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Metal Ions in Unusual and Unstable States of Oxidation and the Steps of Electrochemical Reactions

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Problems associated with the steps of electrochemical discharge and ionisation reactions of metals in aqueous solutions are discussed. Data on the radiation-chemical preparation of metals in unusual and unstable states of oxidation are reported. The results of studies of the physicochemical properties of these species in aqueous solutions and of their reactions with organic and with inorganic compounds are generalised. The effect of metal ions in unusual and unstable states of oxidation on the elementary steps of electrode reactions is discussed. 162 references.

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I. INTRODUCTION

It is generally assumed[1-3] that complex electrochemical oxidation–reduction reactions consist of several elementary (one-electron) electrochemical acts. The intermediate steps of these reactions (for example, the anodic dissolution or the cathodic deposition of metals) give ions in unusual and unstable states of oxidation. Since the direct experimental observation of these short-lived intermediate species is impossible at present, any conclusion as to the steps involved in an electrochemical reaction must be based on an analysis of the kinetics of the process. However, the criteria used to identify the steps cannot usually yield an unambiguous description of the overall mechanism of the process. Nevertheless metal ions in unstable states of oxidation have been obtained by radiation-chemical methods (mainly in aqueous solutions), and their properties have been studied in fair detail. It could be useful to review and discuss these results from the standpoint of a more fundamental understanding of the mechanism of the multi-step discharge and ionisation reactions of metals.

II. STEP REACTIONS IN ELECTROCHEMICAL KINETICS

The theory of multi-step electrode processes is based on the proposition that the transfer of several electrons in a single elementary discharge (or metal ionisation) act is less probable than the sequential transfer through one-electron intermediate steps. Thus a multi-step electrochemical reaction presupposes the formation of metal ions having intermediate valencies.

The fullest discussion of multi-step electrochemical processes can be found in papers[4,5] describing the anodic dissolution of iron in alkaline solutions by the overall reaction

$$Fe + 2OH^- \rightleftarrows Fe(OH)_2 + 2e .$$

The experimental results were explained by postulating the formation (in a one-electron process) of the intermediate surface compound Fe(OH)(ads):

$$Fe + OH^- \rightleftarrows Fe(OH)(ads) + e$$

followed by the slow step

$$Fe(OH)(ads) + OH^- \rightarrow FeO(ads) + H_2O + e$$

and by the fast reactions leading to the formation of the final product

$$FeO(ads) + OH^- \rightleftarrows HFeO_2^- ,$$
$$HFeO_2^- + H_2O \rightleftarrows Fe(OH)_2 + OH^- .$$

The mechanism of a multi-step electrode process on a solid electrode is difficult to study because of the imperfection of real surfaces, and also because the electrochemical discharge (ionisation) reaction is often accompanied by other steps such as diffusion of the species being discharged to crystallisation sites, their incorporation into the lattice, etc. The amalgam electrode is more convenient for theoretical and experimental studies of step reaction mechanisms, and it offers some important advantages over solid electrodes. We shall therefore confine this discussion mainly to data obtained for multi-step electrode processes on amalgams.

1. Criteria of Step Mechanism

The recognition of a step mechanism in an electrochemical reaction is usually based on an analysis of the reaction kinetics. Theoretical rules developed for this purpose[2,3,6-9] have been called the "criteria of step mechanism": they are discussed in detail in Ref. 3.

The step mechanism of a complex electrochemical reaction can be demonstrated by studying the kinetics of the cathodic and of the anodic process. Consider the overall discharge (metal ionisation) reaction

$$M \rightleftarrows M^{n+} + ne \qquad (1)$$

whose rate is limited by the slow step

$$M^{(m-1)+} \underset{k_{cm}}{\overset{k_{am}}{\rightleftarrows}} M^{m+} + e . \qquad (2)$$

