METAL OXIDATION

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It is not intended to give an exhaustive survey of metal–oxygen reactions but to discuss some properties of the metal and oxide, oxygen chemisorption, and the metal–oxide and oxide–oxygen interfaces, and to show how these considerations are relevant to mechanistic studies of oxidation. There is a trend towards treating surface reactions quantitatively before they are completely understood qualitatively and, therefore, certain aspects will be considered which at first sight seem to bear little relation to metal oxidation but which must, with more detailed studies, become important factors in the interpretation of such reactions. The formation of an oxide layer may be tentatively considered to take place as follows: Oxygen molecules adsorbed on the metal surface are dissociated and ionised, incorporation then occurs in which the oxide is formed with the simultaneous formation of cation or anion vacancies. It is, therefore, necessary to consider the properties of the metal, its ability to chemisorb oxygen, the subsequent oxide growth, and the properties of that oxide.

The standard free energy change for the oxidation of all metals except gold is negative, thus a chemisorbed layer should be formed spontaneously on exposing a metal to oxygen even at very low pressures (*e.g.*, $\sim 10^{-6}$mm.). Further oxide growth usually requires an appreciable activation energy, so that the chemisorbed layer remains in a metastable state at much higher oxygen pressures. Reaction beyond the monolayer stage, or incorporation, is therefore kinetically controlled and will be dependent on the characteristics of a diffusion process, *viz*, the diffusion of cations out through the oxide, the diffusion of oxygen inwards (possibly a contribution of both), or electron transport. Since diffusion is synonymous with the inherent defective character of the system, then it is essential to consider first the existence of defects in metals and oxides.

1. Defects in Metals and Oxides

The perfect solid can be regarded as an aggregate of atoms arranged in unbroken lattice array, each cell of the lattice having an identical arrangement of the chemical constituents so that the internal structure is flawless. Solids do, however, exhibit a number of imperfections, the primary ones being vacant lattice sites, interstitial atoms, positive holes, and dislocations. The ratio of the number of defects to lattice atoms is given by eqn. (1),

$$C = \exp\left[-\left(\Delta H_f - T\Delta S_f\right)/kT\right] \qquad (1)$$

where ΔH_f is the heat of formation of the defect, and ΔS_f is the entropy change associated with the defect. On the assumption that $\Delta S_f/k$ is of the order of unity, and by using theoretical estimates of ΔH_f, Broom and Ham[1] have derived the concentrations of vacancy, vacancy pair, and interstitial atom defects in copper at 300°, 800°, and 1300°K (Table 1).

TABLE 1.

	ΔH_f	Number of defects per lattice atom		
	(kcal. mole^{-1})	300°K	800°K	1300°K
Vacancy	22	10^{-17}	$10^{-6 \cdot 2}$	$10^{-3 \cdot 9}$
Vacancy air	35	10^{-27}	10^{-10}	$10^{-6 \cdot 2}$
Interstitial atom	88	10^{-67}	10^{-25}	10^{-15}

Thus, the vacant lattice site may be present in appreciable concentration in thermodynamic equilibrium in metals, since, with rapid quenching, as is the case during the preparation of metal films, the concentration may be as high as 1 in 10^4. The most mobile of these defects is the interstitial type; interstitial atoms produced by irradiation may become mobile at temperatures as low as 40°K, the activation energy for movement being about 2 kcal.mole^{-1}.[2] Single vacancies in copper and gold become mobile only above 240°K and have an activation energy of $\sim$ 20 kcal.mole^{-1}. If the vacancies exist as clusters, which they may well do with evaporated metal films, the activation energy for vacancy-cluster movement is much smaller than for single vacancies, being about 8 kcal.mole^{-1} for a di-vacancy in copper. A value of approximately 4 kcal.mole^{-1} for the activation energy of the sintering of iron films suggests the participation of vacancy-cluster movement in the sintering process.[3]

Few crystals have been prepared with a dislocation density of less than 10^4 per cm.^{2}. This is probably due to vacancies present at the melting point coalescing and finally collapsing to form dislocations. Etching techniques have enabled individual dislocations to be revealed and have also demonstrated the existence of spiral growths on surfaces. The latter have been reported by Forty[4] for the growth of small magnesium crystals from the vapour and also on titanium prepared by fused-salt electrolysis. Measurements of the average step height by the Tolansky multiple-beam interference techniques have a value of about 200 Å. The unique properties of dislocations are of considerable significance in oxidation processes. Their rôle as paths for easy diffusion has been emphasised by Hofman and Turnbull[5] who showed that the rate of silver self-diffusion along sub-boundaries was a million times faster than that of lattice diffusion. The sensitivity of dislocation lines to etching is also evidence of a greater chemical reactivity along such a disarray of atoms. Since atoms associated

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[1] Broom and Ham, Institute of Metals Monograph, 1957, No. 23.
[2] Seitz, *Adv. Phys.*, 1952, **1**, 43.
[3] Roberts, *Trans. Faraday Soc.*, 1960, **56**, 128.
[4] Forty, *Phil. Mag.*, 1952, **43**, 949.
[5] Hofman and Turnbull, *Acta Metallurgica*, 1954, **2**, 419.

with steps are less tightly bound to a surface than others, then such energy differences would be expected to lead to differences in the tendency for surface atoms to react depending on their geometrical arrangement. The rôle of surface kink sites in the oxidation of metals has been discussed by Vermilyea[6] especially in relation to possible stresses that develop at the metal–oxide and oxide–gas interfaces.

The process of self-diffusion in metals most probably occurs by a vacancy mechanism. This requires normal lattice sites, from which the atom is missing, to receive atoms from neighbouring sites, leaving vacant the site from which the atom jumped. The vacancies may cluster in groups of two or more and therefore remain associated through many unit jumps. Two other mechanisms are possible for self-diffusion; they involve either rotation of a coplanar group of atoms which form a closed ring (diffusion therefore occurring by rotation of the ring), or an interstitial mechanism, the diffusing atoms moving through the interstitial spaces between the atoms occupying normal lattice points. For the rotation mechanism the energy barrier to self-diffusion consists of the energy to squeeze the rotating groups of atoms past the interfering atoms. In the interstitial and vacancy mechanisms the activation energy consists of the energy to form the defect plus the energy to move it from one equilibrium site to another.

In oxides the exchange mechanism is less likely, owing to the large repulsion energy associated with the interchange of two ions of opposite sign. If the initial oxide layer is amorphous, as Eley and Wilkinson[7] have suggested for aluminium oxide, then electrostatic repulsion will not be an important factor and the exchange mechanism is feasible. Diffusion in oxides is, however, more likely to occur as a consequence of the existence of Frenkel and Schottky defects; the basic principles of such a mechanism have been developed by Wagner and his co-workers.[8] Since the concentration of lattice defects is relatively low the laws of ideal dilute solutions can be applied, although deviations, mainly because of the electrostatic forces between the imperfections, can occur. The two main classes of defect oxides are those involving excess of metal (n-type) and metal deficiency (p-type). The former include zinc and aluminium oxide in which the excess of metal is located at interstitial positions, while in the latter, examples of which are nickel oxide, cuprous oxide, and cobalt oxide, there occur cation vacancies. Electrical neutrality is maintained in n- and p-type oxides by quasi-free electrons and positive holes, respectively.

2. The Metal and Oxide Surfaces

The most serious difficulty in the study of the early stages of oxidation is to define the metal surface. Not only do uncertainties arise from surface

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[6] Vermilyea, General Electric Research Laboratory, Report No. 57-RL-1704, 1957.

[7] Eley and Wilkinson, *Proc. Roy. Soc.*, 1960, *A*, **254**, 327.

[8] cf. Wagner, *Z. phys. Chem.*, 1933, *B*, **21**, 25.

contamination but also from structural imperfections. A perfect free metal surface, *i.e.*, one containing an ideal arrangement of atoms, in itself represents a defect, since at the surface the continuity of the bulk atoms is absent. Owing to the high chemical activity of the surface atoms oxide is inevitably present unless special techniques have been used in surface preparation. It is only since the advent of ultra-high vacuum methods that the surface contamination factor has been minimised. A number of techniques are now available for the preparation of metal surfaces which are substantially free from presorbed gas. These include the use of flashed metal filaments, metal films deposited from the vapour phase, and the positive-ion bombardment of filaments. Metal filaments are usually no greater than 1 cm.^{2} in area, and, since a monolayer of oxygen could be adsorbed on a metal filament of this area in 100 sec. at a pressure of $\sim 10^{-8}$ mm., a background pressure of $< 10^{-9}$ mm. is necessary. Metal films are prepared by the thermal evaporation of a well-outgassed metal, usually in the form of a filament, and subsequent condensation on a cooled substrate. Such films usually have a high surface area to weight ratio and are intrinsically unstable.

Atoms present in the surface of a metal will tend to rearrange in such a manner that the total free energy is a minimum. The rôle of the surface energy of solids and the consequent surface mobility of atoms has been particularly well demonstrated by Chalmers, King, and Shuttleworth[9] with silver surfaces. When heated to above 500°, silver surfaces, in the presence of oxygen, developed a striated appearance which is attributed to the preferential exposure of (111) planes; heating in nitrogen caused the striations to disappear. Because of the instability of silver oxide it was not considered that an oxidation reaction supplied the motivation for the change, and it was concluded that in the presence of nitrogen a smooth silver surface of any orientation is thermodynamically more stable than a stepped surface of (111) planes, and that with oxygen the situation is reversed. Johnson[10] has shown that tungsten filaments, heated electrically in an inert gas, develop plane facets normal to the $<100>$ and $<110>$ directions; similar facets have been observed with tantalum. The migration of surface atoms has been suggested by Becker[11] to occur only at temperatures above $Tm/3$ where Tm is the melting point of the metal in °K. Investigations of reaction rates as a function of crystal orientation indicate that certain crystal planes are more stable than others. Tragert and Robertson[12] have used electrochemical techniques in an attempt to define the stable planes of copper. They conclude that the (111) plane is the only stable one and that all other planes approach the (111) configuration with time, the process being considered to involve an etch-type mechanism.

