)_M$ = 22 ± 1</td>
</tr>
</tbody>
</table>

*Value of $Q(p)_M$ is obtained from the slope of $\log_{10}$ (parabolic rate constant) against $1/T$, value of $Q(1)_M$ is obtained from the slope of $\log_{10}$ (linear rate constant) against $1/T$."

6.5.1. Activation energy for the oxidation of B.C.C.-iron.

From Engell's work (103), the activation energy for pure vacancy diffusion through wüstite is estimated to be equal to 34 Kcal/mol, which is almost the same as the self diffusion of iron in wüstite. The vacancy diffusion coefficient at a particular temperature has been shown to be
independent of the non-stoichiometry of wüstite (i.e. of the \( y^\Psi \) value, where \( y^\Psi \) represents the vacancies in the sublattice of iron). The \( Q(p)_{M} \) values at \( p_{o2} = 7.6 \text{cm.} \) and 29 cm. are 62 and 33 Kcal/mol. Since the \( Q(p)_{M} \) value is dependent on diffusion-controlled mechanism, the result at \( p_{o2} = 29 \text{ cm.} \) is in good agreement with the activation energy for the diffusion of vacancies (within experimental accuracy). The \( Q(1)_{M} \) values for B.C.C.-iron are 64 and 58 Kcal/mol which are nearly equal to half the dissociation energy of the oxygen molecule. These values are also in good agreement with the value of 60 Kcal/mol obtained by Bénard (50).

Dissociation of an oxygen molecule at the gas/oxide interface therefore appears to be the rate controlling phase-boundary reaction of the linear scaling of B.C.C. - iron. This fact is in accord with the deduction already made (Sec.6.4.3.) that a reaction at the oxide/oxygen interface will be the rate controlling step. The value of \( Q(p)_{M} \) equals to 62 Kcal/mol at \( p_{o2} = 7.6 \text{ cm.} \) still remains unexplained. No plausible interpretation can be given, but it will be worth while to mention that the enthalpy of wüstite formation is also 60 Kcal/mol.
6.5.2. Activation energy for the oxidation of F.C.C.-iron

The \( Q'(p)^M \) - values at the two different pressures of oxygen are 35 and 33 Kcal/mol. These values are similar to the activation energy of vacancy diffusion through wüstite, so that vacancy diffusion through the wüstite layer is one of the rate controlling processes for both \( p_{o2} \) - values in F.C.C.-iron. The value \( Q'(p)^M = 33 \) at \( p_{o2} = 29 \) cm relates to \( n = 2 \pm 0.1 \) i.e. for a true parabolic law, whereas \( Q'(p)^M = 35 \) at \( p_{o2} = 7.6 \) cm relates to \( n = 1.5 \pm 0.1 \) i.e. for a modified parabolic law. Although the activation energy-term is similar in the two cases, the rate constants are different (fig.22&23; Tables 14). This suggests that the difference in the parabolic rate constants in these two cases is perhaps due to a different pre-exponential term in the Arrhenius equation. The \( Q'(1)^M \) - value is 22 Kcal/mol. This value of \( Q'(1)^M \) can be compared with that obtained by Bénard (50) and with the energy required to disrupt an iron-iron bond [Higuchi, et al. (116)]. The metal/oxide interface reaction is therefore the suggested rate controlling phase-boundary reaction (sec.6.4.3.) of the linear oxidation of F.C.C.-iron.

The likely overall reactions are thus considered to be as follows:
(1) \( \frac{1}{2} \, O_2 \rightleftharpoons FeO + Fe^{2+} + 2e^- \), occurring at the oxide/gas interface where the first reaction is the dissociation, followed by simultaneous ionisation of the oxygen molecule.

(2) \( Fe_{\text{atom}} + Fe^{2+} + 2e^- \rightleftharpoons Fe^{+2} + 2e^- \), occurring at the metal/oxide interface where the first reaction is the rupture of iron-iron bond.

(3) \( \left\{ Fe^{2+} + 2e^- \right\}_{\text{oxide/gas}} \rightleftharpoons \left\{ Fe^{2+} + 2e^- \right\}_{\text{metal/oxide}} \) is the diffusion across the oxide layer.

Thus the suggested electrochemical model can be represented as,

<table>
<thead>
<tr>
<th>Iron</th>
<th>Wüstite</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Possible anodic reaction is given by (2) above</td>
<td>( \overset{\text{Fe}}{\text{Fe}^{2+}} )</td>
<td>Possible cathodic reaction is given by (1) above</td>
</tr>
<tr>
<td>( \overset{\text{Fe}}{\text{Fe}^{2+}} )</td>
<td>( \overset{2,e^-}{\text{Fe}^{+2}} )</td>
<td>( \overset{\text{Fe}^{2+}}{\text{Fe}^{+2}} )</td>
</tr>
</tbody>
</table>

6.6. Role of electronic effects

According to Mott (117) the B.C.C. \( \rightarrow \) F.C.C. transition in iron produces no great change either in the number of wave-functions of the 4S-electrons, or the number of holes in the 3d-bond, though the magnetic coupling between their spins may be very sensitive to interatomic distance. Changes in
work function, atomic susceptibility, specific heat, etc.
with change of lattice structure could be considered to
explain the oxidation mechanism and the effect of the space
charge layer at the interfaces can also be considered relevant.
However, the oxide scale in the present case is thick enough
(\(\sim 70\mu\) max.) to consider the oxidation process to be outside
the effect of any electric field-transport mechanism. Thus
results are explained in terms of the geometric factor.

6.7. Effect of oxygen pressure

A decreased oxidation rate is observed with an increased
oxygen pressure. Such a decreased rate is associated with the
corresponding decreased rate-constant values. The slopes of
the plots of \(\log_{10} (\text{rate constant})\) against \(\log_{10} (p_{O_2})\) at
various temperatures lead to the following relations between
the rate constants and \(p_{O_2}\) - values (table-27).

<table>
<thead>
<tr>
<th>Crystal form</th>
<th>Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.C.C.-iron</td>
<td>((K_p)<em>M = (p</em>{O_2})^{-1.6})</td>
</tr>
<tr>
<td>B.C.C.-iron</td>
<td>((K_1)<em>M = (p</em>{O_2})^{-1.2})</td>
</tr>
<tr>
<td>F.C.C.-iron</td>
<td>((K_p)<em>M = (p</em>{O_2})^{-2.5})</td>
</tr>
<tr>
<td>F.C.C.-iron</td>
<td>((K_1)<em>M = (p</em>{O_2})^?)</td>
</tr>
</tbody>
</table>
No relationship could be estimated between \((K_1)_M\) and \(p_{O_2}\) in the F.C.C. range because there was no \((K_1)_M\) value at \(p_{O_2} = 29\) cm in the F.C.C.-iron where only true parabolic law was obeyed. The other relationships in table-(27) must be considered only tentative, since only two \(p_{O_2}\) values were available from the present work.

At increased pressure of oxygen, more oxygen atoms will be available at the oxide/gas interface and so more cation vacancies will be formed and displaced inside the oxide lattice. However, with the same metal substrate the reaction rate at the metal/oxide interface at a particular temperature (but at different \(p_{O_2}\) values) will remain unaltered. Assuming that the reaction rate at the metal/oxide interface is at its saturation limit, then any further incoming of cation vacancies will possibly result in an increased back pressure at the metal/oxide interface. Such a back pressure will ultimately produce a decreasing rate of oxygen dissociation at the oxide/gas interface. This type of inverse relation between vacancy concentration and rate of oxygen dissociation has been recently predicted by Wagner (118) for oxidation when \(n = 1.5\) i.e. in case of a modified parabolic law. Thus for a p-type oxide (as is the case here) if modified parabolic law of oxidation is obeyed, then according to the present work and the corresponding reasoning, a decreasing oxidation rate with increasing \(p_{O_2}\) value can be expected.
7. Discussion on the Oxidation of cobalt

It is assumed here that the experimental results obtained in the present work are only due to the oxidation reaction (i.e. neglecting any solubility of oxygen in cobalt). Such an assumption is reasonable, because the solubility of oxygen in cobalt is low; the maximum solubility in H.C.P.-cobalt is $2 \times 10^{-2}$ wt. % and in F.C.C.-cobalt (at 1000°C) is $0.8 \times 10^{-2}$ wt. %. An X-ray analysis of the as-received metal was carried out and showed the structure of the metal to be consisting entirely of H.C.P.-phase.

7.1. Choice of oxidation law

The conventional graphical method was tried first to find out the relevant law. As shown in fig. (26), plots of $W$ (the weight of oxygen consumed, per unit area of specimen, $\mu$gm/cm$^2$) against time, $t$, give sets of curves. However, semi logarithmic plots of the same set of results (fig. 27) are found to be linear. This indicates that a direct-logarithmic law is obeyed here. The $n$-value of the empirical power equation—(21), varies over a wide range. Such a phenomenon, as mentioned earlier (sec. 6.1.4), can be expected for a set of results which obey a direct-logarithmic law of oxidation. Thus the direct-logarithmic law is taken to be the rate controlling law for the oxidation of cobalt in the initial stages. The values obtained are comparable with those obtained by Gulbransen (75) in the initial stages of oxidation [as replotted by Uhlig (78)]. Many models have been...
proposed to explain a direct-logarithmic oxidation and these are summarised below in table-(28).