According to the slow discharge theory[10], the rates of the anodic and of the cathodic process are given by

$$i_{am} = k_{am}[M^{(m-1)+}]_s \exp\left(\frac{\beta_m F(\varphi - \psi_1)}{RT}\right) , \qquad (3)$$

$$i_{cm} = k_{cm}[M^{m+}]_s \exp\left(-\frac{\alpha_m F(\varphi - \psi_1)}{RT}\right) , \qquad (4)$$

where ψ_1 is the potential at a point one ionic radius away from the electrode surface measured from the potential in the volume of the solution, and α_m and β_m are the true transfer coefficients of the m-th step, for which we can write

$$\alpha_m + \beta_m = 1 . \qquad (5)$$

By using the Nernst equation we can determine the concentrations of intermediate species $M^{(m-1)+}$ and M^{m+}, and thus we can replace Eqns. (3) and (4) (using the subscripts s and v to denote surface and volume concentrations respectively) by

$$i_{am} = k_{am}[M^{(m-1)+}]_v \exp\left(\frac{\beta_m F\varphi}{RT}\right) \exp\left[-\frac{(m-1+\beta_m)F\psi_1}{RT}\right] , \qquad (6)$$

$$i_{cm} = k_{cm}[M^{m+}]_v \exp\left(-\frac{\alpha_m F\varphi}{RT}\right) \exp\left[-\frac{(m-\alpha_m)F\psi_1}{RT}\right] . \qquad (7)$$

The apparent transfer coefficients of the anodic (β) and of the cathodic (α) process are related to the true coefficients β_m and α_m by the expressions

$$\begin{gathered}\beta = m - 1 + \beta_m , \\ \alpha = n - m + \alpha_m , \\ \alpha + \beta = n .\end{gathered} \qquad (8)$$

The criteria for the presence of steps can be formulated by analysing the kinetic features of the electrode process. In the case of a single rate-limiting step the criterion for a step mechanism is the dependence of the ratio of the apparent transfer coefficients (defined by the slopes of the anodic and the cathodic curve) on the number m of the limiting step:

$$\beta/\alpha = (m - 1 + \beta_m)/(n - m + \alpha_m) \qquad (9)$$

and also the fact that the sum of these coefficients is equal to the total number of electrons taking part in reaction (1) [as required by Eqn. (8)].

If in a two-step process the first step is rate-limiting, and the second is a disproportionation reaction, the kinetic equations for the cathodic and the anodic process will be the same as for one-electron reactions. Lastly, if successive steps in a process have comparable rates we observe a discrepancy between the sum of the apparent transfer coefficients and the total number of electrons taking part in the reaction (i.e. $\alpha + \beta < 2$). In this case the most important criteria for a step mechanism are the difference between the exchange currents obtained from the anodic and the cathodic Tafel plot and the difference between the true and the extrapolated value of the exchange current.

The methods of analysing polarisation curves in order to identify the step mechanism of electrochemical processes have been improved. Thus, a computer-aided approach to the analysis of the transition regions of polarisation curves has been developed[11] for studies of fast electrode reactions. Characteristic changes in shape have been established also for the differential curves in the case of a simple one-step process or for two consecutive processes having comparable rates. These changes are found to be adequate criteria for the recognition of step mechanisms.

2. Step Reactions

We shall illustrate the application of the step mechanism criteria to the study of electrochemical processes, and the demonstration of the participation (as intermediates) of metals in unusual states of oxidation, by examining briefly a few specific examples. Studies of the polarisation curves of a labelled zinc amalgam (0.4 M) in 0.1 M $ZnSO_4$ + 0.01 N H_2SO_4 have shown[12,13] that the sum of the apparent transfer coefficients at potentials close to the equilibrium value is approximately 2, and their ratio is approximately 1.6. Similar results were obtained for an indium amalgam in the presence of an excess of $NaClO_4$ [14,15] (found, $\alpha + \beta \cong 3.1$ and $\beta/\alpha \cong 2.4$). It follows from the step mechanism criteria that in both cases we are dealing with a complex electrochemical process in which the rate-limiting step is the removal of the last electron (for the anodic process) or the

addition of the first electron (for the cathodic process), i.e. the results are consistent with the electrochemical formation and with the existence of the ions Zn^+ and In^{2+} in aqueous solutions.

Published data (reviewed in Refs.1–3) clearly show that a substantial difference between the apparent transfer coefficients of the anodic and of the cathodic process is a common feature of all multi-electron discharge (metal ionisation) processes: as a rule, $\beta > \alpha$. For example, for cadmium amalgams β is 1.36–1.78 [16–19] and α lies in the range 0.24–0.28 [20,21], for copper amalgam $\beta = 1.60$ and $\alpha = 0.41$,[22] and for gallium, tin, and lead amalgams α values of 0.23,[23] 0.4–0.6,[24] and 0.5 [25] have been reported, with $\beta = 1.3$–1.6.