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[9] Chalmers, King, and Shuttleworth, *Proc. Roy. Soc.*, 1948, *A*, **193**, 465.
[10] Johnson, *Phys. Rev.*, 1938, **54**, 549.
[11] Becker, *Adv. Catalysis*, 1955, **6**, 135.
[12] Tragert and Robertson, *Trans. Electrochem. Soc.*, 1955, **102**, 86.

Young, Cathcart, and Cunningham[13] have emphasised the dynamic nature of surfaces, especially when used as catalysts. The faces which are stable vary markedly with the reacting gases and the experimental conditions, the surface rearranging to expose these faces. Thus, the nature and structure of a metal surface during reaction may be different from the nature and structure during adsorption although the distinction between adsorption and reaction may be difficult. Interference patterns produced by the oxidation of a copper crystal at 250° show clearly the different crystal regions. Large differences in oxidation rate with crystallographic region have been observed; for example, after 50 min. at 178° the thickness of oxide on the (100) plane was 1000 Å while that on the (311) face was about 60 Å.

It is usual to regard the oxide lattice as a rigid immobile structure, and this may possibly be correct at low temperature ($< 0°$), but there is now considerable evidence from the use of isotopic and other techniques that at higher temperatures ready transfer of lattice oxygen and chemisorbed oxygen will occur. Winter[14] has discussed the experimental evidence for the mobility of lattice oxygen in chemisorption and catalytic studies, and there appears to be no doubt that surface oxygen is extremely mobile in oxide catalysts such as manganese dioxide, cupric oxide, and ferric oxide at temperatures of about 200°. Topographically, the oxide surface may vary from being atomically uneven to grossly rough. In the latter instance protrusions a few hundred Å in length may be observed. Even the formation of the first few oxide layers may disrupt appreciably the surface contour of the metal substrate, and it could conceivably be regarded as a "surface corrosion" process.

3. Oxygen Chemisorption

The precursor of oxidation is the chemisorption of oxygen. A detailed discussion will not be given of the mechanism of oxygen chemisorption. It will suffice to consider only the possible final states.

If, in the adsorbed oxygen, a vacant energy level is present which is below the Fermi level of the metal, an electron can be transferred from the metal to the oxygen. This is the case when oxygen is chemisorbed with a negative dipole pointing away from the surface. There is no unambiguous evidence for the reverse process, *i.e.*, the formation of a positive dipole during oxygen chemisorption. Suhrmann[15] has suggested that the change in the resistance of a bismuth film at 77°K during the adsorption of oxygen can be attributed to the formation of O_2^+. Such a conclusion may not be correct, since, if the bismuth film is an intrinsic semiconductor, the decrease in resistance may reflect the formation of positive holes; on the other hand surface contamination could account for the phenomenon. In

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[13] Young, Cathcart, and Cunningham, *Acta Metallurgica*, 1946, **4**, 145.

[14] Winter, *Adv. Catalysis*, 1958, **10**, 196.

[15] Suhrmann, "Chemisorption", ed. Garner, Butterworths, London, 1957.

covalent bonding the chemisorbed layer is stabilised by electron exchange rather than by electrostatic forces. Such bonds would, nevertheless, be partially ionic, as revealed by the presence of a surface dipole layer, although the latter may only correspond to about 0·5 D. This would suggest that the metal–oxygen bond is predominantly covalent but with a small electron surfeit on the adsorbed oxygen atom. Tompkins[16] concludes that transition metals exhibit definite covalent bonding with both hydrogen and carbon monoxide when these gases are adsorbed at $-195°$ whereas with *sp* metals a predominantly "electrostatic" bond is formed, the dipole moment of which is mainly controlled by the first ionisation potential of the adsorbate.

Since the oxygen molecule has a positive electron affinity of 2—3 kcal.mole^{-1} it is feasible that O_2^- ions could be formed. There is, nevertheless, much speculation regarding the exact nature of a chemisorbed ion, *i.e*,, whether it exists as O_2^-, O^-, or O^{2-}. On the basis of the properties of zinc oxide surfaces Barry and Stone[17] suggest that at room temperature either O^- or O_2^- is prevalent, but between 100° and 400° the O^{2-} species predominates. Experiments with oxygen isotopes at low temperature strongly suggest that dissociative adsorption occurs on the oxide surface, so that O^- is the more likely. The formation of the O^{2-} species at high temperature is in agreement with the conductivity data of von Baumach and Wagner[18] and of Bevan and Anderson.[19]

As a consequence of the surface dipole at the metal–oxygen interface the apparent work function, ϕ, of the metal is altered. The change in ϕ corresponding to a surface coverage θ is given by eqn. (2), where σ_m is

$$\phi = 4\pi\sigma_m\theta M \qquad (2)$$

the total number of sites available, and M is the dipole moment of the adsorbed molecule. The values for the surface potentials of oxygen on metals are all negative; the only system for which there is good agreement between different workers is tungsten–oxygen. In this case values of about $-1{\cdot}8$ v have been obtained by various investigators using different techniques, and this is particularly strong evidence that the value refers to a "clean" surface.[20,21] In general, the variations in the surface potential can be ascribed to the use of contaminated surfaces, although crystal orientation may also be a contributing factor. The presence of a potential V at the gas–metal interface implies that a field F exists, such that $F = V/X$, where X is the adsorbate thickness. With a value of 1 v for V and 3 Å for X, the field approaches 10^8 v/cm. Such a field would, on general grounds,

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[16] Tompkins, Diskussionbeitrag, Bunsengesellschaft, Bad Homburg, 1958.
[17] Barry and Stone, *Proc. Roy. Soc.*, 1960, *A*, 255, 124.
[18] von Baumach and Wagner, *Z phys. Chem.*, 1933, *B*, **22**, 199.
[19] Bevan and Anderson, *Discuss. Faraday Soc.*, 1950, **8**, 238.
[20] Gomer and Hulm, *J. Chem. Phys.*, 1957, **27**, 1363.
[21] Mignolet, *Rec. Trav. chim.*, 1955, **74**, 685.

be expected to have a profound influence on the kinetics of the initial oxidation of metals.

The formation of a chemisorbed oxide layer is usually difficult to separate and distinguish kinetically from second- or third-layer formation. In general, the primary oxide layer is formed at an immeasurably fast rate at temperatures as low as −195° with a high heat of adsorption (> 50 kcal.mole^{-1}). Oxygen chemisorption occurs with all metals; the only possible exception is with gold, but Daglish and Eley[22] have recently suggested that even with gold some sites, possibly gold atoms at dislocation sites, are active in chemisorption. Lanyon and Trapnell[23] measured the extent of oxygen chemisorption by comparing the volume of oxygen adsorption with the uptake of gases such as hydrogen and carbon monoxide. By making assumptions concerning the nature of the chemisorbed gases the extent of the oxygen uptake could be estimated, *i.e.*, whether it involved only the formation of the first layer or whether it involved appreciable incorporation. Making use of physical adsorption techniques in conjunction with chemisorption, Roberts,[24] and Brennan, Hayward, and Trapnell[25] have estimated the extent of oxygen incorporation. The use of physical adsorption as a complementary measurement is of particular significance, especially as chemisorbed gases may induce surface sintering. Table 2 summarises the extent of incorporation using various criteria of coverage and the maximum heat of adsorption for a number of metal–oxygen systems, the oxygen pressure usually not exceeding 10^{-1} mm.

It had been expected that a correlation between the *d*-band structure of metals and chemisorption is a means of systematising adsorption phenomena. Nitrogen, carbon monoxide, ethylene, and acetylene were considered to require *d*-band vacancies, *i.e.*, covalent linkages are formed between the adsorbed molecule and the partly filled *d*-band. This fact was considered to be a distinguishing feature, since oxygen chemisorption occurred on both transition and non-transition metals. There is now evidence[38] that the adsorption of hydrogen atoms occurs on metals in which *d*-bands do not contribute significantly to the electronic structure, namely on copper, silver, and gold. This seems to invalidate any simple correlation between *d*-band structure of the metal and adsorption. There may not be any simple relation between band structure and the formation of surface bonds, since the mere presence of an interface may considerably alter the electronic distribution in its vicinity. That the surface states of metals can sometimes approximate to those of free atoms was suggested by Goodwin;[39] this would imply that activity in chemisorption will be more closely related to the properties of atoms rather than to bulk crystals. In fact,

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[22] Daglish and Eley, Preprint, International Congress Catalysis, Paris, 1960.

[23] Lanyon and Trapnell, *Proc. Roy. Soc.*, 1955, *A*, **227**, 387.

[24] Roberts, *Trans. Faraday Soc.*, 1961, **57**, 99.

[25] Brennan, Hayward, and Trapnell, *Proc. Roy. Soc.*, 1960, *A*, **256**, 81.

[38] Pritchard and Tompkins, *Trans. Faraday Soc.*, 1960, **56**, 540.

[39] Goodwin, *Proc. Camb. Phil. Soc.*, 1939, **35**, 221.