Table-28

Summary of mechanism for the interpretation of direct-logarithmic law of oxidation.

<table>
<thead>
<tr>
<th>Model</th>
<th>Rate determining reaction</th>
<th>Oxide(Limiting) thickness</th>
<th>pressure-dependence</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mott, Hauffe, Ilschner</td>
<td>electron tunneling</td>
<td>films &lt; 50 Å</td>
<td>-</td>
<td>11,14</td>
</tr>
<tr>
<td>Grimley, Trapnell</td>
<td>ion transfer in electric field</td>
<td>thin film of p-type oxide</td>
<td>yes</td>
<td>.15</td>
</tr>
<tr>
<td>Landsberg</td>
<td>chemisorption</td>
<td>thin films</td>
<td>yes</td>
<td>.10</td>
</tr>
<tr>
<td>Evans</td>
<td>diffusion coupled with cavity formation</td>
<td>scales</td>
<td>-</td>
<td>93</td>
</tr>
<tr>
<td>Uhlig</td>
<td>electron transfer at metal/oxide interface</td>
<td>films &lt; 10^4 Å</td>
<td>None</td>
<td>7</td>
</tr>
</tbody>
</table>

In the present work, the oxide thickness varies with temperature from about 400 to 5,000 Å and the oxidation rate is found to be independent of oxygen pressure. These two facts eliminate the applicability of all the above models except those of Evans and Uhlig. Evans has considered that the oxide growth is determined by a process of mechanical breakdown in the oxide layer. But the oxide film is generally regarded as mechanically perfect (12,15).
So the most likely model to explain the present results is the electron-emission theory proposed by Uhlig (7), also derived almost simultaneously by Williams (119) by a slightly different approach. Such a model explains the occurrence of direct-logarithmic law in terms of the space-charge layer formation. Campbell and Thomas (41) also expressed a similar opinion that the initial deviations from the parabolic equation of oxidation for copper, are caused by a space-charge layer in the oxide (about 10^-14 Å thick as determined by electrical capacitance measurements).—The model basically assumes that the oxidation rate is controlled by the electron-emission at the metal/oxide interface. Uhlig's theory is discussed critically in the next section. Certain modifications of the theory are also discussed.

7.2. Criticism of Uhlig's model

Uhlig (7) has derived the direct-logarithmic law of oxidation on the basis of a rate-controlling electron emission mechanism. According to Uhlig, the situation at a metal/oxide contact is similar to the electrical double layer arising at metal surfaces in contact with electrolytes. Therefore in order to explain this model it is worthwhile to briefly mention the double layer phenomena at solid/liquid interfaces. Helmholtz suggested in 1879, a sharp potential gradient i.e. a uniform distribution of positive and negative ions in the double layer at the solid/liquid interface, while modern views are in favour of a
diffuse double layer [Gouy (120)] i.e. a non-uniform distribution of ions. Stern (121) developed a view combining the essential features of both schools of thought, in which the electrical double layer consists of a uniform fixed part (Helmholtz's idea) which is followed by a non-uniform diffuse part (Gouy's idea) (figs. 32 and 33). Here the potential of the solid is indicated by A and that of the bulk of the liquid by B, the fall in potential in between may occur in two ways, (fig. 32 and 33), depending on the character of the ions or molecules which make up the outer portion of the fixed layer. Using Stern's concept, Uhlig proposed that the space charge layer at the metal/oxide interface (analogous with the double layer at the solid/liquid interface) consists of two types of layers, a space charge layer of uniform constant density, followed by a diffuse layer (fig. 34). However, this concept of the two types of layers in the space charge region does not necessarily apply to all the metal/oxide systems. In the present case the oxide is a semi-conductor, so metal/semi-conductor contact theory is more applicable. The space charge layer here consists of only one layer of uniform density at the metal/semi-conductor interface. Thus for a p-type semi-conductor with a high density of surface states, the metal/semi-conductor contact consists of a uniform space charge layer extending into the bulk of the semi-conductor and an induced charge of opposite sign on the metal/semi-conductor.
Energy level diagram for the metal/semi-conductor (p-type) contact.

Notations:
- \( y \) = Oxide-thickness
- \( \delta \) = Thickness of the interface
- \( E_c \) = Conduction level
- \( E_F \) = Fermi level
- \( E_V \) = Valence level

\( V_s \) and \( V_p \) are the potentials across the interface & space-charge layer respectively, while \( \phi_M \) is the work-function of the metal. Positively charged surface states.
interface (fig. 35). So although it is agreed that an electron emission mechanism is the rate controlling process in the direct-logarithmic law of oxidation, Uhlig's idea of two types of layers can be modified in terms of a single uniform space charge layer. In the following the direct-logarithmic law is re-derived on the basis of this concept. Reference is made to the work of Bardeen (122), Cowley (123), Crowell (124), Detwiler (125), Meyerhof (126), Uhlig (7) and Williams (119).

7.3. The direct-logarithmic law

7.3.1. Basic form

During oxidation of a metal, a positive space charge in the oxide is initially formed because of the rapid accumulation of positive metal ions. This is followed by an electron flow from the metal to the oxide. As the oxide grows, a decrease of positive space charge occurs because some of the electrons travelling into the oxide become bound or trapped at oxide lattice imperfections [(Mott and Gurney (127)] which may occur at impurity centres or at lattice vacancies. Such a concept of electron trapping in energy states set up by localised structural defects is now generally accepted and widely applied in semi-conductor theory. The oxide eventually acquires an overall negative charge. Thus although a positive space charge is built up at the onset of oxidation but because of the "trapped" electrons in the oxide, a negative space charge layer is finally formed. When the oxidation rate is controlled by electron flow from the metal, an increasing negative space charge (or decreasing positive space charge) obviously becomes an important factor in
establishing the rate of electron-flow, tending in general to slow down the escape of electrons as the oxide grows and therefore simultaneously slowing down the escape of metal ions and the oxidation process itself. This negative space charge however, induces a "surface-state" charge of opposite sign on the localised electronic states associated with the surface lying in the forbidden region between the conduction and valence bands of the semi-conductor—[Bardeen (22)]. Thus the oxide layer at the surface metal/oxide contact consists of a positive state charge on the semi-conductor i.e. the oxide and a negative space charge layer extending to a depth of \(10^2\) to \(10^4\) Å inside the oxide. At the metal/semi-conductor contact an insulating gap, \(\varepsilon\), equivalent to the average length of individual surface dipoles is assumed to be present [Cowley (123)] (fig. 35). The average length is of the order of spacings, \(3 \times 10^{-8}\) cm. The essential step in the oxidation process is the supply of electrons so that the oxygen molecules or atoms may be ionised and incorporated in the oxide. Electrons may be extracted from the full band of energy levels in the oxide but an alternative source is the metal by thermal emission through the conduction band of the oxide. The number \(N\) of electrons arriving per unit area of the oxide/gas interface per second will determine the rate of growth. The volume of oxide formed when one electron combines with oxygen is denoted by \(\Delta\), so that

\[
\frac{dy}{dt} = N \cdot \Delta.
\]
where, \( y \) denotes the oxide-thickness formed at time \( t \) after an interfacial layer of thickness \( k \) is formed. The rate \( N \) may be calculated from the usual expression for thermionic emission,

\[
N = N_0 \cdot \exp \left\{ -\frac{\Psi_e}{kT} \right\}
\]

where \( \Psi_e \) is the minimum height of the energy barrier which an electron must overcome to reach the oxide/gas interface and \( N_0 \) is the number of Fermi electrons moving toward the barrier per second.

In the present case, the oxide is a p-type semiconductor and a negative space charge layer is formed at the metal/oxide interface. These two facts reflect a rectifying contact with the bands shifting downward (fig. 35). The potential drop across the barrier accompanying the rectifying contact, consists of two parts, \( V_s \) from \( y = -\delta \) to \( y = 0 \) and \( V_p \) from \( y = 0 \) to \( y = \gamma \). The overall potential \( \Psi \) is thus made up of the work function \( \phi_M \) of the metal, a potential drop \( V_s \) (mainly due to surface state charge), a rise \( V_p \) in potential (due to the space charge layer) and another drop, \( V_a \) in potential due to the electron affinity of oxygen at the gas/oxide interface. Thus

\[
\Psi = \phi_M - V_s + V_p - V_a \quad (32)
\]

The potential \( V_p \) across the space charge layer, may be evaluated as a function of the distance \( y \), by applying Poisson's equation,
\[
\frac{d^2 V}{dy^2} = \frac{4\pi N_v e}{\varepsilon}
\]

\(N_v\) being the number of trapped electrons per unit volume of the oxide and \(\varepsilon\) being the dielectric constant of the oxide.