An example of a stepwise redox reaction with two consecutive steps taking place at comparable rates is

$$Tl^+ \rightleftarrows Tl^{3+} + 2e\,.$$

The kinetics of this reaction in 15 *N* H_2SO_4 have been studied on a platinum electrode: after being corrected for diffusion the polarisation curves show linear regions corresponding to $\beta = 0.64$ and $\alpha = 0.36$, i.e. $\alpha + \beta < 2$.[26] Extrapolation of these regions to the equilibrium potential gives very different exchange currents, indicating the presence of one-electron ionisation reactions having comparable speeds:

$$Tl^+ \rightleftarrows Tl^{2+} + e\,,$$
$$Tl^{2+} \rightleftarrows Tl^{3+} + e\,.$$

Similar results have been reported for polarisation measurements in the $Pb^{2+} \rightleftharpoons PbO_2 + 2e$ system in concentrated solutions of $HClO_4$.[27] Here $\alpha = 0.86$, $\beta = 0.24$, and the exchange current found by extrapolating the Tafel portion of the anodic branch of the polarisation curve is higher than the exchange current given by the cathodic branch. These results can be explained by postulating the formation of tervalent lead in an intermediate step of the electrochemical process.

The rate of discharge (or ionisation) of many metals is a sensitive function of pH. One possible explanation assumes that the electrode process is stepwise, and that the rates of the various steps are affected to different extents by the concentration of H^+ ions. Exactly the same explanation has been proposed for the decrease in the rate of the electrode process with increase in the acidity of the medium in the case of an indium amalgam[28,29]. The rate-limiting step does not involve simple In^{2+} ions, but ions which have been partially hydrolysed,

$$InOH^+ \rightleftarrows InOH^{2+} + e\,,$$

this reaction being preceded by the hydrolysis step

$$In^{2+} + H_2O \rightleftarrows InOH^+ + H^+$$

and followed by the chemical step

$$InOH^{2+} + H^+ \rightleftarrows In^{3+} + H_2O\,.$$

The difference in rate between the anodic and the cathodic discharge (or ionisation) of bismuth has also been explained by postulating a step mechanism and by allowing for the hydrolysis of bismuth in intermediate states of valency[30]. The rate of the electrode reactions is affected also by the nature and concentration of the anions present in solution, suggesting complex formation during the intermediate steps of the electrode process, anion effects on the electron transfer conditions, or adsorption of the anions on the electrode[29].

The strongly inhibiting effect of surface-active substances (SAS) on the discharge (or ionisation) of multivalent metals (as compared with the corresponding effect on univalent metals) has been known for a long time[31,32]. This is another indication of a step mechanism, the various steps being affected by the SAS to different extents. The kinetics of electrode processes on a tin amalgam in the presence of camphor (SAS) have been studied in detail[33–35]. Evaluation of the polarisation and adsorption measurements on a computer showed that camphor causes a ~70-fold decrease in the rate of the redox step

$$Sn^+ \rightleftarrows Sn^{2+} + e\,,$$

whereas the rates of formation and of discharge of the singly charged cations,

$$Sn \rightleftarrows Sn^+ + e\,,$$

are decreased only 5-fold. The difference in the effects of the SAS on the different steps is due to the difference in nature of these steps and to the differences in hydration energy of the various steps.

A retardation by SAS in various potential regions (corresponding to different rate-limiting steps) has been observed in a study of the stepwise discharge (ionisation) of bismuth on an amalgam electrode in the presence of hydroquinone[36]. A study of the discharge (ionisation) mechanism of copper[37–39] has revealed the two sequential steps

$$Cu \rightarrow Cu^+ + e\,,$$
$$Cu^{2+} + e \rightharpoonup Cu^+\,.$$

The rate of both these steps is affected by the nature of the solvent (aqueous 2M $HClO_4$ solution, CH_3OH, or glacial acetic acid).

We should stress that the stepwise mechanism criteria are not unambiguous, because they are often based on a large number of assumptions (that the one-electron steps are first-order reactions, and purely electrochemical, i.e. that no additional chemical steps are present; also, that parallel electrochemical reactions are absent, that specific adsorption of the initial, intermediate, and final products is negligible, and that diffusional rate limitation can be ignored). Hence it is very important to establish additional criteria and other methods of studying multi-step electrochemical reactions. For example, electrochemical measurements have been used successfully in conjunction with radiochemical measurements[3] to study isotope exchange effects in a multi-step electrode process[40].