TABLE 2. *Metal–oxygen systems.*

Metal	Temp. of oxidn. (°C)	No. of layers formed	Max. heat of adsorption (kcal. mole^{-1})	Criteria for coverage	Ref.
Al	23*	4·5	210	*b*	25
Rh	−183	1·0	—	*a*	23
Rh	23	1·0	110	*b*	25
Mo	23	1·5	170	*b*	25
Mo	−183	1·0	—	*a*	23
Ta	−183	1·0	—	*a*	23
Ta	23	3·0	220	*b*	25
Fe	23	1·5	100	*a*	26
Fe	23	5·0	130	*b*	25
Fe	23	9·0	—	*b*	24
Fe	0	up to 10	—	*a*	23
Fe	−195	5—10	—	—	27
Fe	−183	—	120	*b*	28
Fe	−78	10·0	—	*b*	29
Fe	−195	6·0	—	*b*	24
Ca	23	~50	—	*b*	30
Ba	35	∞	—	*b*	31
Na	23	>200	—	*b*	30
Si	23	1·5	—	*b*	32
Cu (100 face)	23	4·0	—	*c*	33
Cu	23	up to 6	—	*a*	23
Cu	20	6·0	—	*d*	34
Cu	−183	1·0	—	*d*	34
Ni	23	2·5	105	*b*	25
Ni	23	4·0	120 and 130	*b*	35
Ni	23	1·0	150	*b*	36
Co	25	6·0	115	*b*	37

* The temperature 23° is used for data determined at room temperature if it is not stated precisely. [a]Surface coverage estimated by use of chemisorption. [b]Surface coverage estimated by use of physical adsorption. [c]Coverage calculated from the assumption that 4 Å of oxide is equivalent to one oxide layer. [d]Based on the number of molecules required to form a single layer on a (111) copper surface.

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[26] Bagg and Tompkins, *Trans. Faraday Soc.*, 1955, **51**, 1071.

[27] Emmett, "Structure and Properties of Solid Surfaces," ed. Gomer and Smith, University of Chicago Press, 1953.

[28] Beebe and Stevens, *J. Amer. Chem. Soc.*, 1940, **62**, 2134.

[29] Kummer and Emmett, *J. Amer. Chem. Soc.*, 1951, **73**, 2886.

[30] Roberts and Tompkins, unpublished data.

[31] Bloomer, *Nature*, 1957, **179**, 493.

[32] Green and Maxwell, *J. Phys. and Chem. Solids*, 1960, **13**, 145.

[33] Rhodin, *J. Amer. Chem. Soc.*, 1951, **73**, 3143.

[34] Allen and Mitchell, *Discuss. Faraday Soc.*, 1950, **8**, 309.

[35] Beeck, *Adv. Catalysis*, 1950, **1**, 150.

[36] Klemperer and Stone, *Proc. Roy. Soc.*, 1957, *A*, **243**, 375.

[37] Rudham and Stone, *Trans. Faraday Soc.*, 1958, **54**, 420.

Pickup and Trapnell[40] have correlated the apparent inactivity of mercury and gold in oxygen chemisorption with the high ionisation potentials of the atoms rather than with the work function of the crystals. Some correlation does exist between the number of electronic states near the Fermi level and the susceptibility to oxygen chemisorption of the metalloid elements arsenic, antimony, bismuth, selenium, and tellurium. Apker, Taft, and Dickey[41] have derived the following order of electron densities: Bi>Sb>As>Se>Te. This sequence agrees with the observed order of activity in oxygen chemisorption. Such a correlation is compatible with the fact that, for oxygen to be adsorbed as negative ions, a large electron concentration in the higher occupied states is probably necessary. It is, nevertheless, a very tentative correlation, since the activity of the metals was not strictly defined.

Subsequent to the formation of the first oxide layer, oxygen interaction will occur with a surface oxide. Although there is evidence for the occurrence of O^- and O^{2-} species on an oxide surface, the use of such symbols to describe the surface species is undoubtedly an over simplification since the interaction of a gas with an adsorbate will rarely result in complete electron transfer. Grimley and Trapnell[42] have suggested that neutral pairs may exist on the oxide surface. These could arise from the attraction of positive holes $e\square$ and adsorbed oxygen ions, their formation taking place as shown by eqn. (3), where $O^- e\square$ is the neutral pair and $(\square S)$ is

$$\tfrac{1}{2}O_2 + (\square S) \rightleftharpoons O^- e\square \qquad (3)$$

a possible site for adsorption on the oxide surface.

4. Oxygen Incorporation

It is convenient to discuss the mechanism of oxygen incorporation in terms of the possible rate-controlling processes. Subsequent to the chemisorption of oxygen, and by this is meant the fast initial oxygen uptake at low temperature and which may therefore include multilayer formation, further oxide growth will only occur as a result of the movement of cations outwards through the oxide, oxygen inwards, or possibly a contribution from both processes. Electrochemical and diffusion experiments with oxides, sulphides, or halides have shown that in these phases cations, anions, and electrons are mobile, but their mobilities may differ widely. It would be expected that, in general, owing to the smaller ionic radii of cations, cation diffusion would be energetically more favourable than anion diffusion. Complications arising from the breakdown of a compact oxide lattice may, however, enable direct access of oxygen to the metal covered by a relatively thin oxide layer 100 Å thick. On the other hand it is possible

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[40] Pickup and Trapnell, *J. Chem. Phts.*, 1956, **25**, 182.
[41] Apker, Taft, and Dickey, *Phys. Rev.*, 1949, **76**, 270.
[42] Grimley and Trapnell, *Proc. Roy. Soc.*, 1956, *A*, **234**, 405.

that the flow of electrons through the oxide to the oxide–gas interface is the rate-controlling process.

(a) *The metal–oxide interface.* Cabrera and Mott[43] suggested that the initial energy barrier to be surmounted by a cation entering the oxide lattice was greater than any subsequent barrier, so that cation entry is rate-controlling during the formation of thin oxide films. The situation at the metal–oxide interface may be represented as in Fig. 1, which shows the change in potential energy of a cation as it leaves the metal, enters the oxide, and then diffuses through the oxide. The rate of oxidation at temperature T would, therefore, be expected to be given in the form of eqn. (4), where X is the oxide thickness at time t, E the activation energy,

$$\frac{\mathrm{d}X}{\mathrm{d}t} = \mathrm{c}\exp(-E/\boldsymbol{R}T) \qquad (4)$$

and c a constant.

According to the theory of Eyring,[44] the rate of reaction is given by eqn. (5),

$$r = (\boldsymbol{k}T/\boldsymbol{h})\exp(\Delta S^*/\boldsymbol{R}).\exp(-\Delta H^*/\boldsymbol{R}T) \qquad (5)$$

where ΔS^* is the entropy of activation, ΔH^* the heat of activation, and the other terms have their usual significance. Since the difference between the activation energy and the heat of activation is insignificant, then the general expression for the activation energy of an oxidation process, the rate of which is controlled by the barrier to cationic movement at the metal–oxide interface, is given by eqn. (6), where W is the entry barrier

$$E = \Delta H^* = W - \Delta H + c' - qa'FN \qquad (6)$$

(Fig. 1), ΔH is the heat of oxygen chemisorption, c' is the heat of formation of an anion vacancy (the site for oxygen chemisorption), and $qa'FN$ is the lowering of the energy barrier W by the superimposed field F arising

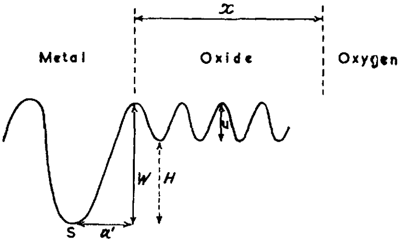

FIG. 1. *The potential energy of a cation on moving from a metal into the oxide.*

from the surface potential of the adsorbed oxygen. a' is the jump distance for the cation, N is Avogadro's number, and q is the charge on the cation. There are very few data relating to the heat of oxygen chemisorption on

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[43] Cabrera and Mott, *Reports Progr. Phys.*, 1948, **12**, 163.

[44] Glasstone, Laidler, and Eyring, "The Theory of Rate Processes," McGraw Hill, New York, 1941.

oxides, *i.e.*, the value of ΔH beyond the monolayer. In, for example, the oxidation of nickel oxide the slow incorporation process occurs with a heat of about 25 kcal.mole^{-1}.[36,37] Since the value of c' is about 1 ev, then $\Delta H \sim c'$ beyond the monolayer, and therefore $E = \Delta H^* = W - qa'FN$. And so eqn. (4) leads to eqn. (7). Cabrera and Mott suggested that

$$\frac{dX}{dt} = c \exp \frac{(W - qa'FN)}{RT} \tag{7}$$

the constant c be given by $N'\Omega\nu$, where N' is the number of special sites from which a cation may enter the oxide (*i.e.*, position S of Fig. 1), Ω is the volume of oxide per cation, and ν is the frequency of vibration of the cations in the lattice. The field F may be replaced by V/X, where V is the surface potential of the chemisorbed oxygen on the oxide, and X is the oxide thickness. The variation of the term $qa'VN/X$ with oxide thickness X, assuming $q = 3e$, $a' = 2{\cdot}5$ Å, and $V = 2$ v, is shown in Fig. 2. Thus, up to an oxide thickness of approximately 30—40 Å the presence of the superimposed field is likely to have a very marked influence on the observed kinetics. The only known attempt to detect any influence of an external field on oxidation behaviour is that of Uhlig and Brenner.[45] An electric field of 15,500 v cm.$^{-1}$ was applied across a copper surface covered by approximately 700 Å in an oxygen environment. No noticeable effect on the oxidation rate was observed, which is in agreement with considerations similar to those of Fig. 2, the lowering of the energy barrier for cation entry being about 1 kcal.mole^{-1}. Such a field would also be insufficient to create defects in the oxide; its rôle would therefore be merely to direct the random movement of ions already taking place in the absence of the field.