Integration of this equation gives:

\[
\frac{dV}{dy} = \frac{4\pi N_v e y}{\varepsilon} + C_1
\]

The field, \(\frac{dV}{dy}\) due to the negative space charge must vanish at the metal/oxide contact i.e. where \(y = -\delta\).

\[
C_1 = \frac{4\pi N_v e \delta}{\varepsilon}
\]

\[
\frac{dV}{dy} = \frac{4\pi N_v e}{\varepsilon} (y + \delta)
\]

On integration, according to Williams (119),

\[
V_p = \frac{4\pi N_v e}{\varepsilon} (\delta y + \frac{y^2}{2})
\]

With thin oxide films, the term involving \(y^2\) can be neglected, so that,

\[
V_p = \frac{4\pi N_v e}{\varepsilon} (\delta y) \quad \quad \quad \quad \quad \quad \quad (33)
\]

With no applied voltage, \(V_s\) can be derived from Gauss's law applied to the surface charge on the metal and oxide,

\[
V_s = \frac{4\pi (n_s e) \delta}{\varepsilon_1}
\]

where \((n_s e)\) is the surface density of charge, \(n_s\) being the
number of surface states per unit area, $\varepsilon_i$ is the dielectric constant of the interfacial layer which is assumed for convenience to be equal to $\varepsilon$ of the oxide. Thus eqn. (32) can be written now as,

$$\psi = \phi_m - V_a + V_p - V_s$$

$$= \phi_m - V_a + \frac{4\pi N_V e (8y)}{\varepsilon} - \frac{4\pi n_s e}{\varepsilon}$$  \hspace{1cm} (35)

It will be shown later (sec.7.6.2) that the electrostatic potential, $V_p$ across the space charge layer has a small magnitude compared with the potential, $V_s$.

7.3.2. Deduction of the law

As given earlier (sec.7.3.1.),

$$\frac{d\psi}{dt} = n_0 \Omega \cdot \exp (\frac{-\psi e}{RT})$$

can be written now on substituting the $\psi$-values as

$$\frac{d\psi}{dt} = n_0 \Omega \cdot \exp \left[ -\frac{e}{RT} \left( \phi_m - V_s + V_p - V_a \right) \right]$$

$$= n_0 \Omega \cdot \exp \left[ -\frac{e}{RT} \left( \phi_m - V_s - V_a \right) \right] \exp \left[ -\frac{e V_p}{RT} \right]$$

$$= n_0 \Omega \cdot \exp \left[ -\frac{e}{RT} \left( \phi_m - V_s - V_a \right) \right] \cdot \exp \left[ -\frac{4\pi N_V \varepsilon (8y)}{RT} \right]$$  \hspace{1cm} (36)

This expression for the rate of oxidation is of the same form as that of the direct logarithmic law:

$$\frac{d\psi}{dt} = A \cdot \exp (-B y)$$  \hspace{1cm} (37)

Integrating on condition that when $y = 0$, $t = 0$, the
direct-logarithmic equation is obtained, thus

\[ y = K_0 \log_e \left( \frac{t}{T} + 1 \right) \]  

where \[ K_0 = \frac{1}{B} = \frac{e^{kT}}{4\pi N_v e^{2.5}} \], \( K_0 \) is the direct logarithmic rate constant,

\[ \frac{1}{T} = AB = \frac{N_0}{K_0} \exp \left\{ -e(\Phi_e - V_A - V_S \right\} \]

[Units of \( K_0 \) and T are \( \mu g/cm^2 \) or Å and minutes respectively.]

Equation (38) is identical to the direct-logarithmic equation given in sec. 2.4 where the thickness of the oxide, \( y \), is replaced by the weight of oxide, \( W \). From eqn. (38),

\[ \frac{dY}{dt} = \frac{K_0}{t + T} \]

or \[ \log_e \frac{dY}{dt} = \log_e K_0 - \log_e (t + T) \]  

From eqn. (37), \[ \log_e \frac{dY}{dt} = \log_e A - B_y \]  

Using equations, (39) and (40), it can be written

\[ \log_e K_0 - \log_e (t + T) = \log_e A - B_y \]

or \[ \log_e \frac{Y}{K_0} = \log_e A - B_y + \log_e (t + T) \]  

Since, \[ B_y = \frac{Y}{K_0} = \log_e \left( \frac{t}{T} + 1 \right) \], therefore eqn. (41) can be written as
\[
\log_e K_0 = \log_e A - \log_e \left( \frac{t}{T} + 1 \right) + \log_e (t + T)
\]

\[
= \log_e A + \log_e T - - - - - - - (42)
\]

### 7.3.3. Significance of \(T\)-term

It will be now worthwhile to consider the significance of the terms such as \(A\) and \(T\). From eqn. (42), it can be written that,

\[
\log_e \frac{K_0}{T} = \log_e A.
\]

or, \(\frac{K_0}{T} = A\).

From eqn. (37), \(\frac{dy}{dt} \bigg|_{y=0} = A\); and \(\frac{K_0}{T} = A\)

and from eqn. (39), \(\frac{dy}{dt} \bigg|_{t=0} = \frac{K_0}{T}\) when \(t = 0, y = 0\).

The term \(A\) thus means the initial oxidation rate with which the oxidation process would start and \(T\) is the time necessary to oxidise the metal to thickness \(K_0\) at the initial oxidation rate.

Variation of \(T\) with temperature is uncertain, because there is no direct relationship in the relative variation of \(K_0\) and \(\frac{dy}{dt} \bigg|_{t=0}\) with temperature. As a result, \(T\) could be independent or directly proportional to temperature.
Case 1. When $T$ is independent of temperature, then eqn. (42) becomes

$$
\frac{d(\log_K)}{d\left(\frac{1}{T}\right)} = \frac{d(\log_A)}{d\left(\frac{1}{T}\right)} - \frac{d\left\{\Omega N_0 \exp \left[ -\frac{e(\phi_M - V_s - V_a)}{kT}\right]\right\}}{d\left(\frac{1}{T}\right)}
$$

The term $(\Omega N_0)$ is independent of temperature, therefore by the Arrhenius equation,

$$
-\frac{E}{R} = \frac{d(\log_K)}{d\left(\frac{1}{T}\right)} = -\frac{e(\phi_M - V_s - V_a)}{kT} - (43)
$$

where $E$ is the activation energy of oxidation.

Case 2. When $T$ is considered to be directly proportional to the temperature $T$, i.e. $T = \alpha T$ or $T = pT$ where $p$ is a constant, independent of temperature, eqn. (42) now becomes

$$
\log_e K_0 = \log_e A + \log_e p T = \log_e A + \log_e p + \log_e T
$$

or,

$$
\frac{\log_e K_0}{T} = \frac{\log_e A}{T} + \log_e p
$$

$$
\therefore -\frac{E}{F} = \frac{d(\log_e \frac{K_0}{T})}{d\left(\frac{1}{T}\right)} = \frac{d}{d\left(\frac{1}{T}\right)} \frac{\log_e A}{T} = -\frac{e(\phi_M - V_s - V_a)}{kT} - (44)
$$

Thus according to eqn. (43), the slope of a plot of $\log_e K_0$ against $1/T$ gives an activation energy of oxidation $E$. A plot of $\log_e \left(\frac{K_0}{T}\right)$ against $1/T$ according to eqn. (44) will give the same $E$-value if there is a uniform variation of $K_0$ with temperature $T$. In the present case, this is so (sec. 7.5.). Thus in both cases, eqn. (43) & (44),
\[ E = e^{(\phi_M - V_a - V_s)} \quad (45) \]

The activation energy of oxidation, \( E \) is thus found to be independent of the potential, \( V_d \) across the space charge layer for a direct-logarithmic oxidation law.

7.3.3.1. Variation of \( \tau \) with temperature

In the present work \( \tau \) is found to vary directly with temperature. Uhlig's (78) plots of Gulbransen's results (75) on cobalt have also shown a direct change of \( \tau \) with temperature. In Table-29, the \( \tau \)-values thus obtained are given, bearing in mind the fact that these values are not the absolute values.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( \log_{10} \tau )</th>
<th>( \tau ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>365</td>
<td>1.440</td>
<td>0.2750</td>
</tr>
<tr>
<td>412</td>
<td>1.799</td>
<td>0.6295</td>
</tr>
<tr>
<td>420</td>
<td>1.860</td>
<td>0.7294</td>
</tr>
<tr>
<td>453</td>
<td>0.930</td>
<td>1.0722</td>
</tr>
<tr>
<td>470</td>
<td>1.968</td>
<td>0.930</td>
</tr>
<tr>
<td>520</td>
<td>0.162</td>
<td>1.450</td>
</tr>
</tbody>
</table>

As shown before, [from eqn. (39)]

\[ \tau = \frac{K_0}{(\frac{dV}{dt})_{t=0}} \]
With increasing temperature both the terms on the right hand side, i.e. the rate constant, $K_o$ and initial oxidation rate, $(\frac{dy}{dt})_{t=0}$ should increase. Since $T$ increases with temperature, $K_o$ must be increasing at a greater rate than $(\frac{dy}{dt})_{t=0}$ (with increasing temperature).

### 7.3.4. Validity of the new derivation

Hauffe (16) has mentioned that a quantitative description of an oxidation system with a p-type oxide layer involves two space charge layers. The inner one in the vicinity of the metal/oxide interface is discussed above. The outer one near the oxide/oxygen interface is a negative surface charge due to the electron affinity of oxygen and a positive space charge layer extending into the oxide. This layer being thin can be assumed to be formed entirely by the electron affinity of the attacking oxygen. Thus the electron affinity term in eqn. (43) and (44) includes the effect that is produced at the oxide/oxygen interface. Hence the equation (43) or (44) can be considered valid over the entire range of the oxide film formed.