More recently the rotating disk electrode with guard ring[41] has been used increasingly in studies of the multi-step anodic dissolution or cathodic deposition of metals, with identification of the unstable intermediate species involved. The multi-step electrode reaction takes place on the central (disk) electrode, and the current i_D is measured as a function of ϕ_D for this electrode. The products of the intermediate steps diffuse from the disk towards the ring, where they react, producing a current i_R. By studying the dependence of i_R on i_D for different speeds of rotation of the disk we can determine the kinetic characteristics of the individual steps in a complex electrode process.

However, in most cases this method also fails to identify the intermediate products directly, and the mechanism of the electrode process has to be inferred from assumed kinetic schemes for the separate reactions. Nevertheless by exploiting recent advances (including progress in computing techniques) we are able to identify the mechanism of the individual steps and the nature of the short-lived intermediate products in a number of electrode processes. For example, evidence has been obtained for the formation of the following lower-valency ions: Al^+ (in the dissolution of aluminium in anhydrous acetic acid[42]), and Be^+ in the dissolution of beryllium[43,44]. An interesting feature of the

dissolution of beryllium is the possibility of a two-electron mechanism (giving Be^{2+}) in parallel with the one-electron mechanism (giving Be^{+}). The lifetime of Be^{+} in solution is $\sim 10^{-2}$–10^{-1} s.

However, the formation of Mg^{+} during anodic dissolution of magnesium in Na_2SO_4 and NaBr solutions could not be established, suggesting that this species is very rapidly removed by a homogeneous reaction (in times ≤ 0.1 s).[45,46] The formation of Bi^{+} ions during the anodic dissolution of the metal in concentrated perchloric acid has been observed[47], and the criteria for the electrochemical and for the chemical mechanism of formation of Cu^{+} in the reaction between Cu^{0} and Cu^{2+} in 1 *N* H_2SO_4 solution have been determined[48].

Current views on the step mechanisms of electrode processes, with formation of intermediate ions in unusual and unstable states of oxidation, are based on the application of multi-step mechanism criteria to a large number of electrochemical processes, not only on amalgam electrodes but also in the dissolution and deposition of multivalent metals on solid electrodes. A detailed discussion of the many publications on this topic lies beyond the scope of the present review, and is largely covered by previous reviews[1,49–52].

The results outlined above suggest that the role of multi-step reactions in electrochemical processes is an important, and even a dominant one. Hence the direct experimental observation of metal ions in intermediate valency states in aqueous or other solutions, even if prepared by non-electrochemical methods, and the study of the nature and properties of these ions may be of great value in the development and validation of our views on the mechanism of step reactions.

III. METAL IONS IN UNUSUAL AND UNSTABLE STATES OF OXIDATION

Recent developments in the pulse radiolysis method and in the matrix stabilisation of short-lived ions and radicals by low-temperature radiolysis have led to the preparation of many metal ions (in aqueous solutions) in unusual and unstable states of oxidation, and to studies of the properties of these ions.

1. Radiation-chemical Preparation

The hydrated electron e^{-}_{aq} and the hydroxyl radical OH, which are formed during the radiolysis of water and of aqueous solutions, have well defined reducing [$E^{0}(e^{-}_{aq}/\frac{1}{2}H_2) = -2.9$ V] and oxidising properties [$E^{0}(OH/H_2O) = 2.8$ V] respectively. Hence the irradiation of many salt solutions can yield, as a result of fast one-electron reduction of metal ions by hydrated electrons

$$M^{n+}_{aq} + e^{-}_{aq} \rightarrow M^{(n-1)+}_{aq} \qquad (10)$$

or fast one-electron oxidation by OH radicals

$$M^{n+}_{aq} + OH \rightarrow M^{(n+1)+}_{aq} , \qquad (11)$$

short-lived metal ions in intermediate states of oxidation which are chemically very active.

The nature and properties of these ions in liquid solutions have been studied by pulse radiolysis with fast recording of the optical spectra and of the changes in electrical conductivity of the medium associated with the formation of these ions[53–58]†. During low-temperature radiolysis of frozen (usually, at 77 K) aqueous salt solutions the metal ions produced by reactions (10) and (11) are stable and can be studied by conventional electron paramagnetic resonance (EPR) and optical spectroscopy methods[57]. The experimental conditions can be chosen so as to favour oxidation or reduction reactions almost totally: this is achieved by adding to the aqueous solution acceptors of e^{-}_{aq} or OH respectively, whose effect is to "transform" the reducing (e^{-}_{aq}) or the oxidising agent (OH) into an oxidising or a reducing agent respectively.