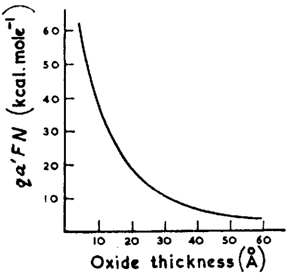

FIG. 2. *The "field effect" as a function of oxide thickness.*

The following would now appear to be relevant to the formation of thin oxide films on metals: (*i*) The structural characteristics of the metal surface since N' is related to surface defects. (*ii*) The surface potential, V, of the chemisorbed gas, since this controls the field, F; the larger the surface potential the more extensive should be the incorporation. In the theory of

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[45] Uhlig and Brenner, *Acta Metallurgica*, 1955, **3**, 108.

Cabrera and Mott, V is assumed to be independent of both temperature and pressure. (*iii*) Since $W = U + H$, where U is the activation energy for cation diffusion through the oxide, and H is the heat of solution of the cation in the oxide, then the value of W will be least for a metal–oxide system where both the heat of solution and the energy for cation diffusion are a minimum. Thus, an open type oxide structure involving a cation of small ionic radius should result in a minimum of the activation energy. (*iv*) Electrons are able to establish an equilibrium between metal and adsorbed oxygen on the oxide in a time small with respect to that required for a cation to diffuse through the oxide.

That the above considerations are applicable to the initial interaction of gases with metals has been shown by a number of investigators. Bloomer,[46] studying the oxidation of barium films at pressures of about 10^{-6} mm., showed that the initial reaction was an acceleratory one, which suggests that a nucleation process was occurring which involved specific sites on the barrier surface. Above 35° oxidation continued until the metal had completely oxidised, but below this critical temperature the oxide thickness approached a limiting value. Such a critical temperature is understandable, since, on rearranging equation (7) and substituting $F = V/X_{\mathrm{L}}$, eqn. (8) is

$$\frac{1}{X_{\mathrm{L}}} = \frac{W(1 - \alpha t)}{Va'qN} \tag{8}$$

obtained, where $\alpha = -(\boldsymbol{R}/W) \ln [(\mathrm{d}X_{\mathrm{L}}/\mathrm{d}t)(1/\nu\Omega N')]$, and $\mathrm{d}X_{\mathrm{L}}/\mathrm{d}t$ is the experimentally defined limiting rate. Therefore, when the temperature is $1/\alpha$, the limiting oxide thickness, X_{L}, is infinite. Critical temperatures of approximately 160° and 400° have been estimated for the nitridation of calcium[47] and the oxidation of iron films[24] respectively.

Since the field is given by $F = 4\pi ne/K$, where n is the number of adsorbed species per unit area, e is the electronic charge, and K is the dielectric constant of the oxide, it would be expected that the contact potential, V, is a function of the oxide thickness. The assumption of Cabrera and Mott, that V is constant during oxide growth, implies that n varies inversely as the oxide thickness, X. Since n is, in general, temperature-dependent, then V should vary with temperature. A recent approach to gas–metal interaction[47] considers the electric field to be confined to narrow tubes, these tubes being associated with field-creating species. Thus, although the number of tubes, n, is temperature dependent, $n \propto \exp(-\Delta H/\boldsymbol{R}T)$, where ΔH is the heat of formation of a field-creating species; the field across any one tube is temperature independent and varies only as the inverse of the oxide thickness. The anodic oxidation experiments of Vermilyea show that, with tantalum, the oxide grows at the electrolyte–oxide interface. This means that the mobile entities are cations, which was *a priori* most likely, owing to the difference between the ionic radii of

[46] Bloomer, *Nature*, 1957, **179**, 173.
[47] Roberts and Tompkins, *Proc. Roy. Soc.*, 1959, *A*, **251**, 369.

Ta^{5+} and O^{2-}. The mechanism of cation transport has been recently investigated by Verkerk, Wenkel, and de Groot,[48] and they concluded that the mechanism was neither pure vacancy nor pure interstitial.

A process termed "place exchange" was suggested by Lanyon and Trapnell[23] to account for the initial oxidation of metals. The adsorbed oxygen is considered to change places with an underlying metal atom, and this process is subsequently repeated, further oxide layers being formed. Similarly, it has been suggested that the initial oxidation of germanium[49] occurs by a "switching" process; this is illustrated in Fig. 3.

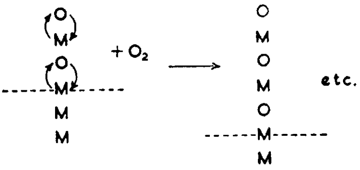

FIG. 3. *Place-exchange mechanism.*

The motivation of the exchange was considered to be derived from the liberated heat of adsorption. Both nickel films and reduced nickel powder exhibit surface regeneration after oxygen chemisorption when kept *in vacuo* ($<10^{-6}$ mm.) at room temperature;[50,51,52] whatever the detailed mechanism of the regeneration process it must involve the re-creation of surface cations. Similarly, Law,[53] and Eley and Wilkinson[54] observed regeneration during the oxidation of silicon and aluminium respectively. It, therefore, seems unlikely that surface regeneration requires that heat be liberated during chemisorption. In the initial oxidation of aluminium, place-exchange is thought only to apply during the formation of the first 6 Å of oxide, after which, recrystallisation of the initially amorphous oxide results in a change-over of the rate-controlling process to electron transport. A recent investigation[55] of the amorphous oxide present on aluminium foil has shown that crystallisation is not observable with the electron microscope until a temperature of about 500° is attained. The process of place-exchange was probably first recognised by de Boer[56] who used photoelectric sensitivity techniques. When oxygen reacts with cæsium the cæsium oxide becomes "buried" in the metal and the mobility of the cæsium atoms is so high that the photoelectric sensitivity remains essentially unaltered, until almost all the cæsium is converted into oxide. This would

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[48] Verkerk, Wenkel, and de Groot, Philips Res. Repts., 1958, **13**, 506.
[49] Green, Progr. in Semiconductors, 1959, **4**, 37.
[50] Roberts and Sykes, unpublished data.
[51] Oda, *Bull. Chem. Soc. Japan*, 1954, **27**, 465.
[52] Anderson and Klemperer, *Nature*, 1959, **183**, 899.
[53] Law, *J. Phys. and Chem. Solids*, 1958, **4**, 91.
[54] Eley and Wilkinson, *Proc. Roy. Soc.*, 1960, *A*, **254**, 327.
[55] Thomas and Roberts, *J. Appl. Phys.*, accepted for publication.
[56] De Boer, "Electron Emission and Adsorption Phenomena," Cambridge, New York, 1935.

indicate that either a layer of cæsium atoms remains on the oxide surface even after extensive oxidation had occurred, or that the cæsium surface was initially oxide and the photoelectric measurements thus referred to an oxide layer rather than to the metal.

Although place-exchange suggests a process quite distinct from cation-diffusion controlled by a superimposed field, the two are at least phenomenologically identical. The place-exchange mechanism has been suggested to involve an activation energy, $E_{\text{exp.}}$, that increases linearly with oxide thickness X so that eqn. (9) holds. This equation clearly has only significance for small values of X. Oxidation, controlled by cation diffusion in the presence of a superimposed field, implies a limiting value for the activation energy, since eqn. (10) is obtained from equation (7). A distinction between two mechanisms, the activation energies of which vary according to equations (9) and (10), is not easy, since the term $qa'VN/X$ decreases almost linearly with X. Now, the kinetic equations which follow from equations (9) and (10) are (11) and (12) respectively,

$$E_{\text{exp.}} = E_0 + \gamma X \tag{9}$$

$$E = W - (qa'VN/X) \tag{10}$$

$$X \propto \log t \tag{11}$$

and

$$1/X \propto \log t \tag{12}$$

X being the oxide thickness at time t, Over restricted ranges of oxide thicknesses, both equations (11) and (12) may be found to describe the results equally well, and a distinction is only possible if constants derived from them are shown to have a reasonable physical significance.

(b) *Electron transport and the logarithmic law.* Electron availability and transport is an essential prerequisite for the occurrence of oxidation. According to wave mechanics a small proportion of the electrons which are incident on a potential barrier will penetrate it. This phenomenon, called "the tunnel effect", is responsible for the flow of electrons between two metals, the surfaces of which are inevitably covered by oxide. Up to an oxide thickness of 30 Å or so, electrons are therefore considered to move through the oxide from the metal by a tunnelling process, and it was Mott[57] who first suggested that the slow step in oxidation was electron transport to the oxide–gas interface by this mechanism. He later abandoned this concept for control by ionic transport. More recently, Hauffe and Ilschner[58] have revived the electron transport rate-controlling process to explain the results of Scheuble for the oxidation of nickel. It is relevant to consider the possible mechanisms by which electrons may be made available.

[57] Mott, *J. Inst. Metals*, 1939, **65**, 333.
[58] Hauffe and Ilschner, *Z. Elektrochem.*, 1954, **58**, 382.

Subsequent to the formation of the initial oxide layer the energy required to remove an electron from the metal is no longer related to the work function of the clean metal. The system is now a composite one involving a metal–semiconductor interface with the possibility of oxygen adsorbed on the semiconducting oxide surface resulting in electron acceptor levels being made available. The potential-energy diagrams shown in Figs. 4, 5, and 6 may, therefore, be considered to represent the conditions for a "clean" metal, a "clean" metal on which oxygen has been chemisorbed, and a metal in contact with oxide on which oxygen is chemisorbed.

