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Oxidative Dissolution of Transition Metals in a Liquid Phase. Role of Oxygen and of the Surface Oxide Layer

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The results of recent studies of the oxidative dissolution of transition metals in a liquid phase are generalised, and an analysis of the role of molecular oxygen and of the oxide film on the metal surface in oxidation processes in donor-acceptor organic media is proposed. The prospects of oxidative dissolution as a direct (single-stage) method of preparation of transition metal complexes are examined. 115 references.

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I. INTRODUCTION

The oxidative dissolution of transition metals in the liquid phase takes place by the reaction

$$M^0 + Ox \xrightarrow[-ne]{mL} L_mM^{n+} + Red + P \qquad (1)$$

where M is the metal, Ox is the oxidiser, L is the complex former, Red is the reduced form of the oxidiser, and P are the products of the interaction between the components of the medium. Oxidative dissolution is an important topic in chemistry and in the chemical industry. It includes problems in catalysis, corrosion, and refining, in the analysis of metals and alloys, in extraction, and in the synthesis of complexes of various types[1]. Many problems in chemical energetics, ecology, and space technology are ultimately determined by metal oxidation processes.

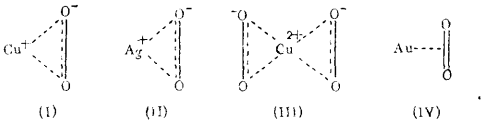
Aqueous media containing inorganic acids, peroxides, and various related composition[2-6] are often used at present for oxidative dissolution. These systems are not always compatible with modern technology, and have some serious limitations (inadequate selectivity, reliance on toxic reagents, etc.). Requirements for non-aggressive and selective processes for the oxidation of metals in the liquid phase are increasing. One promising approach to the development of processes having the required characteristics is the use of non-aqueous media. Unlike the traditional processes in aqueous media, these have not so far been studied in detail.

Interesting influences of dipolar compounds having donor–acceptor properties on the rate and on the direction of chemical reactions have recently been reported: the effects are due to complex formation with organic or inorganic components[7,8]. The use of non-aqueous media allows the choice of a very wide range of donor–acceptor systems and can therefore lead to the development of processes for oxidative dissolution under mild conditions[9].

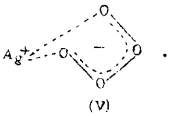
Whether a thermodynamically allowed oxidative metal dissolution process in a liquid phase can be realised, and the rate of the process in practice, are determined by a combination of factors: the nature of the metal and of the oxidiser, the composition of the medium and its donor–acceptor properties, and the state of the metal surface[10]. A real metal surface adsorbs mainly oxygen and water vapour[11]. Therefore an important feature of the process is that it takes place on the surface of an oxide layer. In this review we shall examine the problems arising from the influence of the surface oxide film and of the molecular oxygen on the oxidative dissolution of transition metals in donor–acceptor media, and we shall demonstrate the possibility of the single-stage preparation of transition metal complexes.

II. GAS-PHASE INTERACTION OF MOLECULAR OXYGEN WITH METALS

In order to characterise the interaction between molecular oxygen and a metal surface in a liquid phase, and the type of compound produced by this interaction, we must consider the reaction between metals and oxygen in the gas phase. The atoms of transition metals such as Ni, Cr, Cu, Ag, Au, Pd, Pt, Rh form complexes of the following types with molecular oxygen[12-14]:



Whereas a superoxide anion radical is produced by the interaction of O_2 with Ag and Cu [complexes (I)–(III)], the bond between the oxygen molecule and gold is of the "olefin" type, i.e. the resulting complex (IV) is of the π rather than of the σ type. The possibility of stabilising the bivalent state of the metal leads to the formation not only of $M^+O_2^{\cdot}$ [(I) and (II)] but also of *bis*(dioxygen) complexes such as $Cu^{2+}(O_2^{\cdot})_2$ (III), $Pd^{2+}(O_2^{\cdot})_2$, or in the case of silver (for which this possibility does not exist) we could have the tetra-oxygen complex $Ag^+(O_4^{\cdot})$ (V):



(V)

The formation of complexes of the type of (V) on a metal surface is unlikely for steric reasons. It has been suggested that $AgO_4^{\pm}$ or Ag_2O^{2-} can be formed on a silver surface [i.e. on $Ag(O_2)$(ads)] as a result of the dissociation of the O=O bond[15].

III. LIQUID-PHASE INTERACTION OF MOLECULAR OXYGEN WITH A METAL SURFACE

We have discussed[16] the role of the oxide film on the surface and that of molecular oxygen in the oxidative dissolution of transition metals. Donor–acceptor oxidising systems of two types were studied:

$$\text{DMSO} + \text{RX} \qquad (2)$$

where R = alkyl, H, or CCl_3, and X = Cl, Br, and

$$\text{DMFA} + CCl_4 \qquad (3)$$

In these expressions DMSO is dimethylsulphoxide, and DMFA is dimethylformamide. The system (2), unlike (3), can donate oxygen and thus produce an oxide film on the metal surface:

$$(CH_3)_2SO \rightarrow [O] + (CH_3)_2S.$$

Thus we know that the lower-valency complexes of titanium, molybdenum, and tungsten are effective deoxygenating agents because of the high thermodynamic stability of the M=O bond, and they can reduce $(CH_3)_2SO$ to $(CH_3)_2S$.[17]

We also showed[16] that the metals (M) can be classified into two groups according to their behaviour towards oxidation.

1. Metals which go into solution as complexes of the ionic $[L_pMX_n]_q[MX_m]$ or the neutral type $[L_pMX_m]$. No oxygen is included in these complexes. For the metals in this group, i.e. (Ti), Cr, Mn, Fe, Co, Ni, Cu, (Mo), Rh, Pd, Ag, Cd, (Ir), Pt, and Au, the dissociation energy of the metal–oxygen bond is $E_{MO} < 480$ kJ mole^{-1}.[18] For metals of the first transition series, and also Mo and Re, the rate of oxidative dissolution and the sublimation energy vary in opposite senses.

2. Metals for which the dissociation energy of the M=O bond is $E_{MO} > 480$ kJ mole^{-1} either do not dissolve or go into solution as oxo compounds of the type of $(L_pMO_nX_m)$. This group includes (Ti), V, Zr, Nb, Ru, Hf, Ta, W, (Mo), Re, Os, and (Ir). It was pointed out[18] that the heat of atomisation of O_2 ($E_{OO} = 498.7$ kJ mole^{-1}) lies in this energy range (480–500 kJ mole^{-1}), and therefore a stable M=O bond can be formed in the complexes of these metals.

The mechanism of the oxidative dissolution of the transition metals with the participation of oxygen is extremely complex, and not fully understood[8,9,19,20]. As in the mononuclear complexes of the transition metals with an O_2 molecule we can expect either a labile oxygen-containing molecular complex or a peroxo complex to be formed on the surface[21,22].

The presence of electrons on the oxygen π^* orbitals lowers the bond order in the resulting molecular ions $O_2^{\pm}$ and O_2^{2-}. Accordingly, the distance between the oxygen atoms increases in the series $O_2 < O_2^{\pm} < O_2^{2-}$, and the average energy of the bond decreases[22]. On metals with $E_{MO} \geq E_{OO}$ the states including $O_2^{\pm}$ and O_2^{2-} complexes will have a low stability, and the decomposition of molecular oxygen to form an oxide layer on the surface becomes possible.

The rate of dissolution of metals in the first transition series, and also Mo and Re, in systems (2) and (3) is found to be appreciable. Depending on the energy of the metal–oxygen bond formed on the metal surface by the adsorption of an oxygen molecule in the presence of a donor–acceptor system taking part in the formation of a molecular complex (MC)†, the formation of intermediates and of the final complexes can follow different mechanisms. An analysis of the metal–O_2–MC system has shown[26] that the complex can decompose on the surface either with regeneration of molecular oxygen (if $E_{-O_2-MC} < E_{O=O} > E_{MO}$) or with insertion of oxygen into the products. The formation of a stable oxide ($E_{MO} > E_{MX}$) suppresses this process. Thus, depending on the nature of the metal, oxygen can act as a catalyst (for a number of molecular complexes (MC) in the oxidation of Ag, Au, and Hg with $E_{MO} < 250$ kJ mole^{-1}), as a stoichiometric reactant (for most of the transition metals with $E_{MO} \cong 250$–630 kJ mole^{-1}), and lastly as an oxidative dissolution inhibitor (for Ti, Zr, Nb, Hf, Ta, and W, with $E_{MO} > 630$ kJ mole^{-1}).