Thus, saturating the solution with N_2O produces the reaction

$$N_2O + e^{-}_{aq} \xrightarrow{H_2O} N_2 + OH + OH^{-} , \qquad (12)$$

as a result of which e^{-}_{aq} is transformed into the OH radical. If the solution is saturated with molecular hydrogen at high pressure the OH radicals give a fairly high yield of active reducing species (hydrogen atoms) by the reaction

$$H_2 + OH \rightarrow H + H_2O .$$

However, the most commonly used additives are organic compounds (RH) such as alcohols, formate ions, etc. which react with OH to give organic radicals R:

$$RH + OH \rightarrow R + H_2O . \qquad (13)$$

The reducing power of these radicals increases in the sequence

$$CH_2OH < CH_3CHOH < (CH_3)_2\dot{C}OH < CO^{-}_2 .$$

Even the earliest experiments (in 1963–1965) by the pulse radiolysis method[59–67] demonstrated that e^{-}_{aq} is an active reducing agent towards many metal ions (Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, etc.) in deaerated neutral aqueous solutions of their salts. Later work was concerned with detailed studies of the mechanism of these reactions, and of the nature and properties of the species produced in aqueous solutions of Zn^{2+},[68–70] Cd^{2+},[68,69,71,72] Hg^{2+} and mercury compounds[73–82], Ga^{3+},[83,84] In^{3+},[83] Tl^{+} and Tl^{3+},[85–89] Pb^{2+},[90,91] Bi^{3+},[92] Mn^{2+},[93] Ni^{2+},[68,69,94] Co^{2+},[68,69] Cu^{2+},[95,96] Ag^{+},[97–99] Au^{3+},[100,101] and compounds of Pt[102–105] and Pd.[106]

As well as to these elements, the pulse radiolysis method has been applied to some lanthanides and actinides in unstable states of oxidation, and to a number of complexes (see review in Refs. 53 and 54). It was shown that most of the reactions of e^{-}_{aq} with aquo and chloro complexes of metals are diffusion controlled (10^{9}–10^{10} litre mole^{-1} s^{-1}). The reactivity decreases if water molecules in the coordination sphere of the metal ion are replaced by ligands such as OH^{-}, NH_3, ethylenediamine, glycine, etc. An interesting effect is observed: the rate constant of the reaction between e^{-}_{aq} and M^{n+} falls off most sharply when the last water molecule is replaced by a ligand[67]. Evidently, this arises because the water molecule acts as an electron carrier (from e^{-}_{aq} to the metal ion), being part of the hydration spheres of both species simultaneously. Thus the effect of many ligands (other than water) is to isolate the metal ion from reduction by the e^{-}_{aq} species.

2. Optical Properties

Metal ions in unstable states of oxidation usually absorb in the u.v. region of the optical spectrum with high extinction coefficients (Table 1). The absorption spectrum of metal aquo complexes with an electronic configuration of the outer shells of the $(N-1)d^{10}Ns^{1}$ type, where N is the number of the period (Ag^{0}, Zn^{+}, Ga^{2+}, etc.), consists of a single bell-shaped band. For ions having iso-electronic structures,

†The principles used in pulse radiolysis and various experimental approaches to the determination of the physicochemical parameters of short-lived particles are examined in detail in a special monograph[54].

i.e. for ions of elements in the same period, the absorption band is shifted towards the short-wavelength u.v. region as the charge on the aquo complex increases. An almost linear dependence of the optical transition energy ($E_{\lambda_{max}}$) on the ionic charge is observed[107,108].

Table 1. Optical absorption of metals in unstable states of oxidation in aqueous solutions (λ, nm; ε, litre mole^{-1} cm^{-1}).