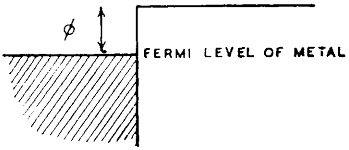

FIG. 4. *Clean metal in a vacuum.*

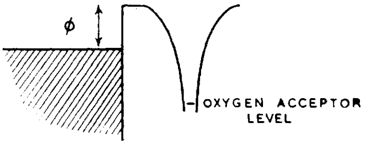

FIG. 5. *"Clean" metal and chemisorbed oxygen.*

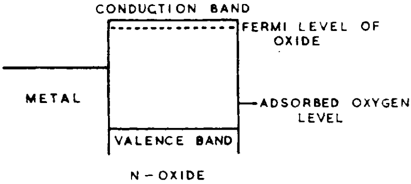

FIG. 6. *Possible non-equilibrium electron energy levels in a metal–oxide–oxygen system.*

In the case of metal + chemisorbed oxygen, electrons may penetrate the potential barrier ϕ, the work function of the metal, by the tunnelling mechanism, O^- ions being formed on the surface. If chemisorption and subsequent incorporation result in the formation of an n-type oxide of low work function electron transfer may occur from the oxide to the metal, and, if a simultaneous movement of cations in the opposite direction does not occur, a space charge, normally called the Schottky depletion layer, is formed. Fig. 6 illustrates a possible non-equilibrium state, Fig. 7 the equilibrium attained between oxide and metal, and Fig. 8 the equilibrium between oxide, metal, and chemisorbed oxygen. The depth of the space-charge layer is related to the density of the donor states in the oxide by eqn. (13), where x_0 is the depth of the Schottky barrier, ϵ is the dielectric constant of the oxide, e is the electronic charge, and $\Delta\phi$ is the height of

$$x_0^2 = \frac{\Delta\phi}{\left(\frac{2\pi}{\epsilon}\right) n_d e^2} \tag{13}$$

the barrier. In the case of a low density of donor states, say 10^{15} per cm.^{3}, then, with $\epsilon = 10$ and $\Delta\phi = 1$ ev, the space charge region is approximately 10^{-4} cm. deep whereas for a site density of 10^{19} per cm.^{3} the depth is only $\sim 10^{-6}$ cm. Equilibrium is established when the Fermi levels in the metal and the oxide are the same.

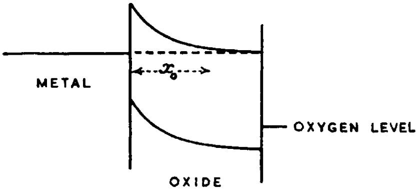

FIG. 7. *Electron transfer from oxide to metal resulting in an energy barrier to further transfer and a space-charge layer of depth x_0.*

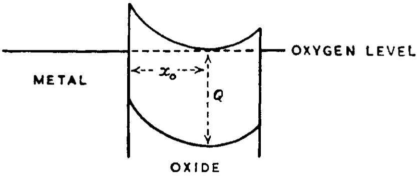

FIG. 8. *Electronic equilibrium established between metal, oxide, and adsorbed oxygen.*

Oxygen chemisorbed on an oxide surface generally results in electron levels being made available which are much lower than the conduction band of the oxide (Fig. 6). At equilibrium the highest filled oxygen level will be at the height of the Fermi level in the semiconductor (Fig. 8). If the semiconductor is an intrinsic semiconductor the effect of the positive space-charge could result in the filled band's being raised sufficiently to donate electrons to the adsorbed oxygen, thus creating holes in the filled band. The latter process could continue until the top of the filled band is at the same height as the Fermi level, so that the height of the barrier is restricted to Q (Fig. 8), the difference in energy between the conduction and filled bands.

Oxygen-ion formation is, therefore, possible either by electron tunnelling from the metal into the conduction band of the oxide, provided the width of the energy barrier is not prohibitive, or, in special circumstances, from the filled band of the oxide.

Garner, Gray, and Stone[59] have suggested that, with an oxide capable of exhibiting variable valency, bonding of oxygen to surface cations may take place with an attendant valency change, *e.g.*, $2Cu^+ + \frac{1}{2}O_2 \rightarrow 2Cu^{2+} + O^{2-}$. That shallow electron-emitting centres do exist on metal surfaces, undoubtedly covered by an oxide layer, is borne out by the ability of certain metals to initiate free-radical reactions at room temperature. This phenomenon, termed exoelectron emission,[60] is thought to account for the formation of hydrogen peroxide from water in the presence of abraded metal, and illustrates the capacity of "freshly prepared" surfaces to act as an electron source.

The boundary layer theory of chemisorption, which is based on the presence of a surface barrier to electron transport, has been applied by Hauffe[61] to derive the kinetics of the uptake of oxygen by oxides. Since oxygen chemisorption increases the work function of the adsorbent, the rate of oxygen chemisorption by the oxide surface is given by eqn. (14),

$$\frac{dX}{dt} = k' \exp\left[-e\frac{(\mu_0 + \Delta\phi)}{kT}\right] \tag{14}$$

where X is the concentration of surface atoms at time t, μ_0 is the height of the energy barrier at the beginning of chemisorption (*i.e.*, $X = 0$), $\Delta\phi$ is the change of the work function of the surface as a consequence of adsorption, e is the electronic charge, T is the temperature, and k is the Boltzmann constant. By expressing $\Delta\phi$ in terms of the concentration of chemisorbed oxygen, the concentration of holes in the oxide, and the potential difference between the interior of the oxide and the surface, Hauffe derived the logarithmic eqn. (15), where $b = 4\pi ea/\epsilon$, ϵ is the

$$X = \frac{2{\cdot}3kT}{eb}\log(1 + t/t_0) \tag{15}$$

dielectric constant of the oxide, and a is the distance between the surface of the oxide and the centres of charge of the chemisorbed atoms. Engel and Hauffe[62] find that eqn. (15) is valid for the first 10 min. of the oxidation of nickel oxide at 25°, after which there is a marked deviation. This logarithmic expression, sometimes referred to as the Elovich or Roginski–Zeldovitch equation, has been shown to be applicable to a large number of systems involving an activated process. Taylor and Thon[63] suggested that the prime function of the adsorbed gas is to create sites which, over the course of the activated process, decay at a bimolecular rate. A similar equation has been derived by Porter and Tompkins[64] and by Jennings and

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[59] Garner, Gray, and Stone, *Proc. Roy. Soc.*, 1949, *A*, **197**, 294.
[60] Grunberg, *Proc. Phys. Soc.*, 1953, **66**, 153.
[61] Hauffe, *Adv. Catalysis*, 1955, 7, 213.
[62] Engel and Hauffe, quoted in ref. 61.
[63] Taylor and Thon, *J. Amer. Chem. Soc.*, 1952, **74**, 4169.
[64] Porter and Tompkins, *Proc. Roy. Soc.*, 1953, *A*, **217**, 529.

Stone[65] who assumed a linear increase in activation energy with surface coverage. More recently, Gundry and Tompkins[66] have invoked the presence of an intermediate chemisorbed state which must be passed through before the adsorbed molecule attains its final equilibrium state. The initial bonding to the surface is thought to involve *d*-orbitals only; this then transforms to a stronger hybridised *dsp* final state. So long as the free energy of adsorption decreases linearly with coverage the Elovich equation can be deduced. The changing hybridisation of surface bonds may play an important rôle in many slow oxidation phenomena.

The Elovich type equation is, however, so frequently obeyed by gas–solid reactions that to invoke a particular mechanistic model merely on the basis of linearity of plots is not a satisfactory criterion of validity. There is also the difficulty of obtaining a unique value for the constant t_0. Landsberg[67] has suggested that the ubiquitous nature of the logarithmic equation in chemisorption reflects the same basic mechanism. He derived the equation (16), where $t_0 = 1/\mathrm{m}Na\beta S_0$, m is a constant, β is the effective

$$q = (1/\beta)\log(1 + t/t_0) \tag{16}$$

area over which the sites become invalidated by the adsorption of a single molecule, N is the number of impacts of the gas molecules with the surface per unit area per unit time, a is the effective contact area between a molecule and the surface, and S_0 is the number of sites per unit area at the commencement of the reaction. This is a denial of the Langmuir hypothesis that the total number of adsorption sites is constant. t_0 would be expected to be inversely dependent on pressure. Another interpretation of the logarithmic equation is that due to Uhlig[68] who considers electron flow to be controlled by a space-charge. The space-charge is envisaged as being composed of two parts: (1) a uniform charge-density layer next to the metal, and (2) a diffuse-charge layer beyond the uniform layer, the latter arising from the presence of electrons trapped at lattice imperfections within the oxide.

5. Dependence of Oxygen Uptake on Pressure

The process of metal oxidation may be considered as three concurrently operating processes, adsorption, desorption, and incorporation. The rates of these processes can be expressed by the following equations

$$V_{\mathrm{ads.}} = k_1 c_{\mathrm{x}}{}^{\alpha} c_{\mathrm{s}} \tag{17}$$

where α is the pressure dependence of the adsorption process, c_{s} is the number of bare sites per cm.^{2}, and $k_1 = (\boldsymbol{k}T/\boldsymbol{h})\,(f^{\ddagger}/f_{c_{\mathrm{x}}}{}^{\alpha}f_{\mathrm{s}})\exp(-E_1/\boldsymbol{R}T)$

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[65] Jennings and Stone, *Adv. Catalysis*, 1957, **9**, 441.

[66] Gundry and Tompkins, *Trans. Faraday Soc.*, 1956, **52**, 1609.