We note that under real conditions (i.e. in a medium of coordinating solvents with donor–acceptor properties) dissolved oxygen forms reversible molecular complexes (for example, $C_6H_5N(CH_3)_2.O_2$ with dimethylaniline[27] and $(C_2H_5)_3N.O_2$ with triethylamine[28]), or associations (for example, $(H_2O)_n.O_2$ with water[29]). The energy degeneracy of the π^* orbitals of molecular oxygen is lifted in solution, but not enough for the paramagnetic properties to be lost. In the adsorption of solvated oxygen on the metal surface the splitting of the energy levels of the oxygen may be so large that singlet oxygen is formed: under these conditions changes in spin multiplicity become possible as a result of the change in the magnetic state of the metal atom (or ion)[30]. The transition $O_2(^3\Sigma) \rightarrow O_2(^1\Delta)$, requires an energy expenditure of ~96 kJ mole^{-1}.[31] Singlet oxygen acts as an electron donor towards strong electron acceptors[32], so that the energy consumed in the formation of a solvated molecule of singlet oxygen bound as a complex to the metal surface is compensated by the energy evolved by the addition of one electron to form an anion radical ($O_2 + e \rightarrow O_2^{\pm}$; $\Delta H^{\circ}_{298} = 63$–88 kJ mole^{-1}.[18–33]

The solvated superoxide ion can exist in two resonance-stabilised states: $O_2^{\pm}L \leftrightarrow O_2.L^{\pm}$ (for example $O_2^{\pm}Py \leftrightarrow O_2.Py^{\pm}$).[34] On the other hand, as we have already pointed out, the compounds which we are treating as "solvents" can form molecular complexes or associations (MC) or charge transfer complexes (CTC) with electron acceptors, for example $Py.SO_3$, $Py.Br_2$,[35] and $DMSO.SO_2$.[36]

We conclude from these results that the important role of molecular oxygen in metal oxidation processes reflects the ability of oxygen to interact with both the metal surface and the components of a donor–acceptor system.

IV. ROLE OF THE OXIDE FILM ON THE METAL SURFACE IN OXIDATIVE DISSOLUTION IN THE LIQUID PHASE

1. Formation of an Oxide Film

The electronic structure of the *d* metals is characterised by the presence of collectivised and of localised electrons. The properties of atoms on the surface of the transition metals play an important role in processes such as adsorption and catalysis, and thermo-electron emission.

The asymmetry of the attractive and repulsive forces towards neighbouring atoms of the crystal lattice gives the surface atoms a high reactivity, resulting from the tendency for the field of interaction forces to restore its symmetry. This tendency manifests itself in the formation of additional

† The molecular complexes are of the DMSO.RX and DMFA. $.CCl_4$ type. The formation of MC or associations and in some cases of an ion–radical salt (IRS) stimulated by the activated metal surface cannot be excluded[23–25].

bonds between the surface metal atoms and other atoms or molecules present on the surface. Complex formation on the surface lowers the thermodynamic potential of the system, and it is therefore an energetically favourable and spontaneous process. A study[37] by γ-resonance spectroscopy of the state of iron atoms on a polycrystalline tungsten surface has shown the presence of broken chemical bonds on the metal surface. This must lead to the formation of reactive centres at which relatively stable surface complexes (or even stable chemical compounds) can be formed.

Metal surfaces are covered with a thin layer of oxide (or, in the case of silver, of sulphide), approximately 100 Å thick. Though this layer is too thin to disguise the "metallic" sheen of the surface, there can be no doubt of its presence, and therefore all the processes known to occur on a metal surface have to take place on the surface of the corresponding oxides, which have the properties of semiconductors[38,39]. Only the oxides Au_2O_3, AgO, and Ag_2O_3 are thermodynamically unstable under normal conditions. On the surface of the precious metals gases such as oxygen and hydrogen form adsorption layers[40]. In some cases the heat of adsorption of oxygen at temperatures close to normal (i.e. the oxygen affinity) is higher than the heat of formation of the oxide: it has been suggested[41] that the thermodynamic properties of oxide films of thickness equivalent to one or a few unit cells of the crystal lattice are different from those of the massive oxides, and that the properties of chemisorbed oxygen are similar to those of oxygen in the thin oxides. The distinction between "chemisorbed oxygen" and "phase oxygen" is becoming blurred. Data on the heat of formation of oxides (expressed per mole of oxygen) and on the heat of adsorption of oxygen on various transition metals are given in Table 1.

Table 1. Heat of adsorption (ΔH_{ads}) of oxygen and heat of formation (ΔH) of transition metal oxides (kJ mole^{-2} O_2).[43,44]

Oxide	$-\Delta H$	$-\Delta H_{ads}$	Oxide	$-\Delta H$	$-\Delta H_{ads}$
Ag_2O	61.1	226.1	NiO	489.0	231.9—628.0
PdO	170.8	100.5	FeO	533.4	314.0
PtO_2	58.6	111.0	CoO	479.0	502.4
Cu_2O	333.7	343.3—502.4	WO	854.1	628.0—649.0

Benard[42] has classified all metals into four groups according to their oxygen affinity (ΔH°_{298}, kJ mole^{-1}): 1) $\Delta H^\circ_{298} < 210$ (the precious metals), 2) $\Delta H^\circ_{298} = 210$–550 (Cu, Fe, Ni, Co, ...), 3) $\Delta H^\circ_{298} = 550$–840 (Mn, Cr, Mo, W, ...), 4) $\Delta H^\circ_{298} > 840$ (Ti, Al, Si, ...). Oxides of the metals in the third and fourth of these groups are difficult to reduce.

The most probable configuration of the adsorption layer varies with the type of crystal plane of the metal, depending on the geometry of the lattice and on the number of bonds which can be formed between the metal and the adsorbed molecule. In the limit of the dissociative adsorption of oxygen the position of the adsorption centres is determined by the crystallographic orientation of the surface. On a close-packed surface, for example on the (111) plane of a face-centred cubic metal like Cu, the most stable adsorption centres are directly above the centres of gravity of groups of three adjacent atoms, and not above the atoms themselves[43] (see Fig.1). This important observation shows that coordination interaction can involve several surface atoms (or molecules): in other words, the conditions in this system are conducive to collective interactions.

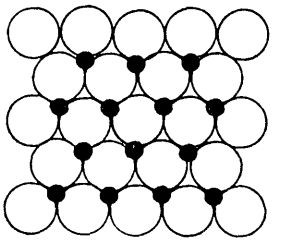


Figure 1. Coordination of the oxygen atoms during the dissociative adsorption of O_2 on the (111) face of a face-centred cubic metal (Cu).[42]

2. Properties of the Oxide Layer

The oxide systems of the transition metals include phases showing substantial deviations from the apparent stoichiometric composition. Typical of these are the homologous series of oxides in which the oxidation number of the metal is not a simple integer[39], for example the titanium oxides[45] Ti_nO_{2n-1} (n = 4–38) and the tungsten oxides[46] W_nO_{3n-2} and vanadium oxides[47] V_nO_{2n-1}, etc., where n is the number of metal atoms in the oxide.

In contrast to the separate amorphous or crystalline oxides, the oxide layers on a metal surface show a number of specific features# when examined as phases in their own right. Near the metal–oxide interface adjacent to the metal surface the oxide has n-type conductivity, i.e. the oxide is non-stoichiometric with an excess of metal. This produces an ohmic contact at the metal–oxide boundary (Table 2), since for most metals the electronic work function is lower than the work function of the oxide. As a result, under thermodynamic equilibrium conditions the oxide layer is enriched with electrons from the metal.

Some of the lower oxide phases of the transition metals, for example TiO,[49] and also the higher oxides of the platinum group metals, for example RuO_2, have a metallic conduction[50]. The possibility and the rate of the oxidation of the metal through the "outer" oxide surface are determined by the difference in work function between the metal and the oxide $\Delta\phi_{OM} = \phi_O - \phi_M$ (where ϕ_M is the electronic work function of the metal and ϕ_O is that of the oxide), and also by the activation energies for conduction (E_C) and for the diffusion of ions (E_d) in the oxide layer.