### 7.3.5. Comparison with Uhlig's deduction.

On the basis of the same assumption as above that the activation energy of oxidation, $E$ is equivalent to transfer of an electron from metal to oxide to oxygen adsorbed on oxide, Uhlig (7) however obtained,
\[ E = e (\phi - V_a) \]

for the initial part of uniform density layer. Here \( \phi \) is the metal work function \( \phi_M \) modified by amount \( \lambda_o \) through contact with the oxide so that \( \phi = \phi_M - \lambda_o \) and \( V_a \) is related to the electron affinity of oxygen.

Thus,

\[ E = e(\phi_M - \lambda_o - V_a) \quad \text{according to Uhlig} \]

and

\[ E = e(\phi_M - V_s - V_a) \quad \text{present work.} \]

Although these two forms are very similar, the equation derived in the present work is however valid for the whole range of the space charge layer, whereas Uhlig's equation is valid only for the uniform space charge layer. According to him, a different Arrhenius equation is required for the diffuse space charge layer and thus Uhlig's model predicts two different equations (Arrhenius type) and hence a two-stage oxidation process.

By contrast, the present work expects a single-stage oxidation process for a direct-logarithmic law, because the space charge layer is taken to be entirely of uniform charge density.

However, instead of a diffuse space-charge layer, Uhlig's model predicts two different equations (Arrhenius type) and hence a two-stage oxidation process.
7.3.6. Role of short circuit diffusion path.

From the transmission electron micrograph the oxide film was found to consist of many small crystallites [(Markali (128) also observed the same on initial oxide film)] and therefore a large number of possible low resistance paths [(Smith (33)]. Thus the greater part of the measured weight gain may be due to short circuit diffusion as opposed to volume diffusion. However the rate controlling process in the oxidation reaction is considered here to be the emission of electrons at the metal/oxide interface and this will be unaffected by the number of such paths. As a result, the activation energy of oxidation, which is related to the rate controlling step, will remain independent of the types of diffusion across the oxide.

7.4. Arrhenius plot

The Arrhenius plots obtained from eqns. (43) and (44) are almost identical. The \( \log_2 K_0 \) against \( \frac{1}{T} \) plot, according to eqn. (43), is shown in Fig. 28. Fig. (36) shows what may be expected if the Arrhenius plots were extrapolated. The upper position of the line obtained on extrapolation from the H.C.P.-phase seems to suggest a higher \( K_0 \) values i.e. higher rate constant, hence a higher oxidation rate for H.C.P.-cobalt as compared with the F.C.C.-phase. Interesting observations were made near the allotropic
transformation point, 386°C. Three points were obtained which do not fit into the curves already drawn through other points (Fig. 28). In the region of 386°C there is a sudden change of $K_0$ values. As a result, three types of curves near 386°C may be drawn (Figs. 37, 38, 39), namely,

Case.1) Here the sudden change of $K_0$ values is ignored and a curve is drawn to join up the H.C.P.-phase with the F.C.C.-phase of cobalt. (fig. 37).

Case.2) Arrhenius plot in the F.C.C.-region goes upward, while that of H.C.P. - cobalt bends downward. (fig. 38).

Case.3) Opposite to case (2), with the plot of F.C.C. - cobalt bending downward while that of H.C.P. - cobalt going upward (fig. 39).

There is no confirmatory evidence to prefer any one of these alterations. However, a selection of the probable ones can be made on the basis of the following argument.

Curve of Case.1) is not the probable one because it ignores the experimental points obtained near 386°C, though there is no reason to believe that these points are less valid experimentally than the others. The results near 386°C show that $K_0$ values drop downward (Fig. 38) from the expected extrapolated value (Fig. 36) in the H.C.P. - phase. Similarly there is an indication to some extent of high $K_0$ values
Possible forms of the Arrhenius plots on the oxidation of cobalt

Fig. 36

Fig. 37

Fig. 38

Fig. 39
while coming down from F.C.C.-end towards 386°C. This experimental evidence therefore supports case 2). However, curve of case-3) is also a possible one, because the H.C.P. - phase shows a higher oxidation rate than the F.C.C.-phase, as expected from the extrapolated Fig. (36). A higher frequency of electron emission in H.C.P.-cobalt with increasing temperature would account for the higher oxidation rate. This phenomenon may well be associated with a build up of "electron pressure". Such a concept of building up of a higher electron pressure in the brillouin zone is consistent with the Fermi surface behaviour at the onset of phase transformation. Thus both cases of (2) and (3) are possible ones in the present case.

7.5. Experimental activation energy of oxidation

The activation energy of oxidation, E has been estimated from the Arrhenius plot (fig.28). The values given in Table-30 are obtained from the Arrhenius plots using both the equations (43) and (44).

<table>
<thead>
<tr>
<th>Cobalt</th>
<th>E-value According to eqn. (43)</th>
<th>E-value According to eqn. (44)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H.C.P.</td>
<td>18 ± 1</td>
<td>18 ± 1</td>
</tr>
<tr>
<td>F.C.C.</td>
<td>20 ± 1</td>
<td>19 ± 1</td>
</tr>
</tbody>
</table>
Activation energies of oxidation of the two allotropic forms of cobalt thus do not differ much; E-values are lower with H.C.P. - cobalt by about 1 to 1.5 Kcal/mol than that with F.C.C. - phase. This difference can be assumed to be within the experimental error. Such similar E-values can be expected from eqn. (45), because the reported thermionic work functions ($\phi_M$-values) of cobalt allotropes are similar and other factors in eqn. (45) can be taken as constants. The plots (Fig 28 and 36) seem to suggest a higher oxidation rate constant, $K_o$ for H.C.P. - cobalt. Since $K_o$ is given by the Arrhenius eqn. as,

$$K_o = G \cdot \exp\left(\frac{E}{RT}\right)$$

it can be said that, because of similar E-values in the oxidation of both structures, the different $K_o$ - values could be attributed to the pre-exponential term, G of the Arrhenius equation. The pre-exponential term is related directly to the entropy of activation term. So it may reflect an increasing measure of the frequency factor or, in other words, a higher probability of an electron emission at the metal/oxide interface and its availability at the oxide/oxygen interface for the oxidation of H.C.P. - rather than that of the F.C.C. - cobalt.

7.6. Calculation of some relevant critical parameters

7.6.1. Density of surface levels, $n_S$

In the present study, the rate of oxidation is explained in terms of an electron emission mechanism at the metal/oxide interface. The electrical double layer is considered to consist of surface charge of atomic dimensions and a space
charge extending to a depth of about $10^2$ to $10^4$ Å into the semi-conductor. Nothing has been mentioned yet about the effect of metal on the formation of such double layer. Bardeen (122) has obtained a relation between the $n_s$ value and the effect of metal on the double layer. According to him, if the density of surface levels is sufficiently high e.g. $n_s > \sim 10^{13}/\text{cm}^2$, the double layer will be independent of the metal. However, for $n_s < \sim 10^{13}/\text{cm}^2$, the double layer will be small and will be determined approximately by the difference in work functions of metal and semi-conductor. To use Bardeen's concept, it is therefore necessary first to evaluate the $n_s$ value. It is known from eqn. (34) of sec. (7.3.1.) that,

$$V_s = \frac{4\pi (n_s e) \delta}{\varepsilon} \quad (34)$$

and from eqn. (45) of sec. (7.3.3.) that,

$$E = e (\phi_M - V_a - V_s) \quad (45)$$

First step will be to evaluate the $V_s$ value from eqn. (45).

**Step 1.** In eqn. (45), $E$ is the activation energy of oxidation, $\phi_M$ is the work-function of the metal and $V_a$ is the affinity of oxygen.

An average value of 19 Kcal/mol i.e. 0.824 eV. is taken for $E$ from the present work (sec. 7.5.). As regards to $\phi_M$ value, the thermionic work-function is to be considered.
The work of Wahlin (129) and Krishnan, et.al. (130) suggests that $\phi_M = 4.4 \text{ eV}$, and is independent of the crystal structure of cobalt. The value $V_a$ can be estimated by considering the likely reactive species (which can be either $O_2^-$ or $O^-\text{ ions}$ amongst other possible forms).

Winter (131) has mentioned the work of Garner, Stone, et.al., Hauffe, et.al. etc. who formulate the charged chemisorbed species as $O^-$ ions. Although Winter himself and Sancier (132) believe the formation of $O_2^-$ ions. However, recent reviews by Smith (133) and Amigues (134) have pointed out the active species to be $O^-$ ions. Grimley and Trapnell (15) subscribe this idea as well. Zettlemoyer, et.al. (80) on their work on the oxidation of cobalt powder, have shown that chemisorption of oxygen occurs with dissociation of oxygen followed by conversion to $O^-$ anions. From all these considerations it may be assumed that $O^-$ anion is the active species which can be finally converted to $O^{2-}$ anions.

Following Cabrera and Mott (13) who assume that the $O^-$ ion has an electron affinity of $2.2 \text{ eV}$, $V_s$ then becomes,

$$e \cdot V_s = e \left( \phi_M - V_a \right) - E$$

$$= 4.4 - 2.2 - 0.824$$

$$\approx 1.38 \text{ eV}.$$
Step 2.