[67] Landsberg, *J. Chem. Phys.*, 1955, **23**, 1079.

[68] Uhlig, *Acta Met.*, 1956, **4**, 541.

where c_x is the gas phase concentration and E_1 the activation energy for adsorption.

$$V_{\mathrm{des.}} = k_2 c_a \tag{18}$$

where $k_2 = (\boldsymbol{kT/h})(f^{\neq}/f_a)\exp(-E_2/\boldsymbol{R}T)$, c_a is the concentration of adsorbed species, and E_2 the activation energy for desorption;

$$V_{\mathrm{inc.}} = k_{\mathrm{inc.}} c_a \tag{19}$$

where $k_{\mathrm{inc.}}$ is the rate constant of the incorporation process. A steady state will be established in the adsorbed layer so that:

$$k_1 c_x^{\alpha} c_s - k_2 c_a - k_{\mathrm{inc.}} c_a = 0 \tag{20}$$

Since $c_s + c_a = N$, the total number of surface sites, then

$$c_s = \frac{N(k_2 + k_{\mathrm{inc.}})}{k_1 c_x^{\alpha} + k_2 + k_{\mathrm{inc.}}}\cdot$$

Thus, the rate of gas uptake, V, is given by

$$\begin{aligned} V = V_{\mathrm{ads.}} - V_{\mathrm{des.}} &= k_1 c_x^{\alpha} c_s - k_2 c_a \\ &= N k_1 k_{\mathrm{inc.}} c_Y^{\alpha} / k_1 c_x^{\alpha} + k_2 + k_{\mathrm{inc.}} \end{aligned}$$

If $k_{\mathrm{inc.}} \gg k_2 + k_1 c_x^{\alpha}$, then $V = N k_1 c_x^{\alpha}$ which means that the rate-determining step is that of adsorption. However, if $k_1 c_x^{\alpha} \gg k_2 + k_{\mathrm{inc.}}$, then $V = k_{\mathrm{inc.}} N$, and incorporation is rate controlling. On this basis alone we would expect the slow step to be adsorption at low pressures and incorporation at high pressures. The influence of phase-boundary equilibria, the nature of the adsorbed layer, etc., complicate these conclusions and are discussed further.

Wagner first directed attention to the pressure-dependence of the chemical composition of the oxide, and according to von Baumach and Wagner[18] interstitial zinc ions are formed in zinc oxide according to the equation (21)

$$\mathrm{Zn}^{2+} + \mathrm{O}^{2-} \rightleftharpoons \mathrm{Zn_i}^{2+} + 2\mathrm{e} + \tfrac{1}{2}\mathrm{O_2(g)} \tag{21}$$

where $\mathrm{Zn_i}^{2+}$ represents an interstitial ion formed from a lattice ion Zn^{2+}. It being assumed that the defects are in dilute solution and do not interact, the equilibrium constant for the formation of interstitial ions is

$$K = \frac{[\mathrm{Zn_i}^{2+}]\,[e^-]^2\, p_{\mathrm{O_2}}^{\frac{1}{2}}}{[\mathrm{Zn}^{2+}]\,[\mathrm{O}^{2-}]}$$

Within the range of composition possible for the zinc oxide phase, $[\mathrm{Zn}^{2+}]$ and $[\mathrm{O}^{2-}]$ do not change appreciably, so the equation can be put in the form

$$K_1 = [\mathrm{Zn_i}^{2+}]\,[e^-]\, p_{\mathrm{O_2}}^{\frac{1}{2}}$$

Since electrical neutrality requires that $[Zn_i^{2+}] = \frac{1}{2}[e^-]$ the change in the concentration of interstitial zinc ions with oxygen pressure should be given by

$$[Zn_i^{2+}] = (K_1/4)^{\frac{1}{3}}\, p_{O_2}{}^{-\frac{1}{6}}$$

Thus, if incorporation proceeds by the diffusion of Zn_i^{2+} the expected pressure dependence is $-1/6$.

Grimley[69] and Grimley and Trapnell[42] have derived growth laws for oxide films by considering the equilibria that may be set up at the metal–oxide and oxide–gas interface. n- and p-type oxides, with rates controlled either by cation transport or by surface reactions, have been examined for two general cases: (*a*) Surface saturated by field-creating ions. The dependence of the derived rate laws on pressure is particularly significant. Linear laws are derived for p-type oxides when surface reaction is rate-determining, similarly for an n-type oxide when the transport of interstitial cations is rate-determining. A logarithmic equation with a pressure dependence of 0·25 is predicted for a p-type oxide when movement of cation vacancies is rate-controlling. (*b*) Neutral pairs in the adsorbed layer. An equilibrium is considered to exist between neutral pairs and field-creating ions. Neutral pairs are considered to arise from the attraction of positive holes and adsorbed oxygen ions, their formation taking place as follows:

$$\tfrac{1}{2}O_2 + (\square S) \rightleftharpoons O^-\, e\square$$

where $O^-\, e\square$ is the neutral pair and $(\square S)$ is a possible site for adsorption on the oxide surface. The neutral pair may subsequently dissociate to form field-creating species, O^-/ads.

$$O^-\, e\square \rightleftharpoons O^-/\text{ads.} + e\square$$

The position of equilibrium in the above equation is important, since, although the oxide surface may be apparently saturated, not all the species need be of the field-creating kind. The derived pressure dependences are shown to be a function of the nature of the adsorbed species; values of $-0{\cdot}75$, $0{\cdot}25$, and 0 are calculated for a system where the surface species are assumed to be O_2^-, O^-, and O^{2-}, respectively. With n-type oxides the growth law is insensitive to the nature of the surface layer.

The formation of thin oxide layers (< 50 Å thick) has been suggested to be controlled in certain cases by electron transport;[58] if tunnelling is the mechanism then the oxygen uptake should be independent of pressure. If tunnelling is not feasible and the electrons have to surmount an energy barrier, E, the rate of electron transport is of the form:

$$\text{Rate} \propto \exp(-E/\boldsymbol{R}T)$$

where E is related to the space charge at the surface. Since the space charge is a function of the concentration of adsorbed species, for an unsaturated

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[69] Grimley, "Chemistry of the Solid State," ed. Garner, Butterworths, London, 1957, 336.

adsorbed layer the rate of electron transport will be some function of the oxygen pressure, although the exact form of the pressure dependence may be difficult to predict. If the concentration, q, of adsorbed species is related to the pressure by $q \propto p^n$, and the rate of electron transport is some linear function of q, then the value of n also gives the dependence of oxygen rate on pressure. Similarly, in rate control by cationic diffusion in the presence of a superimposed field, F, the magnitude of which is a linear function of the concentration of chemisorbed species, the oxidation rate will be related to pressure. If a saturated adsorbed layer is formed the rate will be pressure independent, but if an equilibrium is set up between oxygen molecules, at a pressure p, and oxygen atoms, the surface concentration of atoms and similarly the rate will be proportional to $p^{0\cdot5}$. Table 3 gives values of n for a number of gas–metal systems. There is the general difficulty of formulating a mechanism for a gas–metal reaction which is compatible with the dependence of rate on pressure. Eley and Wilkinson,[7] for example, suggested that, in the oxidation of aluminium, the value 0·6 is evidence for a dilute ideal film of oxygen atoms but that owing to interaction within the monolayer there is a small increase in the value of n over that predicted theoretically. At —80° the oxidation of iron films is independent of pressure, and this has been ascribed to a saturated surface layer of some kind; in the temperature range 0—100° the mean values of 0·2 and 0·28 are compatible with a surface equilibrium involving species which influence cationic diffusion.

TABLE 3. *Gas–metal systems.*

Metal	Gas	Temp. (°C)	Pressure dependence (n)	Ref.
Ca	N_2	23	1·0	47
Fe	O_2	−80	0	24
Fe	O_2	22 to 95	0·28	24
Fe	O_2	0	0·2	23
Al	O_2	20	0·6	7
Cu	O_2	0	0·75	23
Mg	O_2	23	0·8	70
Si	O_2	25	0·52	71
U	O_2	180	0·15	72

6. Nucleation and Anisotropic Oxidation

The realisation that nucleation is an important factor in oxide formation stems from the work of Bénard[73] and his collaborators. As a consequence of the microtopology of metal surfaces it would be expected that pre-

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[70] Sack, Diskussionbeitrag, Bunsengesellschaft, Bad Homburg, 1958.
[71] Law, *J. Phys. and Chem. Solids*, 1958, **4**, 91.
[72] Anderson and Roberts, *J. Chem. Soc.*, 1955, 3946.
[73] Bardolle and Bénard, *Rev. met.*, 1952, **49**, 613.

ferential reaction sites exist on the surface, resulting in the initiation of oxide growth at isolated points on the surface. The number of nuclei formed will depend on the activation energy for surface nucleation, which may vary over the metal surface; whether nucleation is initiated as a two-dimensional monolayer or whether three-dimensional nuclei are formed is not known. Bloomer[74] suggested that since the initial oxidation of barium appeared to start from a fixed number of nuclei the rate of oxygen uptake up to the commencement of the second layer would be expressed by eqn. (22), where X is the volume of oxygen adsorbed at time t, k is a constant,

$$\mathrm{d}X/\mathrm{d}t = kt^{n^*} \qquad (22)$$

and n^* is a non-dimensional parameter. The value of n^* is considered to reflect the geometry of the nucleus and its mode of growth. For flat circular nuclei, n^* has the value 0·5, whereas if the oxide grows into hemispherical caps, *i.e.*, a second-layer process commences before the completion of the monolayer, a value of 0·66 would be expected. Sack[70] has reported values between 0·2 and 0·7 for the oxidation of magnesium at 27°, and Roberts and Tompkins[47] a value of 0·19 for the nitridation of calcium films at 23°. Although a small value of n^* implies a large concentration of nucleating centres it is difficult to give n^* an exact physical meaning.