No direct relationship can be discerned between the $\Delta\phi_{OM}$ values (Table 2) and the ease of oxidation of metals. However, metals for which $\Delta\phi_{OM} \cong 1.0$–2.5 eV and the oxide has an energy gap $W \cong 1$–2 eV (like Mn and Cu) are more readily oxidised than metals with a smaller work function difference ($\Delta\phi_{OM} \cong 0$–1 eV) and a forbidden gap $W > 2$ eV (Ti, W). The relative positions of the energy levels of the metals and oxides are shown in Fig.2.

It has been shown[48] that the lower oxide of iron directly adjacent to the metal and structurally bound to it has a different stability (over thicknesses of the order of a few tens of Å units) than the same oxide in isolation from the metal surface.

Table 2. Physicochemical properties of the transition metal and their oxides[18,51-57].

Compound	φ, eV	$\Delta\varphi_{OM}$, eV	$\Delta H^{\circ}_{f,298}$, kJ mole^{-1}	I, eV	Conductivity*	W, eV
Cu	4.55	—	352.1	7.68	met.	—
Cu_2O	5.15	0.60	—	—	p, (n)	1.85
CuO	5.34	0.79	—	—	p, (n)	2.2
Ag	4.49	—	297.7	7.54	met.	—
Ag_2O	—	—	—	—	p	1.57
AgO	—	—	—	—	p	0.7
α-Ag_2S	—	—	—	—	n, (p)	1.34
Au	5.32	—	354.2	9.18	met.	—
Au_2O_3	5.8	0.48	—	—	n	—
Ti	4.05	—	482.3	6.83	met.	—
TiO	3.1	—0.95	—	—	n, (met.)	0
Ti_2O_3	—	—	—	—	p, (met.)	2.2
TiO_2	4.7	0.65	—	—	n	3.1
V	4.28	—	517.1	6.74	met.	—
VO	—	—	—	—	n, (p)	0.2
V_3O_5	—	—	—	—	n, (met.)	—
V_2O_3	—	—	—	—	n, (met.)	0.3
VO_2	—	—	—	—	n	0.5
V_2O_5	4.1	—0.18	—	—	n, (met.)	0.3
Cr	4.56	—	346.7	6.76	met.	—
CrO	—	—	—	—	p	—
Cr_2O_3	5.9	1.34	—	—	p, (n)	1.9
CrO_2	—	—	—	—	n, (met.)	0.3
CrO_3	—	—	—	—	n	3.2
Mo	4.21	—	672.0	7.35	met.	—
MoO_2	—	—	—	—	p	—
MoO_3	4.25	0.04	—	—	n	2.8
W	4.55	—	868.3	7.98	met.	—
WO_2	4.95	0.40	—	—	n	—
WO_3	4.5	—0.05	—	—	n	2.9
Mn	4.0	—	293.5	7.43	met.	—
MnO	6.5	2.5	—	—	n, (p)	1.25
Mn_2O_3	—	—	—	—	p	0.3
β-MnO_2	—	—	—	—	n	0.3
γ-MnO_2	—	—	—	—	n	0.6
Fe	4.6	—	415.8	7.90	met.	—
FeO	3.85	—0.75	—	—	p, (n)	0.4
Fe_3O_4	—	—	—	—	n, (p)	0.4
α-Fe_2O_3	—	—	—	—	n	1.9
β-Fe_2O_3	—	—	—	—	—	2.1
γ-Fe_2O_3	3.9	—0.70	—	—	n	2.2
Co	4.97	—	451.3	7.86	met.	—
CoO	—	—	—	—	p, (n)	0.8
Co_3O_4	4.9	—0.07	—	—	p	0.9
Co_2O_3	—	—	—	—	n	—
Ni	5.06	—	437.1	7.63	met.	—
NiO	5.55	0.49	—	—	p	1.9
Ni_2O_3	—	—	—	—	n	—
Ru	4.66	—	687.5	7.36	met.	—
RuO_2	—	—	—	—	met.	0.1
Rh	4.76	—	593.3	7.46	met.	—
Rh_2O_3	—	—	—	—	—	—
RhO_2	—	—	—	—	met.	—
Pd	4.98	—	400.3	8.33	met.	—
PdO	—	—	—	—	—	0.04
Os	4.55	—	749.8	8.7	met.	—
OsO_2	—	—	—	—	—	—
Ir	5.0	—	710.1	9.2	met.	—
IrO_2	—	—	—	—	met.	—
Pt	5.42	—	524.6	8.96	met.	—
PtO	—	—	—	—	—	—
Pt_3O_4	—	—	—	—	—	—
PtO_2	—	—	—	—	n	—

Symbols: ϕ is the work function, $\Delta H^{\circ}_{f,298}$ is the sublimation energy, I is the ionisation energy, W is the width of the forbidden energy gap, and met. denotes metallic conduction. *The brackets denote a conductivity type not confirmed independently.

In general the rate-limiting step in the oxidation of metals whose oxides are electronic conductors is the breaking of bonds in the crystal lattice of the metal. If the oxide has a mixed (ionic–electronic) or an ionic conduction (as in Nb, Ta, and Zr) the transport of electrons through the oxide layer can be rate-limiting. Unfortunately, very little information is available on the activation energies for conduction and self-diffusion of metal ions in oxides containing metals in different states of oxidation.

Activation energies for conduction and metal diffusion in oxides measured at high temperatures are listed in Table 3. We can distinguish the group of electronic semiconductors (the oxides of Mn, Fe, Co, Ni, Cu) for which the activation energy for conduction is $E_{\sigma} < 83.7$–125.6 kJ mole^{-1} and the activation energy for the diffusion of the cation is $E_d < 210$ kJ mole^{-1}. Metals of this group show the characteristic relationship between the rate of oxidative dissolution and the sublimation energy of the metal[16]. In the case of the electronic semiconductors TiO_2, WO_3, and Ta_2O_5 and of the semiconductors of mixed or ionic type Nb_2O_5 and ZrO_2, which have relatively high values of E_{σ} (>83.7–125.6 kJ mole^{-1}) and of E_d (>209.3 kJ mole^{-1}), the oxidation of the metal is slow[16].

The stability of the oxide formed on the metal surface towards the replacement of oxygen by another counter-ion (for example, Cl^-) generated by electron transfer from the metal to the components of the donor–acceptor medium plays an important role in the oxidative dissolution of metals. Obviously, if the stability of the oxide is higher than that of the corresponding chloride (allowing for the effects of complex formation on the surface and in the solution) the dissolution will be suppressed.

Table 4 gives the standard heats of formation ΔH°_{298} of the chlorides and oxides of some transition metals. We note that the metals can be divided into two groups with respect to the relative stability of the corresponding oxides and chlorides (for the same degree of oxidation):

1) Co(III), Mn(IV), Cr(III), Fe(III), Mo(IV, VI), Ti(III, IV), V(III, IV, V), W(VI), Nb(V), Ta(V), Zr(IV), Rh(I, III), and Ru(IV) (chlorides less stable than oxides);

2) Ag(I), Au(I, III), Co(II), Ni(II), Mn(II), Pd(II), Cr(II), Fe(II), and V(II) (chlorides more stable than oxides).

The importance of the relative stability of the lower and the higher chlorides and oxides should be stressed. During the transfer of an electron from the metal to the oxide surface the metal ions in the oxide are reduced, and the stability of the oxides of the first group of metals decreases ("destabilisation" of the oxide layer): this improves the conduction properties of the layer, and the reactions leading to the formation of metal chlorides and their complexes become energetically preferred. If atmospheric oxygen is present in the system the degree of oxidation of the metal in the oxide layer increases, and the rate of formation of chlorides or oxide chlorides decreases. Under these conditions the rate of the oxidative dissolution process can be a function of the rate of the relevant rate-limiting step: either the supply (by diffusion) of oxygen to the surface or the dissolution of the oxide in the liquid phase containing chloride ions.

For the metals in the second group the characteristic reaction is the replacement of oxygen by chlorine: "stabilisation" of the oxide layer is produced by the oxidation of the metal ions by oxygen in the oxide layer, i.e. by the formation of higher oxides. This lowers the rate of the oxidation. The addition of oxygen to the donor–acceptor system suppresses the reaction in the first case and assists it in the second[9,16].