In order to evaluate $n_s$ from eqn. (34) it only remains now to find out the values of $\varepsilon$ and $\delta$. The dielectric constant of the oxide, which may be a mixture of two oxide in the present case, is not well confirmed around the temperature of interest here. However, from the $\varepsilon$-values used by Uhlig (7,42,78) for different oxides such as nickel oxide, copper oxide, zinc oxide, $\varepsilon$-value of cobalt oxide is taken to be equal to 12, because of the very similar electro-static behaviour of the oxides. Rao et al. (135) found the $\varepsilon$-value of CoO is of that order. The $\delta$-value is of atomic dimension, $3 \times 10^{-8}$ cm. Thus $n_s$ is estimated from eqn. (34) as,

$$n_s = \frac{\varepsilon \cdot V_s}{4\pi \varepsilon_0 \cdot \delta} = \frac{\varepsilon \cdot (e \cdot V_s)}{4\pi \varepsilon_0 \cdot e^2 \cdot \delta}$$

$$= \frac{12 \times 1.38 \times 1.6 \times 10^{-12}}{4 \times 22 \times (4.8 \times 10^{-10})^2 \times 3 \times 10^{-8}}$$

$$\approx 3 \times 10^{14} / \text{cm}^2.$$

Since $n_s > 10^{13} / \text{cm}^2$, therefore in accord with Bardeen's concept, the double layer will be independent of the metal, and will be the same as that for the surface of the semiconductor. Either phases of cobalt, H.C.P. or F.C.C, thus have little influence on the space charge region in the present study.
7.6.2. Potential across the negative space charge layer, \( V_p \)

It is expected that in the case of a simple metal-semiconductor junction, contact potential difference is largely balanced by the surface states charge rather than by the space charge, [Bardeen (122)]. It is considered worthwhile to verify the validity of the statement in the present case. Thus values of the potential contributed by the surface charge, \( V_s \) and that by the space charge, \( V_p \) are estimated. From the preceding section (7.6.1) value of \( V_s \) is known. So here the value of \( V_p \) is to be estimated.

The potential across the space charge layer can be approximately calculated from the relation \( V_p \)

\[
V_p = \frac{4 \pi N_v e^2 \delta}{\varepsilon}
\]

[eqn. (33) of sec. (7.3.1)]. To find \( V_p \), it is first necessary to estimate the value of \( N_v \), which is the number of trapped electrons per unit volume of the oxide.

Step 1:

To evaluate \( N_v \) it is useful to start with the following eqn. (eqn. 38 of sec. 7.3.2.)

\[
K_0 = \frac{1}{B} = \frac{\varepsilon kT}{4 \pi N_v e^2 \delta}
\]

or,

\[
N_v = \frac{\varepsilon kT}{K_o \cdot 4 \pi e^2 \delta}
\]

By taking \( K_0 \) at 470°C to be equal to 24.42 \( \mu \text{gm/cm}^2 \). (Sec. 5) which is equivalent to \( \sim 3660 \text{ \AA} \) (Sec. 4.7.3.) and \( \varepsilon = 12 \) (Sec. 7.6.1.),
\[ N_v \approx 4.5 \times 10^{17}/\text{cm}^3. \]

This is a reasonable figure for the density of trapping centres in the oxide, and may be compared with \( N_v \approx 5 \times 10^{17}/\text{cm}^3 \), obtained in copper oxide [Williams (119)].

Using the value of \( N_v \), the potential across the space charge layer becomes,

\[
V_p = \frac{4 \times \frac{22}{\pi} \times 4.5 \times 10^{17} \times (4.8 \times 10^{-10})^2 \times (3 \times 10^{-8}) \times y}{12} \times \frac{1}{1.6 \times 10^{-12}} \text{ eV.}
\]

On the basis that \( y = 26.388 \ \mu\text{gm/cm}^2 \) i.e. \( 4 \times 10^3 \ \AA \) at the end of 10th minute (sec. 4.7.3.),

\[ V_p \approx 0.08 \text{ eV.} \]

Thus a low value of \( V_p \) is obtained as compared to the value of \( V_s \) which is equal to 1.58 eV. Such a lower \( V_p \) value shows, in accord with Bardeen's concept, the validity of the assumption of a metal/semi-conductor contact in the present system instead of adopting the solid/liquid contact phenomenon, as used by Uhlig (7).
8. Investigations besides the Kinetic Studies

Besides the kinetic studies, the effect of oxygen on metals in the region of the allotropic transformation temperature has also been investigated in terms of the oxide colour, metallography of the oxide, etc.

8.1. Iron

8.1.1. Colour of the oxide

Below 890°C the surface layer had a velvet, dark-red appearance on slow cooling after the oxidation test [Evans & Chatterjee (104)]. Above 890°C, the colour was metallic gray. Formation of a velvet oxide was also observed in the present study. Its appearance, however, depends on the particular experimental conditions. The following factors are found important to control the formation of velvet oxide, namely temperature of oxidation, pressure of oxygen during the oxidation test, oxide thickness, the cooling rate and the cooling atmosphere. With different possible combinations of these various experimental conditions, the following conclusions are drawn from the experimental results:

1) Under any set of conditions, formation of the velvet oxide will never be observed when the temperature of oxidation is in the region of F.C.C. - iron.
2) There is a specific temperature range from 740°C to 820°C in B.C.C.-iron where the velvet oxide will be formed predominantly, at an oxygen pressure of 7.6 cm Hg. Below and above this temperature range, the relative amount decreases gradually and metallic gray oxide appears in increasing amount.

3) Even in the temperature range where the formation of velvet oxide is expected there is some optimum thickness of the oxide which must be formed at the temperature of oxidation to obtain any trace of velvet oxide subsequently. The higher the temperature the greater is the optimum thickness of the oxide required to produce the velvet oxide.

4) At higher pressure of oxygen i.e. $p_{O_2} = 29$ cm Hg, the maximum temperature, at which velvet oxide can be observed on cooling, is lower than that at a lower $p_{O_2}$ - value.

8.1.2. Metallography of the oxide

Metallography does not reveal the structure of the oxide formed at the experimental temperature, because wustite is not stable below ~600°C on cooling [Vallet and Raccah (61)]. At a particular $p_{O_2}$ - value, the oxide structures at room temperature did not differ much from each other when the experimental temperatures were different. However with change of $p_{O_2}$ - values, different micro-structures were obtained (figs. 40 and 41) on cooling down the oxide under the same experimental conditions. Coarser grains are formed when the
Optical micrographs
of iron oxide

Fig. 40
At
$p_{O_2} = 7.6$ cm.

Fig. 41
At
$p_{O_2} = 29$ cm.
specimen is oxidized at higher $p_{O_2}$ value, also the structure (fig 41) shows a pattern of thermal etching unlike photomicrograph (40) where fine grains only are observed. Thermal etching phenomenon is usually associated with the preferential oxide growth on certain crystallographic planes.

8.2. Cobalt

8.2.1. Colour of the oxide

With increasing thickness of the oxide film, the colour of the oxide changes. Complex oxide colours were observed. It is difficult to describe them precisely, but the observed colour sequence with the change of temperature and film-thickness is given below.

1) Oxidation in the temperature range of the H.C.P. - cobalt phase produced,
   a) blue-green film up to about $330^\circ C$ where the film thickness is about 1000 Å,
   b) blue-green film is associated with brown-pink colour up to $386^\circ C$.

2) At the allotropic change point of $386^\circ C$,
   a) pink film was observed when the corresponding kinetic data showed a high rate of oxidation,
   b) blue-green film with pink edges was observed for a corresponding low oxidation rate.

3) Oxidation in the temperature range of the F.C.C. - cobalt phase produced,
   a) pale blue metallic gray film up to around $450^\circ C$ with the film of about 2000 Å thickness,
   b) dark gray film above $450^\circ C$. 
The oxide film was found unstable when cooled in air after the oxidation in the F.C.C - temperature range but not while cooling down from the H.C.P. - temperature range. However in both cases, the oxide film was stable when cooled down in vacuum or in an oxygen atmosphere.

8.2.2. Metallography of the oxide

To ascertain the structure of the as-received metal, X-ray diffraction pattern was taken (Fig.42). The structure as revealed was pure close-packed hexagonal.