Particle	pH	λ_{max}	$10^{-3}\varepsilon$	References
Ag^0	5—7	360	—	[66, 97]
Zn^+	5—7	300	7.5	[68]
Zn^+	5—7	300	13	[70]
Cd^+	3—7	300	13	[68]
Hg^+	2—4.3	255	14	[74]
HgOH	5.5—7.0	233; 265 sh.	10; 5 sh.	[76]
HgCl	1—7	245; 330 sh.	7.5; 2.3 sh	[75]
HgBr	1—7	280; 350 sh.	5.1; 4.3 sh.	[78]
HgI	1—7	360	5.5	[79]
HgCN	1—7	285	(3.5—3.8)	[77, 81]
HgCNS	1—7	415	4.4	[81]
$Hg_2(I)$	1—3.5	285; 300 sh.	14; 9	[82]
Ga^{2+}	$\leqslant$2.3	265	6.4	[83, 84]
GaOH$^+$	2.9—3.9	265; 300 sh.	5.7	[84]
In^{2+}	$\leqslant$2.0	$\sim$250	20	[83]
Tl^{2+}	$<$1.0	$\leqslant$225	12	[86]
TlOH$^+$		$<$250; 360 sh.	3.0	[89]
TlCl$^+$	1 M $HClO_4$	263; 342 sh.	7.7; 4.4 sh.	[87]
$TlCl_2$	1 M $HClO_4$	280; 342 sh.	6.4; 4.7 sh.	[87]
$TlCl_3^-$	1 M $HClO_4$	304; 362 sh.	10; 9.3 sh.	[87]
Pb^+	3—4	300	3.0	[90, 91]
Pb^{3+}	3—4	200		[91]
Bi^{2+}	5—7	335		[92]
Co^+	5—7	320; 375	2.3 (311 nm)	[68]
Ni^+	5—7	300	3.6; 6	[68, 94]
Cu^{3+}	2	265	1.1	[66, 95]
CuOH$^+$	5, 7	295	5.7	[95]
Mn^+	5—7	$\sim$300		[63]
Mn^{3+}	5—7	$<$250	2.1 (258 nm)	[93]
$AuCl_2$	$<$2	270	5	[101]
$AuCl_3^-$	$<$2	260	8	[101]
$AuCl_4^{2-}$	$<$2	330	5	[101]
Pt(III)	1—13, Cl^-	410	$\sim$3.5	[102, 103]
Pt(III)	7, Cl^-	450	2.8	[103]
Pt(I)	1—12, Cl^-	310	$\sim$3	[102, 103]
Pt(I)	12, CN^-	360; 295 sh.	8.4 (360 nm)	[102]
Pd(I)	7, Cl^-	$\sim$340		[106]
Pd(III)	7, Cl^-	320	4.7	[106]
Pd(III)	1 M HCl	340	18	[106]

The absorption of the aquo complexes of metals in the *s* and *p* blocks, i.e. elements in subgroups IB—VB of the Periodic Table, in the $^2S_{1/2}$ electronic state (with an unpaired electron in the *s* orbital), is due to a transition of the $a_{1g}^* \rightarrow t_{1u}^*$ type[108]. This transition can be interpreted qualitatively as the transfer of electron density from the central metal ion towards the ligands. In the case of aquo complexes with an octahedral structure a substantial covalent contribution to the formation of the M—OH_2 chemical bond has been demonstrated by the semi-empirical variant of the MO method. This contribution increases with the charge on the central metal ion.

The chloro complexes of Group IB—VB metals show a large number of absorption bands due to $2t_{1u} \rightarrow a_{1g}^*$ and $3t_{1u} \rightarrow a_{1g}^*$ transitions (for complexes with an octahedral structure), i.e. the electron transfer is from the ligands towards the central atom. In contrast to the aquo complexes, the energy of the optical transition ($E_{\lambda_{max}}$) decreases along an isoelectronic series of metal ions as the formal state of oxidation increases[109].

In the optical spectra of the hydroxo complexes (MOH^{m+}, where $m = [(n-1)\pm1]$) we observe a splitting of the fundamental band, characteristic of the $M^{(n\pm1)+}$ ions (Table 1). The compounds HgX (where X = Cl, Br, I, CN) behave similarly[81].