We note that the rate of dissolution of oxides depends less on the concentration of oxidiser than on the nature and concentration of the complex-forming ligand. For example, in spite of the relatively low concentration of proton oxidiser, the rate of dissolution of BeO is much greater in oxalic acid than in hydrochloric acid[66].

3. The Oxide Layer on the Surface of a Transition Metal as a Carrier of Electrons from the Metal to the Acceptor

Compounds of the transition metals such as the oxides have a characteristic valence band due to metal ions in an intermediate state of oxidation, for example M^{2+}, and not to O^{2-} ions, since the M^{2+} level is 5–8 eV higher than the O^{2-} level. In these compounds holes are formed more readily in the high

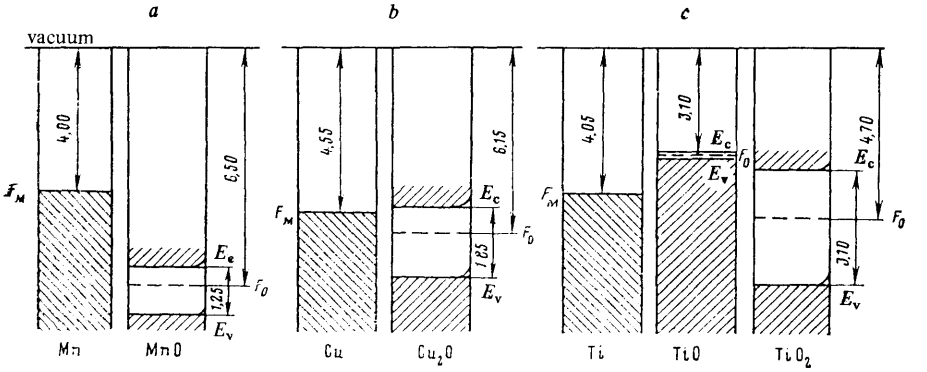


Figure 2. Energy level diagram (eV) for metals and their oxides: *a*) Mn/MnO, *b*) Cu/Cu_2O, *c*) $Ti/TiO/TiO_2$;[51-57] F_M and F_0 are the Fermi levels in the metal and the oxide, E_v and E_c are the edges of the valence and of the conduction band.

M^{2+} level or in the V'_M or V''_M levels (where V'_M and V''_M are vacancies with a negative and a double negative effective charge respectively). In any case, the emission of electrons from the M^{2+} level in transition metals[67] has an energy advantage equal to double the quantity $\Delta E_{OM} = E_O^{2-} - E_M^{2+}$. Thus, since the oxygen 2*p* band in transition metal oxides lies below the valance band of the metal, the first possible electron transition to give a polar state is (for nickel, say) from the Ni^{2+} ($3d^8$) to the Ni^+ ($3d^9$) band by the reaction[68]

$$Ni^{2+} + Ni^{2+} + h\nu \rightarrow Ni^{3+} + Ni^+ \qquad (4)$$

This transition is dipolar, and allowed by the selection rules[69], since it is from a $^3F(3d^8)$ to a $^2D(3d^9)$ state. On the other hand a transition from the $O^{2-}(2p^6\,{}^1S)$ to the $Ni^+(^2D)$ band is either forbidden by the selection rules or (if treated as quadrupolar) it should have a much lower intensity[70].

Whereas reduction of a non-transition metal (M^{3+}) causes electrons to appear at the M^{2+} level, and oxidation produces holes in the O^{2-} band, in the oxides of transition metals (for example, in magnetite, Fe_3O_4) both processes are accommodated in the M^{2+} band, which is half-filled.

Table 3. Activation energies for conduction (E_σ) and for diffusion (E_d) of cations in metal oxides (kJ mole^{-1}).

Metal oxide	E_σ	E_d
TiO_2 [57]	106.3÷152.8	257.1
V_2O_3 [57]	31.0	—
V_2O_5 [57]	19.3÷96.7÷28.9	—
Cr_2O_3 [57]	19.3÷154.5÷47.3	—
CrO_2 [57]	19.3	—
MnO [58]	35.6	125.6÷146.5
Mn_3O_4 [57]	56.1	—
MnO_2 [57]	28.9	—
FeO [57]	32.7	—
Fe_3O_4 [59]	7.5÷28.9÷19.3	124.3
CaO [60]	64.9÷28.9	144.4÷160.8
NiO [61]	90.0; 75.4	182.1
Cu_2O [62]	15.5÷24.3; 25.1÷33.5	151.1
CuO [57]	67.8	—
WO_3 [57]	57.8; 159.1	—
ZrO_2 [63]	—	—
Nb_2O_5 [64]	125.6÷159.1	—
Ta_2O_5 [65]	209.3	—

Notes: The width of the forbidden gap is 2.0 eV for ZrO_2 and 2.2 eV for Nb_2O_5,[57] with mixed conductivity; the energy gap for Ta_2O_5 is 3.6 eV.[57]

Table 4. Standard heats of formation ΔH°_{298} (kJ mole^{-1}) of the chlorides and oxides of the transition metals.

Chlorides	$-\Delta H^\circ_{298}$	Oxides	$-\Delta H^\circ_{298}$
AgCl	127.0	Ag_2O	30.6
—	—	(Ag_2S)	29.3
AuCl	35.2	—	—
$AuCl_3$	118.5	Au_2O_3	−80.9
$CoCl_2$	325.7	CoO	239.5
—	—	Co_3O_4	879.2
CuCl	134.8	Cu_2O	166.6
$CuCl_2$	206	CuO	155.3
$NiCl_2$	316.1	NiO	244.5
$MnCl_2$	482.7	MnO	388.5
—	—	MnO_2	521.3
$PdCl_2$	190.1	PdO	85.4
$CrCl_2$	395.9	CrO	272.1
$CrCl_3$	563.5	Cr_2O_3	1129.2
$MoCl_4$	479.8	MoO_2	589.5
$MoCl_5$	529.6	—	—
$MoOCl_4$	644.8	MoO_3	754.9
MoO_2Cl_2	724.3	—	—
$FeCl_2$	341.2	FeO *	266.7
$FeCl_3$	405.3	Fe_3O_4 **	1117.9
$TiCl_3$	714.7	TiO	525.0
$TiCl_4$	800.5	Ti_2O_3	1519.0
$TiOCl_2$	765.3	TiO_2 ***	941.6
VCl_2	452.2	VO	427.5
VCl_3	573.6	V_2O_3	1256.0
$VOCl_3$	720.1	V_2O_5	1561.1
VCl_4	577.8	V_3O_5	1574.2
WCl_5	573.6	WO_2	570.7
WCl_6	682.5	WO_3	840.9
WO_2Cl_2	837.4	—	—
$WOCl_4$	745.3	—	—
$NbCl_5$	798.0	Nb_2O_5	1904.2
$NbOCl_3$	880.1	—	—
$TaCl_5$	862.5	Ta_2O_5	2046.5
$ZrCl_4$	963.0	ZrO_2	1081.0
RhCl	67.0	RhO	90.9
$RhCl_3$	234.5	Rh_2O_3	286.0
$RuCl_3$	205.2	RuO_2	305.6

*Wüstite.
**Magnetite.
***Rutile.

From these considerations we can formulate the main features of the oxidation of transition metals in the liquid phase with allowance for the catalytic role of the oxide film in the transfer of an electron from the metal to the oxidiser.

1. The oxide film on the metal surface acts as a catalyst§ for the oxidation of a transition metal in the liquid phase. Metal ions in the oxide film are reduced by the electrons flowing from the metal under the influence of the oxidiser¶ adsorbed on the surface. The adsorption of oxygen on the surface of a thin oxide layer produces a negative charge in the film. The outer surface of the oxide receives electrons both from the bulk of the film and from the metal, and the metal acquires a positive charge relative to the film[71]. Transition metals in a lower state of oxidation show a characteristic tendency to form metal–metal bonds, especially in the lower halides and oxides of Nb, Ta, Mo, W, and Re, though at least one such compound is known for every element of the *d* group[72]. We may assume that electron transfer is produced either by the formation of clusters in the lattice of transition-metal lower oxides containing M–M bonds with an energy similar to the bond energy of the transition metal lattice[73], or through the 2*p* band of the oxygen sublattice, which allows continuous exchange of electrons between the iron ions through the oxygen ions[74].