With reference to the morphology of the oxides formed at different temperatures, no difference could be observed using an electron microscope with a magnification as high as 45,000. Typical structures are shown in Figs. 45 & 50, which are comparable to Gulbransen's work (59). These structures show the oxide to consist of many small crystallites. With higher magnification, a difference in morphology was observed for oxides formed above and below the allotropic change point, Tc. The electron diffraction patterns [Figs. (44 and 48)] cannot provide quantitative information with regard to the oxide structure, since a standard was not used on the same grid. This was done purposely, as otherwise; the diffraction pattern arising from the oxide and the standard would have so many lines that it
would be almost impossible to identify each of them correctly. The oxide structure is thus, determined from the corresponding X-ray diffraction patterns (figs. 43 & 47), which show the presence of lines from two oxides, CoO and Co$_3$O$_4$. From the relative intensity of the lines as given by ASTM-Index on X-ray Powder Data File it has been estimated qualitatively that the oxide formed above $T_c$ has about 50% of each oxide (fig.43) and about 90% Co$_3$O$_4$ in the oxide formed below $T_c$ (fig.47). Electron diffraction patterns show strong spots co-existing with tangentially streaked portions of rings. This indicates that the oxide consists of fine grain size and single crystals. The oxide formed on a particular metal grain tends to become a single crystal as the oxide thickens [Smeltzer, et.al. (33)] i.e. as the temperature is increased (figs. 44 & 48). Dark field transmission electron micrograph, fig. (49), also confirms the single crystalline nature of the oxide. According to Smeltzer (117), as the oxide grows dislocation tangles can be observed. At higher temperature for a relatively thicker oxide of cobalt, dislocation tangles are observed (fig.46) whereas Moiré fringes are observed (figs 51 & 52) below $T_c$. The periodic structure of a crystal can be revealed of Moiré patterns from overlapping crystals, even when the actual lattice periodicities are below the
resolution limit of the microscope. Such indirect lattice resolution can provide information about dislocations, because a Moiré pattern, formed by superimposing a perfect on an imperfect crystal, represents a magnified image of the imperfect crystal \( \text{[(Hashimoto & Uyeda (126)]} \). The Moiré pattern may be interpreted as arising from,
1) two parallel lattices of different spacing, 
\[
D = \frac{d_1 d_2}{d_1 - d_2}
\]
where \( D = \text{Moiré spacing} \), and 
\( d_1, d_2 \) are lattice spacings.
2) two similar or dissimilar, lattices with a slight relative rotation of \( \theta \),
\[
D = \frac{d}{\theta} \quad \text{or} \quad D = \frac{d_1 d_2}{\sqrt{d_1^2 + d_2^2 - d_1 d_2 \cos \theta}}
\]
Some elaborate work is necessary before any conclusion on the interpretation of the observed Moiré fringes may be drawn. However, an idea may be developed here with regard to the type of Moiré fringes. From the magnified photograph (fig. 52), the Moiré-spacing was found to be \( 30 \pm 2 \text{ Å} \). The small rotational angle between two overlapping flakes was measured \( \text{[according to Seki (136)]} \) as the intersectional angle of their long edges and found out to be \( 11 \pm 1^o \) degrees. Using different equations, it has been found that the following eqn. is the suitable one, namely \( D = \frac{d}{\theta} \) where 
\( d = \text{lattice spacing} \), and the following result is obtained.
<table>
<thead>
<tr>
<th>Type of Moiré</th>
<th>Moiré-spacing calculated from x-ray parameter</th>
<th>Mean observed Moiré-spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}_Co_3O_4</td>
<td>24 Å</td>
<td>30 ± 2 Å</td>
</tr>
</tbody>
</table>

Each dislocation in a Moiré-pattern corresponds to a single dislocation in an atomic lattice [Hashimoto (137)]. However, the oxide formed from F.C.C.-cobalt has dislocation tangles and therefore can be considered to have higher dislocation density than that formed from H.C.P. - cobalt. Also the oxide, formed from F.C.C.-cobalt, was found to be mechanically very unstable, indicating the presence of heavy strain. Highly strained material will have high stored energy and so high dislocation density. Thus both the electron micrographs and mechanical property show the oxide produced from F.C.C.-cobalt has higher dislocation density than that formed from H.C.P. - phase. So for short-circuit diffusion controlled oxidation, a higher rate of oxidation is expected with F.C.C. - phase. On the other hand, for a non-diffusion controlled process such as, an electron emission mechanism, the rate, as for example in the present study, is found to be higher with H.C.P. - phase.
X-ray diffraction pattern
of the as-received metal.

Low angle

High angle

Lines for H.C.P.-cobalt

Fig. 42
Metallography of cobalt oxide
(forming on oxidation of cobalt above the allotropic change point)

Lines for cobalt oxide (CoO)

Lines for cobalt oxide (Co₃O₄)

X-ray diffraction pattern

Fig. 43

Electron diffraction pattern

Fig. 44

Electron micrographs

Fig. 45

Fig. 46
Metallography of cobalt oxide
(formed on oxidation of cobalt below the allotropic change point)

Lines for cobalt oxide (CoO):
111 220 311 400 331 420

Lines for cobalt oxide (Co₃O₄):
220 400 440 622 731 751
311 422 620 444 800 555
222 511 531 642 822 660

X-ray diffraction pattern

Fig. 47

Electron diffraction pattern

Fig. 48

Dark field electron micrograph

Fig. 49
Electron micrographs of cobalt oxide (formed on oxidation of cobalt below the allotropic change point)

Fig. 50

Fig. 51

Fig. 52
CONCLUSION
9. Conclusion

This section is divided into three parts, namely,
a) conclusions drawn from the work on iron
b) conclusions drawn from the work on cobalt
c) effect of allotropic transformation on the oxidation from the works on iron and cobalt.

9.1. Iron

A modified parabolic law governs the initial oxidation of pure iron in dry oxygen at temperatures where wüstite is the main oxide. For such a law, both mechanisms of diffusion-controlled (parabolic rate law) and phase-boundary reactions (linear rate law) operate simultaneously. With increasing temperature and $p_\text{O}_2$ values, the true parabolic law appears at the expense of the modified parabolic law; in other words, the phase-boundary reactions and diffusion-controlled reactions no longer contribute equally, the former occurring at a faster rate as the temperature and $p_\text{O}_2$ values are increased. An anomaly in the Arrhenius plot at the allotropic change point is attributed to the influence of the phase-boundary reactions.

For a modified parabolic rate law, the metal/oxide interface-reaction is slower in F.C.C.- and the oxide/gas interface-reaction is slower in B.C.C.-iron. Distribution of vacancies and their subsequent movement characterize the type of metallic structure. The concept of vacancy concentration inside the metal explains the mechanism of the
reaction at the metal/oxide interface and the distribution of vacancies in the oxide may be applied to develop a possible explanation for a decreased oxidation rate with increased pressure.

9.2. Cobalt

A direct-logarithmic law governs the initial oxidation rate of pure cobalt. The rate-law is explained in terms of an electron emission mechanism involving space-charge effects. A change in the activation energy of oxidation can be shown to be directly related to a change in the thermionic work function of the metal, provided the oxide formed is of about the same composition and the potential drop across the space charge layer is small. The constancy of activation energy in the present work agrees with the fact that there is no reported change in the thermionic work function above and below the allotropie transformation temperature of cobalt. In the present-case, an electron emission mechanism is established as the rate-controlling process and a higher oxidation rate of H.C.P.-cobalt than F.C.C. is expected. This is attributed to the pre-exponential term (namely, the entropy of activation) of the Arrhenius equation, which would provide a higher probability of electron emission from the Fermi surface of H.C.P.-cobalt than that of the F.C.C.-phase
The electron micrographs and the mechanical stability of the oxide have qualitatively indicated a higher dislocation density in the oxide formed, from F.C.C. than from H.C.P. -cobalt. Dislocations which are considered as short-circuit diffusion paths, act as sinks of vacancies. As a result, a higher oxidation rate of F.C.C. - cobalt as compared with the H.C.P. -phase can be expected, if instead of the electron emission, a short-circuit diffusional process was the rate-controlling mechanism.

9.3. Effect of allotropic transformation

Any change in the crystallographic structure of a metal can be associated with a change in the rate of oxidation of the metal if one of the rate controlling processes is a phase-boundary reaction. Such a phase-boundary reaction may be limited by an electron emission mechanism at the metal/oxide interface when the oxide-film is thin and when a direct-logarithmic law of oxidation is obeyed (of the present work on cobalt). Alternatively, a concept of vacancy distribution in the metal can be used to explain the mechanism of the phase-boundary reaction (of the present work on iron). A change in the linear oxidation rate (which is controlled by a phase-boundary reaction) at the allotropic change point has been shown in the Arrhenius plots for other metals, such as titanium [D'yachkov (107)], manganese [Voitovich (138)] and plutonium [Thompson (139)].
The relevant Arrhenius plots in the case of cobalt (figs. 53, 54) and iron (fig. 55) as obtained in the present study are reproduced. Both the possibilities for the plots in case of cobalt are considered (figs. 53 & 54). The Arrhenius equation applies only in the region where the plots is a straight line (dashed lines in figs. 53, 54 & 55). The curves produced in both cobalt and iron near the transformation are considered as non-Arrhenius zones which are of considerable interest, in the present section. In order to discuss the indication in the trends of oxidation behaviour of metals at the allotrophic change point, it will be worthwhile to consider this from two points of view:

Case 1. Oxidation behaviour in the vicinity of allotrophic transformation point,

Case 2. Oxidation at the allotrophic transformation point.

Case 1.