3. State of the Metal Ions in Aqueous Solutions

Metal ions in aqueous solutions react with water molecules or with the anions present in solution to give complexes whose composition and structure are determined to a large extent by the nature and concentration of the anions and by the pH. Reduction or oxidation of the metal ion alters its electronic configuration, often leading to a change in the coordination number, polarisability, and other related characteristics of the ion. The crystallographic radii of the metal ions of Groups IB—IVB in their higher state of oxidation [$(N-1)d^{10}$ electronic configuration] and in a state of oxidation one unit lower [$(N-1)d^{10}Ns^1$ electronic configuration] are compared in Table 2. In the latter case the radii for the iso-electronic series were calculated[108] by the Pauling formula[110]

$$r_Z = \frac{C_{N-}}{Z^*_{\text{eff}}} Z^{-2/(N_B-1)} ,$$

where Z^*_{eff} is the effective charge on the nucleus, Z is the atomic number of the element, N_B is the Born repulsion coefficient, and C_N is a constant coefficient for the iso-electronic series of ions of the elements of periods 4, 5, and 6, determined from the known radii of Cu^0, Ag^0, and Au^0. Since $r[M^{(n-1)+}] > r(M^{n+})$, we can expect the acid-base properties of metal ions in unusual states of oxidation to be different from those of the same ions in the higher states of oxidation. The tendency of the ions to form complexes with dissolved ligands, and other properties, will also be different. This conclusion is borne out by pulse radiolysis studies.

Table 2. Crystallographic radii of the ions of Group IB—IVB metals[108].

M^{n+}	Cu^+	Zn^{2+}	Ga^{3+}	Ge^{4+}	Ag^+	Cd^{2+}	In^{3+}	Sn^{4+}	Au^+	Hg^{2+}	Tl^{3+}	Pb^{4+}
$r(M^{n+})$	0.96	0.74	0.62	0.53	1.26	0.97	0.81	0.71	1.37	1.10	0.95	0.84
$M^{(n-1)+}$	Cu^0	Zn^+	Ga^{2+}	Ge^{3+}	Ag^0	Cd^+	In^{2+}	Sn^{3+}	Au^0	Hg^+	Tl^{2+}	Pb^{3+}
$r(M^{(n-1)+})$	1.278	1.063	0.908	0.791	1.445	1.224	1.059	0.934	1.442	1.244	1.094	0.975

Table 3. Stability constants of chloro complexes for Tl(I), Tl(II), and Tl(III) in aqueous solutions.

Complex	Medium	K_I	K_{II}	K_{III}	K_{IV}	Refs.
$TlCl_3^{2-}$	4 M $NaClO_4$	0.8	0.2	0.1	—	[111]
$TlCl_3^-$	1 M $HClO_4$	$6.2\cdot10^4$	$1.9\cdot10^3$	13	—	[87]
$TlCl_4^-$	0.5 M $HClO_4$	$5.2\cdot10^6$	$1.3\cdot10^5$	553	44	[112]

Dodson and Schwarz[87] studied the chloro complexes of Tl(II)# and calculated their stability constants:

$$Tl^{2+} + Cl^- \overset{K_I}{\rightleftarrows} TlCl^+ ,$$

$$TlCl^+ + Cl^- \overset{K_{II}}{\rightleftarrows} TlCl_2 ,$$

$$TlCl_2 + Cl^- \overset{K_{III}}{\rightleftarrows} TlCl_3^- .$$

#Throughout this paper we shall use a Roman numeral in brackets to denote the state of oxidation of the element.

The constants are compared in Table 3 with the corresponding values for the stable forms Tl(I) and Tl(III). We note that the stability constant increases very rapidly with the charge on the central thallium ion. The tendency of the metal ions to hydrolyse in aqueous solutions varies in a similar way.

For example, the pK values of the reaction

$$M(H_2O)_6^{n+} \rightleftarrows M(H_2O)_5OH^{(n-1)+} + H^+ \qquad (14)$$

for Hg^{2+}, Ga^{3+}, and Tl^{3+} are 3.5, 2.6, and 1.3 respectively[113], and those for Hg^+, Ga^{2+}, and Tl^{2+} are 5.1,[75] ≥3.3,[84] and 4.6.[88] Thus the tendency of metal ions to replace water molecules in their coordination sphere by OH^- ions is decreased by one-electron reduction of the ions, i.e. the ions become less hydrolysable than ions in the higher state of oxidation. Conversely, Cu^{3+} ions obtained from the oxidation of Cu^{2+} by OH radicals [reaction (11)] are more readily hydrolysed than Cu^{2+} ions. The pK of reaction (14) for Cu^{3+} is ~2.9,[64,95] i.e. it is much lower than the pK value for Cu^{2+} (given[113] as 7.5).