2. A metal atom incorporated into the crystal lattice loses enough electrons to convert it into its stable lower state of oxidation, for example

$$Cu^0 - e \rightarrow Cu^I; \quad Fe^0 - 2e \rightarrow Fe^{II}.$$

3. As a result of the donor–acceptor properties of the complex on the surface the reduction of the metal ions in the film is accompanied by a stimulated, synchronous transfer of electrons to the conduction band, yielding a pair of metal ions in states of oxidation differing by two units [see Eqn.(4)].[67,75] Since the postulate of a purely ionic bond in transition metal oxides is only a rough approximation we cannot exclude the interaction between the oxidiser and a virtual Mott exciton as the mechanism of this process. The formation of ions in different states of oxidation at very short distances apart may be equivalent to the formation of an active centre (which consists of a number of pairs of these ions, i.e. a cluster)[76].

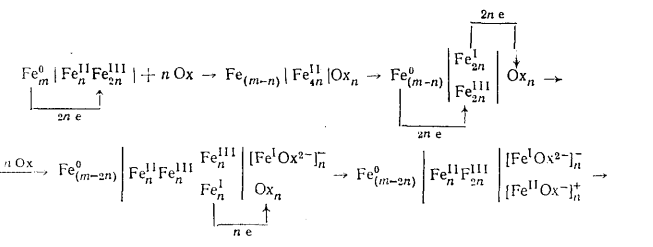
4. Stabilisation of the excited state of the ions (or ion) is obtained by the transfer of one or two electrons from the surface of the oxide layer to the oxidiser, and depends on the nature of the latter (one-electron or two-electron acceptor).

5. Stabilisation of the counter-ions takes place through the formation of neutral complexes (for example, $[M^{n+}Ox_n^-]^0$, $[M^{2n+}Ox_n^{2-}]^0$), or of an ionic complex of the type $[M^{n+}Ox_{(n-m)}^-]_p^{m+} \cdot [M^{n+}Ox_{(n+p)}^-]_m^{-p}$ in the solvated state, which assists the diffusion of the complex into the solution.

6. Diffusion of an oxidised metal ion into the solution in the form of a neutral complex takes place when the stability of the complex is higher than the stability of the oxide on the surface, since this process requires the breaking of M–O bonds and formation of new M–Ox bonds.

7. Saturation of the free valencies of the oxygen atoms on the surface takes place through the diffusion of metal ions along vacancies in the layer by the replacement pressure ("crowdion") mechanism[77].

According to the proposed mechanism, the oxidation of metals can be described by the following scheme (in which the metal is a two-electron donor, iron (Fe^0), the oxidiser is a one-electron or two-electron acceptor, and the vertical lines denote the boundaries of the oxide phases):



In this process the oxidised state of the layer is regenerated. The scheme allows the formation of univalent iron, stabilised in an ionic complex by bivalent iron.

Evidently, further oxidation of the complex can take place in solution. However, further oxidation on the surface is also possible, giving Fe(II)–Fe(III) iron complexes of different valency in which the stabilisation of the bivalent iron[10] depends on the donor–acceptor properties of the solvent included as a ligand in the complex cation (for example, $[Fe^{II}(CH_3CN)_6].[Fe^{III}Cl_4]_2$) or in the complex anion (for example, *cis*-$[Fe^{III}Cl_2(DMSO)_4]_2[Fe^{II}Cl_4]$).

As the scheme shows, the active centre on which the oxidation takes place contains at least two metal atoms (or ions).

Inspection of the catalytic properties of oxide layers of the transition metals in the light of the above mechanism reveals the possibility (in principle) of selective oxidation of the transition metals. The basis of the selective oxidation process is the requirement of complementarity of the reaction† *with respect to the active centre*, i.e. the retention of the one- or two-electron mechanisms for the electron transfer to the oxidiser, irrespective of the number of electrons removed in the stabilisation of an atom from the crystal lattice of the metal. The realisation of this process depends on the properties of the complex on the metal surface (or on those of the oxide layer), i.e. on the possibility of redistributing the electron density in the surface complex by transferring one or two electrons. This redistribution leads to the decomposition of the complex, giving oxidised forms of the metal in solution in a lower state of oxidation than the ions on the metal surface (for example, those in the oxide layer). Several examples consistent with this interpretation of the role of the film on the metal surface can be quoted.

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§ We shall use the term "catalyst" to denote a compound formed on the surface from the metal ion newly created in the oxidation process and from the O^{2-} ion set free, so that the "composition" of the compounds on the surface stays constant but its constituent metal ions are replaced.

¶ The term "oxidiser" (Ox) refers to a complex (or association) between the components of a donor–acceptor system in the liquid phase, for example $(DMFA)_n(RX)_m$.[23,24]

† A reaction is called complementary or non-complementary depending on whether the oxidation states of the oxidiser and of the reducer change by the same amount. The complementarity (or electronic correspondence) principle states that the replacement of a non-complementary by a complementary process leads to a faster reaction[78,79].

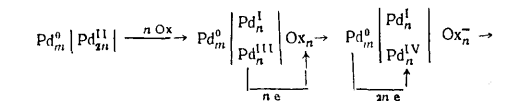
A study[80] of the cathodic reduction of oxide layers on an iron surface has shown that the outer layer of oxide contains ions in a higher state of oxidation, and that its oxygen content is higher than the stoichiometric composition Fe_2O_3 (oxide with an excess of cation vacancies).

We also know that the removal into an acid medium of the higher-valancy oxide from an iron surface involves the reductive dissolution rather than the direct dissolution of hematite and magnetite. A study of the solubility of the oxide Fe_2O_3 showed[81] that the direct action of acid on this oxide is slow, and gives Fe^{2+} ions in solution, though the oxide formally consists of Fe_2O_3. In a short-circuited model cell consisting of Fe_2O_3 and Fe^0 the iron was found to be the anode, and the oxide the cathode. Under these conditions the transfer of an electron from the metal to the oxide leads to the formation of structure defects of Fe^{3+} in the oxide lattice (i.e. to an increased concentration of Fe^{2+}). The appearance of Fe^{2+} ions upon dissolution of an oxide containing only Fe^{3+} is explained by assuming that the dissolution is confined to the structure defects. This explanation is consistent with our mechanism of electron transfer from the metal to the oxidiser through a layer of oxide.

It has been shown[82,83] that the transfer of an ion from the surface to the solution is assisted by a decrease in its valency. In the dissolution of precious metals in the presence of strong-field complexing ligands (for example, the dissolution of gold by the cyanide method with oxygen as the oxidiser, see p.12 of Ref.48) a layer of intermediate products is formed (mainly, the thermodynamically unstable[48] higher oxide of gold(III), Au_2O_3), and the cyanide complex of univalent gold goes into solution[2]. The thickness of this layer varies from 100 (on silver) to 1000 conventional monolayers (on copper), and depends on the concentration of cyanide and oxygen, on the rate of stirring, and on the temperature and duration of the reaction. It has been stressed[82,83] that the exact mechanism of action of these films is not understood, though their permeability to oxygen has been established. The rate of dissolution of the film itself plays an important part in the metal oxidation process.

A dynamic equilibrium is created on the surface, and the film adopts a constant thickness, depending on the conditions of the reaction[84].

The complementarity of the oxidation process with respect to the active centre which we have postulated can be further tested by considering the oxidation of a platinum group metal in which the metal is a two-electron donor (palladium) and the oxidiser is a one-electron acceptor:



As a rule the oxidation of Pd^0 with a two-electron acceptor produces a slower reaction, despite the fact that Pd^0 is a two-electron donor. The reaction follows a one-electron mechanism because the active centre formed on the surface is a one-electron donor.

The above considerations lead to the conclusion that the oxidation can be accelerated by adding to the system a compound able to act simultaneously as a one- and two-electron oxidiser and reducer[79]. Thus a much faster reaction is obtained by adding to the oxidation–reduction system a catalytic carrier which converts the one-electron electron-transfer mechanism into a two-electron mechanism (catalytic carrier, copper and iron ions (M); oxidiser, molecular oxygen)[85,86]:

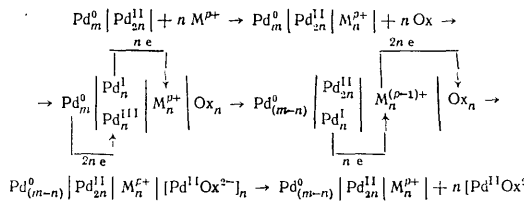


Table 5. Characteristics of electron transfer from a metal through an oxide layer to an oxidiser.