The orientation of alien crystals by an anisotropic substrate surface, termed epitaxy, is important in relation to the occurrence of anisotropic oxidation and the possibility of stresses that arise in oxide films subsequently leading to cracking. van der Merwe[75] developed a theory of epitaxy that involved as a necessary prerequisite the formation of a pseudomorphic layer. According to this theory such an oriented layer will occur provided the misfit is not greater than about 14%; it also predicts increasing instability of strained layers with increasing thickness. Rhodin explains the anisotropic behaviour of thin oxide layers on copper in terms of the van der Merwe[75] model of epitaxial growth.

Oxidation is undoubtedly dependent on the crystallographic plane being oxidised. Rhodin,[33] Gwathmey and Benton,[76] and Lustman and Mehl[77] showed that, of the most commonly occurring planes in a copper surface, the (110) is the most readily oxidised and the (111) plane the least. Young, Cathcart, and Gwathmey[78] found that at 150° the rate of oxidation of the (100) plane is four times that of the (311) although the limiting oxide thickness on the former is ten times that on the latter. Bénard and Talbot[79] observed at 900° that the oxidation rates for different planes of copper decreased in the following order: (210), (211), (110), (111), (100), (123).

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[74] Bloomer, *Brit. J. App. Phys.*, 1957, **8**, 321.
[75] van der Merwe, *Discuss. Faraday Soc.*, 1949, **5**, 208.
[76] Gwathmey and Benton, *J. Phys. Chem.*, 1941, **46**, 969.
[77] Lustman and Mehl, *Trans. Amer. Inst. Mining Met. Engrs.*, 1941, **143**, 1.
[78] Young, Cathcart, and Gwathmey, *Acta Metallurgica*, 1946, **4**, 145.
[79] Bénard and Talbot, *Compt. rend.*, 1948, **225**, 411.

Such a sequence was similarly reported earlier by Gwathmey and Benton at 1000°. The difference in behaviour at low and high temperatures suggests that different mechanisms are operating. The concept of metal atoms entering the oxide lattice only at kink sites possibly accounts for the anisotropic behaviour; a surface with a large number would be expected to oxidise faster than one with fewer. This is implicit in the theory of Cabrera and Mott. Anisotropic behaviour may, in some cases, be complicated by the crystallisation of an initially amorphous layer, or of recrystallisation. Such processes have recently been observed with copper at 150°. Crystallisation of an amorphous film could result in the oxide's becoming less protective, since movement can occur more easily along grain boundaries than within grains.

Gulbransen and Coplan[80] have used electron optical techniques to investigate the possible influence of dislocations, defects, and internal stress on the chemical reactivity of the metal surface. Thin oxide whiskers 100—150 Å in diameter occur when pure iron reacts with oxygen at 400°; these whiskers may grow to a length of 10^5 Å. With water vapour at 400° oxide platelets are formed. These observations, together with those of Pfefferkorn,[81] strongly suggest a growth mechanism in which the metal structure itself determines the progress of growth, the growth of a whisker taking place only at the tip where one or more screw dislocations emerge. Bénard, Grønlund, Oudar, and Duret[82] have studied the formation of oxide and sulphide nuclei on copper. A rather surprising feature is the constant rate of formation of nuclei at 550° and an oxygen pressure of 6×10^{-3} mm. With aluminium, Roberts and Thomas[83] have observed the formation of nuclei at temperatures around 550°, the geometrical form of the nuclei being dependent on the pressure conditions. At a pressure less than 10^{-6} mm. needle-shaped nuclei appear, and at atmospheric pressure an oxide layer composed of contiguous crystals of diameter $\sim 0{\cdot}2\ \mu$ are formed. Recrystallisation of the initial amorphous film is suggested, since electron diffraction shows that crystalline aluminium oxide of lattice parameter 7·9 Å is formed.

7. Thick Oxide Films

Although the general practice of discussing oxidation regions in terms of kinetic laws is an ambiguous one, the parabolic growth law is correctly associated with oxidation occurring in the presence of a thick oxide layer, usually 1000 Å or more deep. The oxide layer must be coherent and pore-free, and, above about 300°, the kinetics should conform to eqn. (23),

$$dx/dt = k_1/x \qquad (23)$$

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[80] Gulbransen and Coplan, *Discuss. Faraday Soc.*, 1960, **28**, 229.

[81] Pfefferkorn, *Naturwiss.*, 1953, **40**, 551.

[82] Bénard, Grønlund, Oudar, and Duret, Diskussionbeitrag, Bunsengesellschaft, Bad Homburg, 1958.

[83] Thomas and Roberts, *J. Appl. Phys.*, accepted for publication.

where x is the oxide thickness at time t, and k_1 is a constant. If $x = x_0$ at $t = 0$, then

$$x - x_0 = x = 2k_1(t/x) - 2x_0$$

This is probably the best way to express the law as it enables the initial uptake to be discarded since the origin of time may be set at any desired oxide thickness. Thus, a plot of t/x against x gives a straight line of slope $2k_1$. It may well be that the value of y_0 from the intercept has little quantitative significance in view of uncertainties regarding non-isothermal conditions and departures from parabolic behaviour at small times.

Wagner suggested that diffusion in oxide (or sulphide) phases may, in general, be interpreted as migration processes of ions and electrons, whereas the migration of electrically neutral atoms or molecules can be neglected. There are, therefore, two limiting cases which are illustrated in Fig. 9: (1) Positively charged cations and electrons may migrate in the same direction from the metal–oxide interface to the outer surface. (2) Negatively charged anions migrate inwards and electron movement occurs in the opposite direction.

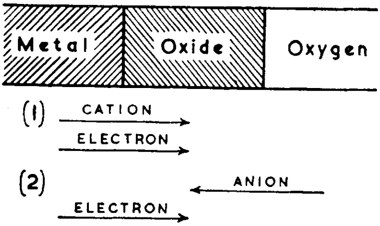

FIG. 9. *Diffusion in oxide phases.*

Wagner applied the model of a compact oxide layer with lattice defects to the derivation of the parabolic rate law assuming that cation diffusion within the oxide is rate controlling, so that a concentration gradient exists between the metal–oxide and oxide–oxygen interfaces. The concentration of defects is generally so low that analytical procedures are of little value. Engel,[84] using an electrochemical method, has succeeded in measuring the defect variation in an iron(II) oxide layer. He has shown a linear increase of defect concentration from the metal–oxide to the oxide–gas interface. It is significant that the defect concentration at the metal interface was not in fact 0 but at 900° amounted to 6%. Such a gradient of defect concentration apparently exists only when the iron(II) oxide layer is in intimate contact with the metal phase; poor adhesion results in equilibrium being established with the Fe_3O_4 phase which leads to a constant defect concentration in these positions of the iron(II) oxide layer.

If transport processes (electron, cation, or anion movement) within the oxide are more rapid than any of the possible phase boundary equilibria,

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[84] Engel, *Z. Elektrochem.*, 1959, **63**, 835.

non-equilibrium conditions then exist at the interface. The oxidation of iron under different conditions demonstrates clearly the influence of phase-boundary conditions. In oxygen at high temperature a number of oxide phases are formed and the parabolic law is obeyed; in carbon monoxide–carbon dioxide mixtures above 900° a linear rate law with only iron(II) oxide occurs, while in a hydrogen–water environment above 950° parabolic dependence with iron(II) oxide formation takes place. Evidently the high defect concentration in iron(II) oxide ensures a high diffusion velocity compared with the surface equilibria existing in a carbon monoxide–carbon dioxide environment whereas in a water–hydrogen atmosphere the surface equilibrium proceeds sufficiently rapidly so that the diffusion of cations through the iron(II) oxide layer represents the slower process.

That diffusion through an oxide film was not solely responsible for the oxidation rate was first emphasised by Evans[85] who obtained a more general equation by solving the simultaneous equations which represented the law of mass action at the boundary and transport across the film. The mixed parabolic equation (24), which expresses a reaction influenced

$$\alpha y^2 + \beta y = kt \qquad (24)$$

by both diffusion and boundary processes, has two obvious limiting cases, the simple parabolic law and the rectilinear law. The occurrence of the latter would suggest that the replenishing of the oxidising gas cannot keep up with the rate at which oxide growth occurs, so the oxygen-replenishment rate takes over control. Gulbransen[86] has recently developed Wagner's diffusion picture of oxidation by combining it with the transition-state theory. This development gives an expression for the parabolic rate constant involving absolute physical constants, two entropy and two heat of activation terms. In the case of the formation of nickel oxide, a p-type oxide, vacancies are formed according to equation (25); one cation

$$\tfrac{1}{2}O_2(g) \rightleftharpoons O^{2-} + \square c + 2\oplus \qquad (25)$$

vacancy $\square c$ is formed together with two positive holes and one oxygen ion O^{2-}. The concentration of vacancies is, therefore, given by:

$$n_c = (\boldsymbol{N}/4^{\frac{1}{3}})(p_{O_2})^{\frac{1}{6}} \exp(-\Delta H^\circ/3\boldsymbol{RT}) \exp(\Delta S^\circ/3\boldsymbol{R})$$

where ΔH° and ΔS° are the standard heat and entropy of formation respectively, N is Avogadro's number, $\boldsymbol{R}$ the gas constant, T the temperature, and p_{O_2} the oxygen pressure.