In the case of cobalt, oxidation rate of both F.C.C.- and H.C.P. - phases decrease with increasing temperature (shown by arrows in fig. 53) in the non-Arrhenius zone, or according to fig. (54) the rate increases in both the structures with increasing temperature. By contrast, the oxidation of B.C.C. - iron increases with temperature while that of F.C.C. iron decreases with temperature in the
vicinity of change point (shown by arrows in fig. 55). These facts indicate that some properties of F.C.C.- and cobalt H.C.P., which are important in the (phase-boundary reaction controlled) oxidation study, are similar, while that of B.C.C.- and F.C.C.- iron differ widely. It is found from structural point of view that both forms of cobalt are very similar, as compared to the case of iron. For example, the magnitude of the enthalpy change, the volume change per unit volume of the low temperature phase on allotropic transformation, in the case of iron is larger by some order than for cobalt. From the transformation volume change of the allotropes and the number of atoms per unit cell, it can be said that F.C.C.- iron is more close-packed than B.C.C.- iron whereas both H.C.P.- and F.C.C.- cobalt have almost similar volumes. Relating these facts to the oxidation behaviour, it can be concluded that for (phase-boundary reaction controlled) oxidation, an open-packed structure will show faster rate of oxidation with temperature in the vicinity of allotropic change point as compared to the corresponding allotropes of a closely-packed structure (for example, the case of iron). On the other hand, for almost identical packing of allotropic structures, the oxidation rate will change (either decrease or increase) in the same direction, with temperature in the region of transformation (for example, the case of cobalt).
In the case of cobalt, the oxidation rate of the allotropes diverge at the allotropic transformation temperature, $386^\circ C$ (points A & B of figs. 53 & 54). By contrast, the oxidation rates of iron-allotropes converge together (fig.55) at the change point, $911^\circ C$. Such behaviour seems to be related to the type of relevant mechanism of allotropic transformation. And the type of transformation mechanism, to be considered, basically depends upon the oxidation mechanism followed. Thus electronic mechanism of allotropic transformation is relevant in the case of cobalt here, because the oxidation results are explained in terms of an electron-emission mechanism. The concept of building up of "electron pressure" in the H.C.P. with temperature explains fig.(54) if 100% H.C.P. - cobalt is assumed to be stable up to $386^\circ C$ and undergoes a transition to F.C.C. - phase at $386^\circ C$. Alternatively, it may so happen that with increasing temperature the F.C.C. - phase may begin to form at the expense of H.C.P. - structure before $386^\circ C$ is reached. As a result, instead of a change from pure H.C.P. -phase to F.C.C. - cobalt at $386^\circ C$, it will be a transformation from a mixture of the two phases to a single phase of F.C.C. - cobalt. In such a case, a divergence of the other type in the oxidation behaviour can be obtained fig.(53).

In the case of Iron, the change in the lattice geometry involving allotropic modification appears to be the relevant
mechanism, because the oxidation results are explained in terms of the geometric factor. The number of interfaces, vacancy diffusion and distribution in the interior of the metal and other similar structural factors are very much the same in the allotropes of iron at the transformation temperature, where the allotropes are in meta-stable stage. Thus although the structural packing, the volume etc., of the two allotropes of iron differ in their respective stable region, the differences however disappear to a large extent in the meta-stable condition. As a result, the oxidation rates in the Arrhenius plot tend to converge at 911°C.

Therefore the conclusions that can be drawn in this section are

1) in the vicinity of the transformation temperature, a change in the oxidation behaviour of a metal with temperature necessitates a phase-boundary reaction as one of the rate controlling processes, and

2) at the transformation temperature, a study on the change in the oxidation behaviour necessitates not only phase-boundary reaction as a rate controlling process (as in the previous case) but also a knowledge of the mechanism of the applied oxidation law.
Arrhenius plots illustrating the non-Arrhenius zones

**Cobalt**

Non-Arrhenius zone

\[ \text{F.C.C.} \quad \text{B.} \quad \text{H.C.P.} \]

\[ \text{Log}_{10} K_0 \]

\[ \frac{1}{T} \quad (\text{K}) \]

**Iron**

Non-Arrhenius zone

\[ \text{F.C.C.} \quad \text{B.C.C.} \]

\[ \text{Log}_{10} (K_1)_M \]

\[ \frac{1}{T} \quad (\text{K}) \]

Notations:

- \( K_0 \) = Direct-logarithmic rate constant
- \( (K_1)_M \) = Linear rate constant
- \( T_c \) = Temperature of allotropic change
- \( T \) = Temperature

Fig. 53, Fig. 54, Fig. 55
10. Further Work

(1) It should be of interest to study the initial oxidation kinetics of other metals in the region of allotropic change points. Selection of the metal is important. A better insight can be obtained only by choosing a metal which has a wide difference in the electronic and geometric structures of its allotropic modifications. In the present work, oxidation result of cobalt is explained in terms of the electronic factor while that of iron in terms of the geometric factor. It would be interesting to find out the theoretical limitations of these two factors when applied simultaneously to explain oxidation results.

(2) It has been shown in the case of iron that of the two phase-boundary reactions, the metal/oxide interface is rate-controlling in F.C.C. - iron, whilst in B.C.C. - iron the oxidation is controlled by the oxide/gas interfacial reaction. It would be worthwhile to verify this by using inert-markers. Studies on the inert-marker movement must be made with extreme care, isolating the effects due to the two types of kinetics, (as involved in the case of a modified parabolic law) linear and parabolic types.

(3) In the case of the direct-logarithmic oxidation of cobalt, it would be interesting to carry out a measurement on the thermionic work function in the region of the transformation temperature. Such measurements should be associated as far as
possible with the measuring of oxidation kinetics so as to make sure that the thermionic data obtained relates to the same condition as the oxidation of cobalt.

(4) It might be worthwhile using single crystals to study the oxidation behaviour of different crystal planes near the transformation region. Atomic packing and electronic configuration of a particular plane should only emphasize the effect of electronic and geometric factors.

(5) It would be interesting to carry out analogous investigations on the initial stages of halogenation, sulphidization and similar processes. The halogens and sulphur, like oxygen, are electronegative. So a relationship between the oxidation behaviour and halogenation or sulphidization of the same metal around the allotropic change point could be expected.
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Text books

Appendix - I

To show that a modified parabolic law of oxidation can be expected when \( n = 1.5 \) of the empirical power law, \( W^n = Kt \).

**Stage 1. Basic Form**

**Case (A):** For a true linear rate-law, \( W \propto t \) and the equation is given by

\[
W = K_1 t + C' \quad \text{(a)}
\]

Where \( K_1 \) is the linear rate constant and \( C' \) is a constant. This equation can be replaced by a similar equation such as,

\[
W = \frac{(K_1)_M}{2} t + C_1 \quad \text{(b)}
\]

Where \( (K_1)_M \) is a rate constant but different from \( K_1 \) and \( C_1 \) is a constant and different from \( C' \).

Equation (b) can be re-written as,

\[
\frac{W}{(K_1)_M} = \frac{1}{2} t + \frac{C_1}{(K_1)_M} \quad \text{(c)}
\]

**Case (B):** For a true parabolic rate-law, \( W^2 \propto t \) and the equation is given by

\[
W^2 = K_p t + C'' \quad \text{(d)}
\]

where \( K_p \) is the parabolic rate constant and \( C'' \) is a constant. This eqn. (d) can be replaced by a similar equation, such as

\[
W^2 = \frac{(K_p)_M}{2} t + C_2 \quad \text{(e)}
\]
where \((K_p)_M\) is a rate constant but different from \(K_p\) and \(C_2\) is a constant and different from \(C^\prime\).

Equation (e) can be re-written as

\[
\frac{W^2}{(K_p)_M} = \frac{t}{2} + \frac{C_2}{(K_p)_M} \quad \text{(f)}
\]

Stage 2. Equations (c) and (f) are multiplied in one case and added in the other case:

Case (C): When eqns. (c) and (f) are multiplied, then

\[
\frac{W^3}{(K_p)_M(K_1)_M} = \frac{t^2}{4} + \frac{t}{2} \left\{ \frac{C_1}{(K_1)_M} + \frac{C_2}{(K_p)_M} \right\} + \frac{C_1 \cdot C_2}{(K_1)_M \cdot (K_p)_M}
\]

\[
= \frac{t^2}{4} + \frac{t}{2} A + B \quad \text{where,} A = \frac{C_1}{(K_1)_M} + \frac{C_2}{(K_p)_M}
\]

and

\[
B = \frac{C_1 \cdot C_2}{(K_1)_M \cdot (K_p)_M}
\]

\[
= \left( \frac{t + A}{2} \right)^2 + B - \frac{A^2}{4}
\]

\[
= \frac{1}{4} (t + A)^2 - \left\{ \frac{C_1}{2(K_1)_M} - \frac{C_2}{2(K_p)_M} \right\}^2 \quad \text{(g)}
\]
Case (D): When eqns. (c) and (f) are added, then
\[ \frac{W}{(K_1)_M} + \frac{W^2}{(K_p)_M} = t + \left\{ \frac{C_1}{(K_1)_M} + \frac{C_2}{(K_p)_M} \right\} \]
\[ = t + \frac{A}{h} \quad \text{ (h)} \]
Therefore,
\[ (\frac{t + A}{h})^2 = \frac{1}{4} \left\{ \frac{W}{(K_1)_M} + \frac{W^2}{(K_p)_M} \right\}^2 \]
or,
\[ (\frac{t + A}{h})^2 - \left\{ \frac{C_1}{2(K_1)_M} - \frac{C_2}{2(K_p)_M} \right\}^2 = \frac{1}{4} \left\{ \frac{W}{(K_1)_M} + \frac{W^2}{(K_p)_M} \right\}^2 - \frac{\left\{ \frac{C_1}{2(K_1)_M} - \frac{C_2}{2(K_p)_M} \right\}^2}{\frac{1}{4}(K_1)_M^2} \]
\[ = \frac{1}{4(K_1)_M^2} \left\{ W^2 - C_1^2 \right\} + \frac{1}{4(K_p)_M^2} \cdot \left\{ W^4 - C_2^2 \right\} + \frac{1}{2(K_p)_M^2(K_1)_M} \cdot \left\{ W^3 + C_1C_2 \right\} \quad \text{ (i)} \]

Stage 3. Identity of case (c) and case (d):
At the initial stages of oxidation, when time t is small, the W-values are low as well. As a result, the values of the constants C_1 and C_2, which are obtained from the intercept values of the relevant W against t and W^2 against t plots respectively, can be considered comparable with the W-values. In other words, at the initial stages of oxidation
\[ C_1 \approx W \]
and \[ C_2 \approx W^2 \]
Thus the first two terms of the right hand of the eqn. (i) become negligible as compared to the third term and eqn. (i) becomes
\[
\left(\frac{t + A}{t}\right)^2 - \left\{ \frac{C_1}{2(K_1)M} - \frac{C_2}{2(K_2)M} \right\}^2 \approx \frac{W^3 + C_1 \cdot C_2}{2(K_2)M \cdot (K_1)M}
\]

\[
= \frac{W^3}{(K_2)M \cdot (K_1)M}. \quad -(j)
\]

(since \(C_1 \cdot C_2 \approx W^3\))

Equation (j) and (g) are identical. Origin of equation (j) is the equation (h) i.e. Case (D) and that of eqn. (g) is case (C). So the identity of the two cases, (C) and (D) are shown.