Surface reaction	Number of electrons*				E/E'	$\Delta E_i = E_i - E_i'$	Optimum conditions ($\Delta E_i < 0$)	Element	E_i/E_i'	ΔE_i, eV
	M^0	M^n	M^{n-1}	Ox						
$M^0 + 2M^n \rightarrow M^{2+} + 2M^{n-1}$ (5)	2	1	2	2	$\frac{W + I_0 + I_+ + I_{n-2} - I_{n-1}}{I_0 + I_+}$	$W + I_{n-2} - I_{n-1}$	$W < I_{n-1} - I_{n-2}$	Fe	$\frac{W + 9.7}{24.1}$	$W - 14.4$
$M^0 + M^n \rightarrow M^{2+} + M^{n-2}$ (6)	2	2	2	2	$\frac{W + I_0 + I_+ + \frac{1}{2}[I_{n-2} + I_{n-3}]}{I_0 + I_+ + I_{n-2}}$	$W + \frac{1}{2}[I_{n-3} - I_{n-2}]$	$W < \frac{1}{2}[I_{n-2} - I_{n-3}]$	Fe	$\frac{W + 36.15}{40.3}$	$W - 4.15$
$2M^0 + M^n \rightarrow 2M^+ + M^{n-2}$ (7)	1	2	1	1	$\frac{W + 2I_0 + I_{2+} - I_{n-1} + I_{n-2}}{I_0 + \frac{1}{2}[I_+ + I_{2+} - I_{n-1} - I_{n-2}]}$	$W + I_0 + \frac{1}{2}[I_{2+} - I_0 - I_{n-1} - I_{n-2}]$	$W < \frac{1}{2}[I_+ + I_{n-1} + I_{n-2} - I_{2+}] - I_0$	Au	$\frac{W - 2.1}{9.2}$	$W - 11.2$
$M^0 + M^n \rightarrow M^+ + M^{n-1}$ (8)	1	1	1	1	$\frac{W + I_0 + \frac{1}{2}[I_{n-1} - I_{n-2}]}{I_0}$	$W + \frac{1}{2}[I_{n-1} - I_{n-2}]$	$W < \frac{1}{2}[I_{n-2} - I_{n-1}]$	Au	$\frac{W + 13.95}{9.2}$	$W + 4.75$

Symbols: I_0 is the ionisation energy (eV) of the neutral unexcited atom by the reaction $M^0 \rightarrow M^+ + e$; I_+ is the ionisation energy (eV) of the singly charged (positive) unexcited metal ion by the reaction $M^+ \rightarrow M^{2+} + e$; $I_{(n-1)}$ is the ionisation energy (eV) of the unexcited metal ion with $(n - 1)$ positive charges by the reaction $M^{n-1} \rightarrow M^{n-2}$; W is the width of the forbidden energy gap (eV); E is the energy required for the electron transfer process with allowance for the formation of an electron–hole pair; E' is the same energy without the correction for the formation of an electron–hole pair.
*The numbers of electrons taking part in the catalytic process in the oxide layer are shown; M^0 is the metal (electron donor), M^n is the metal ion (electron acceptor), M^{n-1} is an active centre (electron donor), Ox is the electron acceptor in the liquid phase.

4. Role of the Surface Oxide Film as an Intermediate Electron Trap

The role of the surface as a direct participant in a chemical reaction, and in particular the metal oxidation reaction, includes the provision of a site for the localisation of free current carriers and excitons, since the Madelung constant (μ) on the surface is smaller than in the bulk, and therefore an electron–hole pair (or exciton) has a lower energy on the surface. In the case of an ionic cubic lattice we have $\mu = 1.74$ for the bulk and $\mu = 1.68$ for the surface, which is the cause of excition transport from the surface[87].

It can be shown that the oxidation of a metal covered with a layer of a semiconducting compound of variable composition and containing ions of the metal in different states of oxidation (e.g. an oxide) is energetically more favourable if it takes place through the formation of an electron–hole pair than by direct oxidation without preliminary excitation of the atoms (or ions). If all the other conditions stay the same (composition of the oxidation–reduction medium, composition of the layer on the metal surface, Madelung energy) two alternative paths are available for the oxidation of iron.

1) Oxidation through the formation of an electron–hole pair (in the case of a two-electron mechanism for the transport of electrons to the oxidiser):

a) reduction of Fe_3O_4 to FeO

$$Fe^0 + 2Fe^{3+},\ (Fe^{2+}) \rightarrow 3Fe^{2+},\ (Fe^{2+}) + E_v$$
$$E_v = I_0 + I_+ - 2I_{2+} = 7.9 + 16.2 + 2 \cdot 30.6 = -37.1\ \text{eV}$$

b) formation of an electron–hole pair

$$2Fe^{2+} \rightarrow Fe^+ + Fe^{3+} + W\ ,$$

where W is the width of the forbidden energy gap for FeO (Fe_3O_4) = 0.4 eV (see Table 2)

c) oxidation of Fe^+

$$Fe^+ \rightarrow Fe^{3+} + 2e + E_{OC}$$
$$E_{OC} = I_+ + I_{2+} = 16.2 + 30.6 = 46.8\ \text{eV}\ .$$

The total energy requirements of the first path are

$$E = E_v + W + E_{OC} = -37.1 + 0.4 + 46.8 = 10.1\ \text{eV}.$$

2) Oxidation without formation of an electron–hole pair, replacing the two-step process (b), (c) by the oxidation of two Fe^{2+} ions:

d) $$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e + E'_{OC}$$
$$E'_{OC} = 2I_{2+} = 2 \cdot 30.6 = 61.2\ \text{eV}$$
$$E' = E_v + E'_{OC} = -37.1 + 61.2 = 24.1\ \text{eV}\ .$$

The gain in energy $\Delta E = E - E'$

$$\Delta E = 10.1 - 24.1 = -14.0\ \text{eV}.$$

In idealised limiting cases of oxidation in the absence of oxygen and of an oxide layer on the metal surface, or of a rate of dissolution of the oxide layer in the donor–acceptor medium greater than the rate of oxidation of the metal, the complex formed by the components of the liquid phase with the surface atoms of the metal can also be a catalyst for the oxidation process if it can be treated as a semiconductor. We can assume that the lower the activation energy for conduction and the energy gap in the complex, the more marked will be the catalytic effect.

Calculated values of the energy required for the electron transfer process in the film on a metal surface are shown in Table 5 for a one-electron (e.g. Au^0) and a two-electron donor metal (e.g. Fe^0), without allowance for the electron affinity of the oxidiser or for the solvation energies of the initial and the final products, which are assumed constant.

If the metal ions present in the film in a higher state of oxidation act as one-electron acceptors [for example, according to reaction (5)] the energy gain for iron (with $W = 0.4$ eV) is 14 eV.

If the metal ions in a higher state of oxidation act as a two-electron acceptor in the film [for example, by reaction (6)] the energy gain for iron becomes (W – 4.15) eV. Since $W \leq 3$ eV for semiconductors, in this case the energy gain is >1 eV. Comparing the electron transfer systems (5) and (6), assuming in both cases the formation of electron–hole pairs, we conclude that the first path offers an energy advantage:

$$\Delta E_{1,2} = E_1 - E_2 = {}^1/_2(I_{n-2} - I_{n-3}) - I_{n-1}\ .$$

For iron $\Delta E_{1,2} = -26.45$ eV, i.e. the one-electron reduction of the metal ion in the higher state of oxidation is preferred in this case. A similar analysis for gold suggests that reaction (7) is preferred to reaction (8) as an electron transfer path ($\Delta E_{3,4} = -16.05$ eV), whereas for a process not involving the formation of an electron–hole pair the two reactions are energetically equivalent ($E'_3 = E'_4$)#.

Our analysis justifies the following conclusions.

1) The transfer of an electron from the metal to the oxidiser through the surface film is energetically more favourable (if the film has semiconductor properties) than the "normal" transport process found in oxidation–reduction reactions in the liquid phase.

2) the most favourable process in terms of energy is the transfer of an electron through a layer of oxide with a very small decrease in the degree of oxidation of the metal ions in the layer [Table 5, Eqns.(5), (6), and (7), (8)].