Since the parabolic rate constant is, according to Mott, given by $k_1 = 2\Omega D(n_1 - n_2)$ where n_1 and n_2 are the number of vacancies per cm.^{3} at the oxide–gas and oxide–metal interfaces respectively, and Ω is the volume of the oxide per cation, then

$$k_1 = [2\Omega DN(p_{O_2})^{\frac{1}{6}} \exp(-\Delta G^\circ/3\boldsymbol{RT})]/4^{\frac{1}{3}}$$

where ΔG° is the standard free energy of formation of vacancies.

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[85] Evans, *Trans. Electrochem. Soc.*, 1924, **46**, 247.

[86] Gulbransen, Proc. Gothenburg Conference on Solid State Reactions, 1952.

From Zener's[87] theory of diffusion the diffusion coefficient, D, is related to the vibration frequency, ν, of the lattice, the free energy, ΔG^*, of the diffusion process, and the distance, a, between the jumps by:

$$D = \gamma a^2 \nu \exp(-\Delta G^*/\boldsymbol{R}T)$$

where γ is a constant characterising the nature of the jumps. Thus, the rate constant is given by equation (26)

$$k_1 = 2\gamma a^2 \Omega \nu N(p_{\text{O}_2})^{\frac{1}{6}} \exp[(\Delta S^\circ/3 + \Delta S^*)/\boldsymbol{R}] \exp[-\Delta H^\circ/3 + \Delta H^*/\boldsymbol{R}T] \tag{26}$$

Two metal–oxide systems have been considered in the light of the above theory. For nickel the agreement between the experimentally determined ΔS^*, the entropy of activation of diffusion, and the calculated value is good. With cobalt the agreement is poor, which possibly suggests that the assumed mechanism is not the correct one.

A second model for an oxide assumes it to be composed of macroscopic as well as lattice defects. These macroscopic defects are considered to be pores, cracks, or blisters formed as a consequence of internal stresses in the oxide film. Pilling and Bedworth's rule,[88] which still arouses much discussion, is a consequence of such considerations. It states that an oxidation process will obey a linear law if the oxide occupies a smaller volume than that of the consumed metal. A linear law can also occur if the metal forms an oxide of larger volume than that of the consumed metal, but stress relief results in breakdown of the oxide film. This breakdown may be complete or partial and in the latter case a porous oxide would be formed over a compact oxide film with the result that the rate will be controlled by ionic diffusion which occurs by a defect mechanism in a compact oxide film of constant thickness; hence the linear law. Aylmore, Gregg, and Jepson[89] have recently investigated the porosity of a number of oxides. Metals such as calcium, magnesium, tungsten, and uranium form porous oxides which oxidise at a linear rate, while cobalt and copper form coherent non-porous oxides and obey the parabolic law. A phenomenon which has, as yet, no unambiguous explanation, is that of breakaway. This has been observed during extensive studies[90] of the high-temperature oxidation of magnesium in which a rate process which has been constant for maybe 10 hours or more suddenly accelerates. Cracking and recrystallisation of the oxide, and stress relief, have been suggested as the cause. The exact origin of the stress is uncertain, but factors such as thermal gradients, phase changes at the metal–oxide interface, and differences in thermal expansion of oxide and metal may be important.

Evans[91] considers that "breakdown" of an oxide scale can occur in one

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[87] Zener, *J. Appl. Phys.*, 1951, **22**, 372.
[88] Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 529.
[89] Aylmore, Gregg, and Jepson, *J. Electrochem. Soc.*, 1959, **106**, 1010.
[90] Gregg and Jepson, *J. Inst. Metals.*, 1958, **87**, 187.
[91] Evans, *Trans. Electrochem. Soc.*, 1947, **91**, 547.

of three ways: (*a*) Blistering, which involves detachment of the oxide but no real breakage, may be expected where adhesion is poor and cohesion good. Rectilinear thickening should occur, $\mathrm{d}X/\mathrm{d}t = K_1$, if the cracks in the blister wall admit oxygen to the cavities so that new oxidation starts at the base of each blister; but otherwise it should obey a logarithmic growth law since the outward movement of cations, although aided by rifts normal to the surface, is interrupted by cavity barriers parallel to the surface. (*b*) Shear cracking involving breakage but no detachment, which may be expected where adhesion is good and cohesion poor. This should lead to a rectilinear, a parabolic, or an intermediate growth law. (*c*) Flaking is probably rare and may be considered to be that process likely subsequent to blistering. It involves the separation of the oxide as a flap so that the oxidation should resume at the initial rate.

If the assumption is made that an expression of the form of (27) describes the rate of cracking at an oxide thickness x, where E is the activation energy of the cracking process, then, for a linear growth law, the rate of oxide cracking and formation must be equal. By comparing equations (27) and (7) it is seen that the experimentally determined activation energy is a composite quantity involving the terms F, W, and E.

$$\frac{\mathrm{d}x}{\mathrm{d}t} \propto \mathrm{f}(x)\exp(-E/RT) \tag{27}$$

The ideas of Evans on scaling have been extended, and equation (28) has been derived by Haycock[92] to describe the kinetics of a scaling process:

$$x = \frac{k_\mathrm{p}}{k_1} \ln \frac{k_\mathrm{p}}{k_\mathrm{p} - k_1(x - k_1 t)} \tag{28}$$

where k_p and k_1 are the parabolic and interface reaction rate constants. The interface reaction which depletes the barrier layer may be either vaporisation of the primary reaction product or the formation of a porous scale possibly by crystallisation, grain growth, or mechanical cracking. If vacancies remain at the metal–oxide interface they may coalesce and form cavities; this would ultimately lead to considerable porosity at the interface, which in turn would lead to considerable decrease in contact area. These irregularities should affect the kinetics of the reaction, and Birchenall[93] has developed a number of kinetic equations based on simple models of pore growth at the interface. The ability of porosity to form is thought to be related closely to the plastic properties of both metal and oxide.

A minor constituent present in the metallic phase may influence oxidation in the following possible ways: (1) A new oxide of the minor component is formed on the outer surface, and if cation diffusion is rate

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[92] Haycock, *J. Electrochem. Soc.*, 1959, **106**, 771.
[93] Birchenall, *J. Electrochem. Soc.*, 1956, **103**, 619.

controlling the new oxide layer will influence the oxidation rate. Quarrel[94] has suggested that the oxidation resistance of heat-resisting steels is due to the formation of a stable surface spinel. On the other hand, Wagner[95] has recently shown that if an alloy consisting of two metals, A and B, is oxidised one oxide only may be formed; with alloys rich in A only AO is formed, and with alloys rich in B only BO occurs. At intermediate compositions of the alloy, the formation of an oxide does not correspond to a stable state and therefore the two oxides AO and BO are formed simultaneously. Under these conditions diffusion, and hence oxidation, rates will depend on the spatial distribution of the two oxides in the scale. (2) The effect of substituting ions of valency different from the cations of the parent oxide is to change the cation vacancy and positive-hole concentration and hence the reaction rate. In an oxide containing cation vacancies the introduction of a minor constituent of higher valency than the parent metal will increase the number of vacancies and hence the oxidation rate (Fig. 10). Conversely, in an n-type oxide a minor constituent of lower valency will increase the oxidation rate and one of higher valency will diminish it. The predicted influence of alloying elements on the concentration of vacancies and hence the rate of oxidation is due to Hauffe[96] and is known as the "Valency Rule". Wagner and Ziemens[97] have shown that the addition of chromium to nickel alloys in small concentrations increases the oxidation rate, presumably by increasing the cation vacancy concentration in nickel oxide when some Ni^{2+} ions are replaced by Cr^{3+}. Alloying elements may decrease the oxidation rate of iron above 700° by lowering the composition range of wüstite which constitutes 95% of the oxide scale and therefore most probably is the phase with the greatest natural growth rate. Additional protection could be observed if the alloying element lowers the range of defect concentration in the spinel phase or decreases the ion mobilities. If the mobilities of the cations are sufficiently

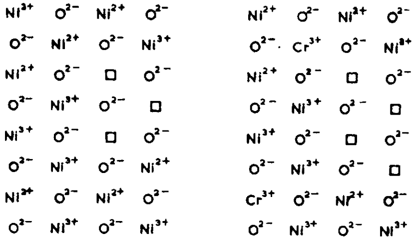

FIG. 10. *The influence of the addition of* Cr^{3+} *on the defect structure of nickel*(II) *oxide.*

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[94] Quarrel, *Nature*, 1940, **145**, 821.

[95] Wagner, *J. Electrochem. Soc.*, 1952, **99**, 369.

[96] Hauffe, *Prog. Metal Physics.*, 1952, **4**, 71.

[97] Wagner and Ziemens, *Acta Chem. Scand.*, 1947, **1**, 547.

decreased a changeover to anion control could occur. (3) If the minor component oxide is incompatible with the parent oxide, embrittlement with subsequent cracking can occur thus leading to a possible "breakaway" reaction. (4) If the alloying element has a greater affinity for oxygen than the solvent metal the minor element may oxidise below the surface oxide in an area where the partial oxygen pressure is too low to cause oxidation of the parent metal. This phenomenon, termed internal oxidation,[98] has been suggested to occur when (*a*) oxygen is soluble in the alloy and is able to diffuse fairly rapidly within the alloy, and (*b*) the minor constituent forms an oxide which is thermodynamically more stable than the parent metal.

It is a pleasure to acknowledge many stimulating discussions with Professor F. C. Tompkins, F.R.S.

[98] Rhines, *Trans. Amer. Inst. Min. Met. Engrs.*, 1940, **137**, 246.