Stage 4. To show that eqn. (g) and (h) are approximately empirical and modified parabolic equations respectively.

Although \(C_1\) and \(C_2\) have values comparable to \(W\) - values but these values themselves are low as compared to the experimentally obtained values of \((K_1)M\) and \((K_2)M\). As a result, the ratios \(\frac{C_1}{(K_1)M}\) or \(\frac{C_2}{(K_2)M}\) can be considered negligible with respect to the values of time, \(t\).

This simplifies eqn. (g) to
\[
\frac{W^3}{(K_2)M \cdot (K_1)M} \approx \frac{t^2}{4} \quad \text{assuming that if } C_1 \quad \text{and } C_2 \quad \text{are}
\]

\[
\frac{(K_1)M}{(K_2)M}
\]

negligible, then square of these terms would also be negligible.
or, \[ w^3 = \frac{(K_p)_M \cdot (K_l)_M}{4} \cdot t^2 \]

or, \[ W^{1.5} = \sqrt{\frac{(K_p)_M \cdot (K_l)_M}{2}} \cdot t \]

\[ = K t \quad \text{(m)} \]

And eqn. \((h)\) simplifies to

\[ \frac{W}{(K_l)_M} + \frac{W^2}{(K_p)_M} \equiv t \quad \text{(n)} \]

Equations \((m)\) and \((n)\) are typical empirical and modified parabolic equations respectively. So in Stage \((4)\) it is shown that Case - (C) represents an empirical equation while Case - (D) represents a modified parabolic equation.

Identity of case (C) and (D), as shown in stage - 3, thus shows that the empirical eqn. \((m)\) where \(n = 1.5\) reflects a case of a modified parabolic law. The analysis thus given is one of the many approaches to solve the problem, but the present analysis has the advantage that it is made on the basis of two reasonable assumptions only, one in stage - 3 and the other in stage - 4.
Nomenclatures (besides those used for the apparatus)

A. Thermodynamic terms and associated terms

\( \Delta G \) = Change in the free-energy of formation of the oxide from its elements
\( \Delta G^\circ \) = Standard free-energy of formation of the oxide
\( \Delta H^\circ \) = Standard heat of formation of the oxide
\( \Delta S^\circ \) = Standard entropy of formation of the oxide
\( S^* \) = Entropy of activation

\( H_{vap} \) = Head of Vapourisation
\( H_{fus} \) = Heat of fusion
\( K_{eq} \) = Equilibrium constant

\( p_{o2} \) = Partial pressure of oxygen in gaseous phase

\( \{p_{o2}\}_E \) = Decomposition pressure of oxide

\( \{p_{o2}\}_s \) = External pressure of oxygen (at Cu\(_2\)O/O\(_2\) interface), viz. \( p_{o2} \)

\( \{p_{o2}\}_m \) = Equilibrium dissociation pressure of Cu\(_2\)O
\( \{p_{o2}\}_1 \) = Equilibrium dissociation pressure of wüstite

B. Electrochemical terms

\( t_c \) = Transference number of cations
\( t_a \) = " " anions
\( t_e \) = " " electrons

\( l_c \) = Speed of cations
\( l_a \) = " " anions
\( l_e \) = " " electrons
C. Semi-conductor terms

- $n_0$, $Zn^{\text{+}}$ = Symbols related to interstitial ions
- $n^\circ$, $Cu^{\text{+}}$, $Fe^{\text{+}}$ = Symbols related to cation vacancies
- $\oplus$ = Holes
- $n_\text{e}$, $\bar{e}$, $(-)$ = Symbols related to electrons
- $\delta$ = Gap at the metal/semi-conductor contact
- $N$ = Number of electrons arriving per unit area of the oxide/gas interface per unit time
- $N_0$ = Number of Fermi electrons moving towards the barrier per unit time
- $\Omega$ = Volume of oxide
- $\gamma$ = Minimum height of the energy barrier for an electron to reach oxide/gas interface
- $e$ = Charge associated with an electron
- $V_S$ = Potential due to surface state charge
- $V_P$ = Potential due to space charge layer
- $V_a$ = Potential due to Electron affinity of oxygen
- $\phi_M$ = Work function of the metal
- $N_V$ = Number of trapped electrons per unit volume of the oxide
- $n_S$ = Number of surface states per unit area
- $\epsilon$ = Dielectric constant of the oxide
- $\lambda_0$ = Amount by which the metal work function is modified through the contact with the oxide
D. Terms used in oxidation chemistry

D.1. General constants and rate constants

- $R = \text{Gas constant}$
- $k = \text{Boltzmann's constant}$
- $h = \text{Planck's constant}$
- $\lambda = \text{Interatomic spacing}$
- $M_o = \text{Atomic weight of oxygen}$
- $M_{ox} = \text{Molecular weight of wustite}$
- $\rho_{ox} = \text{Density of oxide}$
- $V_f = \text{Vacancies in the sublattice of iron}$
- $C_{2e} = \text{Equilibrium vacancy concentration at the oxide/gas interface}$
- $C_{1e} = \text{" } \text{ " } \text{ at the metal/oxide interface}$
- $K_a = \text{Velocity constant at the metal/oxide interface}$
- $K_b = \text{Velocity constant at the oxide/gas interface}$
- $A_1, K_1 = \text{Constant terms in inverse-logarithmic law}$
- $\ell = \frac{1}{A_B} = \text{Constant term in direct - logarithmic law, while A, B are constants}$
- $\beta = \text{Constant in the relation of } T \text{ with temperature, } T$

- $K_2 = \frac{1}{K_3} = \text{Direct - logarithmic rate constant}$
- $K_3 = \text{Asymptotic rate constant and } K_4 \text{ is a constant}$
- $K_5 = \text{Empirical rate constant, while } C \text{ is the integration constant}$
- $K_p = \text{True parabolic rate constant, while } C^2 \text{ is the integration constant}$
\[ K_p' = \text{Rational rate constant} \]
\[ K_6 \text{ or } (K_p)^M = \text{Parabolic rate constant of the modified parabolic law} \]
\[ K_1 = \text{True linear rate constant, while } C' \text{ is the integration constant} \]
\[ K_7 \text{ or } (K_1)^M = \text{Linear rate constant of the modified parabolic law} \]
\[ n = \text{constant term of the empirical power law} \]
\[ a, \beta = \text{Two roots of the quadratic equation of the modified parabolic law} \]

\textbf{D.2: Activation energy-terms}

\[ Q = \text{Activation energy of a parabolic oxidation for a true parabolic law} \]
\[ (Q_p)^M \text{ or } (Q(p))^M = \text{Activation energy of a parabolic oxidation for a modified parabolic law} \]
\[ Q_l = \text{Activation energy of a linear oxidation for a true linear law} \]
\[ (Q_l)^M \text{ or } (Q(l))^M = \text{Activation energy of a linear oxidation for a modified parabolic law} \]
\[ Q_D = \text{Activation energy of vacancy diffusion in iron} \]
\[ E^* = \text{Energy of vacancy formation in iron} \]
\[ E = \text{Activation energy for direct logarithmic rate-law, where } G \text{ is the pre-exponential term of the Arrhenius equation.} \]
D.3. Diffusion-terms

\( D_{\text{eff.}} \) = Effective diffusion co-efficient of vacancies through the oxide.

\( D \) = Diffusion co-efficient of vacancies through the oxide

\( D_c = \) Self-diffusion co-efficient of cation through the oxide

\( D^* = \) Self-diffusion co-efficient of iron

\( D_0 = \) Pre-exponential term for an eqn. \( D^* = D_0 \exp(-Q D/RT) \).

\( D_{\text{vac.}} = \) Vacancy diffusion co-efficient in iron

D.4. Other terms

\( C_2 = \) Vacancy concentration at the oxide/gas interface

\( C_1 = \) " " metal/oxide "

\( F_1 = \) Flux of vacancies arriving at the metal/oxide interface

\( F_2 = \) " " oxide/gas "

\( F_3 = \) " " across the oxide

\( n = \) Number of lattice vacancies

\( N^* = \) Total number of sites

\( W = \) Weight of oxide per unit area of the specimen

\( y \) or \( x = \) Defining oxide layer-thickness

\( t_h = \) Measured oxide thickness

\( l = \) Length

\( b = \) Breadth

\( B'_c = \) Cathetometer value

\( x^* = \) Conversion factor