V. ROLE OF SURFACE DEFECTS

A real surface differs from an idealised surface by perturbations in the periodicity of the structure, i.e. by the presence of surface defects[88]. The defects can participate directly in surface processes, since they can act as centres for the coordination of the components of the donor–acceptor medium. Vacancies in the cation sublattice may also play a part in the formation of electron–hole pairs by the quasi-chemical equation

$$V^0_M + V''_M \rightleftarrows (V'_M, h)^{\cdot} + (V'_M, e)'' \rightleftarrows 2V'_M + h + e$$

where V^0_M, V'_M, and V''_M are vacancies with a zero, a negative, and a double negative effective charge.

Transition metals containing *d* electrons and able to transfer electrons reversibly form characteristic associations (or complexes) of defects of the same kind because the attractive forces arising from quantum-mechanical exchange interaction are large enough to overcome the elastic and Coulombic interactions.

In the non-stiochiometric lower oxide of iron the holes, which are localised on iron ions as Fe^{3+}, can interact with the cation vacancies bearing an effective negative charge. This interaction leads to the formation of a composite complex defect: an interstitial ion bound to two vacancies, $[V'_{Fe}Fe^{3+}V''_{Fe}]'$. A complex with this configuration is more stable than the simple vacancy; it is a structure element of the phase $Fe_{3-y}O_4$ into

For gold $I_+ + I_2 - I_{n-1} - I_{n-2} = 0$ (see Table 5).

which $Fe_{1-y}O$ is converted when the critical metal deficit is exceeded. In these oxides the defects show long-range order, and the electrical conductivity is abnormally large (125 $Ohm^{-1}\,cm^{-1}$).[89] It has been suggested[90] that under these conditions the conductivity is due to the exchange of electrons between two adjacent iron ions (Fe^{2+} and Fe^{3+}). Evidently, analogous effects are possible in other oxide phases with a metal defect, $[M_{1-y}O]$, which include oxides with structure defects of the cation vacancy type[77] such as MnO, NiO, and Cu_2O.

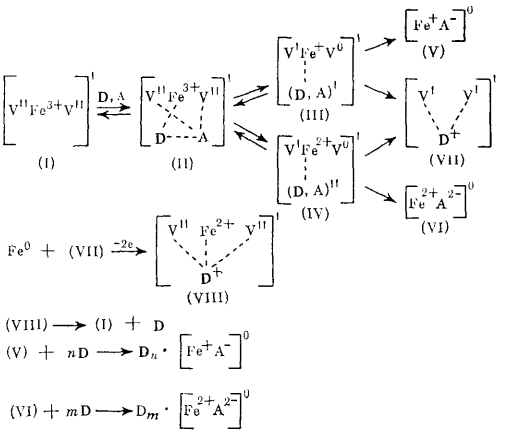
It has been shown that the active dissolution of iron covered with FeO involves an increase in the non-stoichiometry of the surface oxide and an increased concentration of surface defects: anion vacancies (Fe^{II} ions) and free electrons. Photoelectric polarisation measurements have established that the passivation of iron, copper, and silver is accompanied by changes in the surface oxide towards a stoichiometric composition, and by a decrease in the concentration of non-stoichiometric defects[88].

Experimental data[91,92] indicate the formation of the anion radicals ($Ox^{\dot{-}}$) on the surface of metal oxides in the presence of acceptor molecules (O_2, SO_2, quinones). However, complex formation takes place mainly on charged surface defects (negatively ionised cation vacancies) rather than on ordinary lattice atoms, The assumption of charge transfer from an ionised defect to a molecule of the oxidiser is confirmed by the formation (for example, with benzoquinone or fluoranil) of charge-transfer complexes (CTC) of the same structure on both typical semiconductor (Ge, TiO_2, ZnO) and typical insulator surfaces (MgO, Al_2O_3).[93,94] For donor molecules the most probable coordination is on ordinary lattice atoms and on ions in interstitial sites.

Donor molecules (for example, triphenylamine) form cation radicals when adsorbed on zeolite surfaces, and acceptors such as tetracyanoethylene, trinitrobenzene (TNB), and *m*-dinitrobenzene form anion radicals. It is interesting to note that previous adsorption of donors (anthracene and perylene) on the zeolite causes a ten-fold increase in the number of TNB anion radicals as compared with the adsorption of TNB on a fresh zeolite surface[95]. Under these conditions an additional TNB anion radical is formed for every three anthracene or perylene cation radicals. This effect can be explained by the cooperative interaction of vacancies on a solid surface[95]. The adsorption of SO_2 and benzene leads to the formation of the corresponding ion radicals, i.e. $SO_2^{\dot{-}}$ and $C_6H_6^{\dot{+}}$. The adsorption of one oxygen molecule produces one perylene cation radical, but $O_2^{\dot{+}}$ is not formed under these conditions. We interpret this as evidence of the cooperative nature of the interaction on the solid surface, since additional electron transport from the donor to the surface without involving an acceptor suggests a surface with a high capacity for electrons and controllable donor–acceptor properties.

Evidently, the formation of surface complexes in a donor–acceptor medium leads to electron transfer from the negative pole of the resulting dipolar MC (or CTC) to an ordinary lattice atom or ion, and from the vacancies to the positive end of the dipole. The formation of this coordination bond is accompanied by substantial changes in crystal field, with corresponding changes in the parameters of the defects, causing localisation of free carriers on the defects closest to the molecules held by coordination forces. This influences the strength of the bonds and the distortion in the complex, and weakens the intramolecular bonds of the MC. As a result of this coordination and collective interaction effect the localisation of holes near a metal ion in the lower state of oxidation and the emission of the ion from the surface into the liquid phase can take place within a unified quantum-mechanical system.

The participation of surface defects in complex formation with the oxidised form of the metal can be described (in the case of iron) by the following scheme:

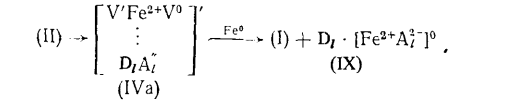


In step (9) the complex (II) is formed on the surface. It includes the components of the oxidation–reduction system (the donor D and the acceptor A), the metal ion, and defects with double negative charges. This is followed by redistribution of the charge density in the complex, in which the charge on the active centre is retained. In the ground state the two components of the complex are bound by ion–dipole, hydrogen, and dispersion forces, and also (to a small extent) by electrostatic and covalent forces arising from electron transfer from DA to the metal. This transfer is largely determined by the electronegativity of the metal and also by the donor–acceptor properties and by the polarisability of the components of the medium (strictly speaking, of their associations) involved in complex formation on the surface. Depending on the relative stability of the complexes (III) and (IV), and on the donor–acceptor properties of DA, neutral complexes of univalent and of bivalent iron [(V) and (VI)] will diffuse into the solution. This stabilises the cation vacancy complex (VII) containing a positively ionised molecule of the donor [step (9)]. Two-electron transfer from a metal atom to the complex (VII) causes the donor to be transferred to the solution [steps (10) and (11)] and regenerates the active centre I.

This scheme ignores the redistribution of electron density in the complex on the surface, which can lead to a weakening of the intramolecular bonds and to the ejection of fragments of the donor (D_f) and of the acceptor (A_f) by the reaction

$$(II) \rightarrow D_f + A_f. \qquad (12)$$

Reaction (13) brings into the solution the complex (IX) between the metal and the decomposition products of the oxidation–reduction system:



The reaction

$$(II) \rightarrow (IVa) \rightarrow (I) + D_I + A_I \qquad (14)$$

causes catalytic conversion of the components of the donor–acceptor system: in other words, the metal surface can stimulate (or accelerate) the interaction between D and A with

formation of the fragments D_f, D_l, A_f, and A_l. This reaction path does not lead to oxidation of the metal, and may even suppress it.

The possibility of controlling the direction of the interaction between a metal surface and the components of the liquid phase offers a real prospect of achieving selective oxidation of the transition metals.

VI. PROSPECTS OF OXIDATIVE DISSOLUTION AS A DIRECT METHOD OF SYNTHESIS OF TRANSITION METAL COMPLEXES IN THE LIQUID PHASE

The traditional methods of dissolving transition metals in a liquid phase, which give oxidised forms of the metal, rely on the use of aqueous media containing strong oxidising agents. The range of complexes which can be obtained in this type of system is very narrow, and the method is unsuitable for the direct (single-stage) synthesis of complexes by reaction (1).

Developments in the chemistry of the coordination compounds of transition metals have stimulated new approaches, based on non-aqueous aprotic media. The interest in these media stems mainly from the wide range of physicochemical properties which they offer: 1) their dielectric constants ε cover the range from 2.2 (1,4-dioxan) to 182 (*N*-methylformamide), 2) the dipole moments μ lie between 1.75 (tetrahydrofuran, THF) and 5.39 (hexamethyl phosphorotriamide, HMPA), 3) the region of existence of the liquid phase extends from −48.8 to +242 °C (for propylene glycol carbonate, PC), 4) these media offer specific donor–acceptor properties§, the *DN* varying from 2.7 (nitromethane) to 28.8 (HMPA) and the *AN* varying from 3.9 (diethyl ether) to 20.5 (nitromethane).

As we have shown[1], donor–acceptor systems containing dipolar aprotic compounds can be very effective in the oxidative dissolution of transition metals: dimethylsulphoxide, dimethylformamide, dimethylacetamide (DMA), tetramethylenesulphone (TMS), 2,4-dimethyltetramethylenesulphone (DMTMS), ethylene glycol carbonate (EC), PC, HMPA, acetonitrile (AN), benzonitrile (BN), and halogenated hydrocarbons (for example, CCl_4).[97] The most distinguishing feature of these organic solvents is their ability to form molecular complexes or associations[24]. This property also favours any thermodynamically allowed process¶ in which an easily polarisable solvent[104] acts as a bridging ligand and thus makes possible the transfer of an electron from the surface to an acceptor[25,105].

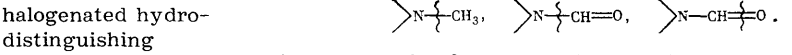
The oxidative dissolution of metals can yield two types of complex: neutral or ionic. The complexes may contain (as ligands) the components of the medium in their original state, or intermediate products formed by the interaction of these components[16,23,106].

1. Neutral complexes with an unchanged component as ligand. This case is most often met with copper, nickel, cobalt, molybdenum, and tungsten. Examples of complexes which have been synthesised in this way include the compounds L_2MX_2 (where M = Cu, Co, Ni) and $L_2MO_2X_2$ (where M = Mo, W), with X = halogen and L = DMFA, DMA, DMSO, and AN.

2. Ionic complexes with an unchanged component as ligand. Examples of complexes of this type which have been synthesised include the iron and cobalt compounds *cis*- and *trans*-$[Fe^{III}(DMFA)_4Cl_2][Fe^{III}Cl_4]$, $Fe^{III}(DMFA)_3Cl_2][Fe^{III}Cl_4]$, *cis*- and *trans*-$[Fe^{III}(DMSO)_4Cl_2]Cl$, $[Fe^{III}(DMSO)_3Cl_2].[Fe^{III}Cl_4]$, *trans*-$[Fe^{III}(DMSO)_4Cl_2][Fe^{III}Cl_4]$, *cis*-$[Fe^{III}.(DMSO)_4Cl_2]_2[Fe^{II}Cl_4]$, $[Fe^{III}(DMSO)_5Cl][Fe^{III}Cl_4]_2$, $[Fe^{II}(AN)_6][Fe^{III}Cl_4]_2$, $[Fe^{II}(BN)_6][Fe^{III}Cl_4]_2$, and $[Co^{II}.(DMSO)_6][Co^{II}Cl_4]$.

Further examples may be quoted to illustrate the special features of the direct method of synthesis. The metal being oxidised stimulates the interaction between the components of the oxidising system. The intermediates formed during the reaction are stabilised by ionic or coordination interaction with the metal ion. The possibility of including these "fragments" as ligands can lead to the formation of unusual complexes, both neutral and ionic. Thus by oxidising metals with a system containing DMSO the following complexes have been obtained: with iron, $[Fe^{III}(DMSO)_5Cl][Fe^{II}_2Cl_6O]$,[106] and with palladium $[(CH_3)_2S]_2PdBr_2$,[107] showing that the $>S \rightarrow O$ bond is broken. Stabilisation of the intermediates formed by this reaction is found also in the complex $[(CH_3S)_3C][Fe^{III}Cl_4]$ formed by the oxidation of iron during chlorination of cyclohexane in the DMSO + CCl_4 system: the H_3C-S bond is broken in this reaction[108].

It is interesting to note that in the dinuclear bridge complex $[cis\text{-}Cu(DMFA)_2Cl_2]_2$ formed during the oxidation of copper, one of the DMFA molecules bound to the copper atom through oxygen is in an anomalous state, all its bonds being longer than those of the other DMFA molecule in the *cis*-position. This suggests a weakening of the bonds as a result of complex formation, and the possibility of dissociation of the DMFA molecule into fragments under the influence of temperature and of the medium[106]. In fact, the following complexes containing fragments of the DMFA molecule have been isolated and characterised in DMFA systems[109,110]: $[(CH_3)_2.NCH\}_2CCl][Fe^{III}(DMFA)_6][Fe^{III}Cl_4]_4$ and $[CH_3NH_3]_4[Fe^{II}Cl_6].H_2O$. The reaction involves bond breaking as follows:



As an example of the potential use of this method we may consider the complex dimethyldibenzylammonium tetrabromopalladate, obtained[107] in the $C_6H_5CH_2Br$ + DMFA system. In this case the $>N-CHO$ bond in DMFA is broken, and stabilisation of the "fragments" $(CH_3)_2N-$ and $C_6H_5CH_2-$ takes place in the $[(CH_3)_2N(C_6H_5CH_2)_2]^+$ cation.

The use of chelating ligands in aprotic dipolar solvent–halogenated hydrocarbon systems widents the range of complexes which can be synthesised by this method. In the presence of α,α'-dipyridyl (α-dipy), dimethylglyoxime (DMGH), 8-oxyquinoline (8-oxin H), acetylacetone (acac H), cyclo-octa-1,5-diene (COD) the following complexes have been obtained: $(\alpha\text{-dipy})NiCl_2$, $Ni(DMG)_2$, $Co(8\text{-oxin})_2(H_2O)_2$, $Co(\alpha\text{-dipy})(acac)_2$, $H[Co(DMG)_2Cl_2]$, $Cu(DMG)_2$, $Cu(acac)_2$, $[Cu(COD)Cl]_2$, $(\alpha\text{-dipy})PdBr_2$, $(\alpha\text{-dipy})PtBr_4$, etc.[111,112] Another promising direction is the direct synthesis of transition metal complexes by catalytic oxidation with oxygen. This process has been demonstrated for a group of metals including some platinum group metals (Pd^0 and Pt^0) with which oxygen behaves as a "stoichiometric" reagent[16].

In the $M^0 + O_2 + HX + L + Kt$ system, where L = DMFA, pyridine (Py), pyridine oxide (PyO), AN, trimethylamine oxide $(CH_3)_3NO$, or the salt of an onium base ($>\overset{|}{N}X$, $\rightarrow SX$,

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§ *DN* is the donor number and *AN* is the acceptor number on Gutman's scale[7,96].

¶ The Gibbs free energy (ΔG°_{298}) calculated for the reaction $Fe^0 + 2CCl_4 \rightarrow FeCl_2 + C_2Cl_6$ without allowing for complex formation is −229.4 kJ mole^{-1}.[98,103]

X = Cl, Br, I), and Kt = Fe, Cu, a series of palladium and platinum complexes has been synthesised. With [HX[> [L] ionic complexes were isolated in which the oxidised metal was in the anion, and the cation was produced from L by protonation (L = Py, PyO), hydrolysis (L = DMFA, AN), dissociation [L = $(C_2H_5)_3NHBr$, $(CH_3)_3SBr$], or protonation of the deoxygenated form of L[$(CH_3)_3NO \rightarrow (CH_3)_3N$ + [O]]. With [HX] < [L] neutral complexes were obtained, for example $(\alpha\text{-dipy})PdCl_2$.[85,86]

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Our study of the possible mechanisms of electron transfer from a metal to an oxidiser during the liquid-phase oxidative dissolution of transition metals, allowing for the semiconductor properties of the oxide layer, for the adsorption of molecular oxygen, and for the donor–acceptor interaction between the components of the medium has identified both complementary and non-complementary processes for the oxidation of metals in organic complex-forming media by which a wide range of coordination compounds can be synthesised.

The oxidative dissolution of transition metals in organic media and the direct synthesis of complexes are currently attracting intensive study from which interesting developments can be expected from the practical as well as the scientific aspect[113–115].

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