We should stress that the formation (during intermediate steps) of metal ions in unusual and unstable states of oxidation almost invariably makes the kinetics of the overall electrode process a function of pH and of the concentration of anions. This may be due to the large difference between the acid–base properties of metal ions in unusual states of oxidation and those of the same ions in their normal states of oxidation. Evidence for this suggestion was given above in connection with the discharge (ionisation) reactions of In [28,29] and Bi [30] on an amalgam electrode. The adsorption of OH^-, Cl^-, SO_4^{2-}, and other anions on the electrode surface and the formation of complexes with the metals in solution can affect the kinetics of the electrochemical act. It is thought, for example, that the adsorption of OH^- groups on an electrode assists the transfer of Fe,[114–116] Ni,[117] and Co [118] into the solution through the intermediate formation of the hydroxo complexes MOH, i.e. that the OH^- ions favour the dissolution of the metal by a multi-step mechanism (see reviews in Refs. 49–51).

The stability of metal ions in unusual states of oxidation in aqueous solutions is determined by the nature of the ligand and by the extent of complex formation by the ion. Thus, the rate constant of the disproportionation of the Tl^{2+}, $Tl(OH)^+$, and $Tl(OH)_2$ ions increases very markedly with the number of hydroxyl groups in the coordination sphere[89]. A similar effect is produced by Cl^- ions in the chloro complexes of Tl(II) [87] and Au(II).[101] Thus by varying the pH or the concentration of ions in solution we can influence the stability of metal ions in unusual states of oxidation, their steady-state concentration, and therefore also the kinetics of the electrode process.

4. Oxidation–Reduction Potentials

The step mechanism of complex electrochemical processes arises, essentially, from differences in the thermodynamic conditions appropriate to each of the constituent acts: in other words, if the redox potentials of the M^+/M and M^{2+}/M^+ pairs in the overall electrode process

$$M \rightleftarrows M^{2+} + 2e \qquad (15)$$

are significantly different we can expect a difference also in the rates of the ionisation and discharge reactions

$$M \rightleftarrows M^+ + e, \qquad (16)$$

$$M^+ \rightleftarrows M^{2+} + e. \qquad (17)$$

Of course, the probability of transfer of several electrons in the same elementary act is in general smaller than the probability of one-electron transfer. Furthermore, the activation energies for the one-step discharge of the M^{2+} ions may be higher than those for the multi-step process involving the formation of intermediate M^+ species[3]. The rate of the slowest step will determine the rate of the electrode process. We shall assume, as usual, that diffusional limitations are absent, i.e. that the reactants diffuse rapidly and their concentrations at the surface and in the volume of the solution are equal. For the metal ionisation–discharge reaction considered here the rates of steps (16) and (17) in the anodic and the cathodic process are given by Eqns.(6) and (7) respectively.

To determine the redox potential of the reaction

$$Red^- + Ox \underset{k_-}{\overset{k_+}{\rightleftarrows}} Red + Ox^- \qquad (18)$$

we need to know the equilibrium constant $K_p = k_+/k_-$. Since metal ions in unusual states of oxidation are active and short-lived particles, reactions involving these ions are usually irreversible, and it is very seldom possible to determine k_+ and k_- simultaneously. It is more usual to determine the rate constant of the forward reaction (for example, the reduction of the metal ions, or their oxidation by the OH radicals to ions in unstable states of oxidation) and that of the subsequent reaction (disproportionation, or interaction with other species present in solution). In any case, the concentrations of different participants in a fast reaction of the type of (18) are always difficult to measure simultaneously because of the overlap of the optical spectra, which interferes with the determination of K_p.

The equilibrium constant of the reaction

$$Tl^{3+} + Fe^{2+} \rightleftarrows Tl^{2+} + Fe^{3+}$$

was determined[86] as 4.1×10^{-8} in 1 M $HClO_4$ solution, and by combining this value with the potential of the Fe^{3+}/Fe^{2+} couple we obtain a potential of 0.3 V for the Tl^{3+}/Tl^{2+} couple. The reactions of Zn^+ and Cd^+ ions with $Co(NH_3)_6^{3+}$ were studied by Navon and Meyerstein[119]: using the standard rate constants for the $Co^{3+} \rightleftharpoons Co^{2+}$, $Zn^{2+} \rightleftharpoons Zn^+$, and $Cd^{2+} \rightleftharpoons Cd^+$ exchange reactions they determined K_p by the Marcus theory[120,121] and they calculated $E^0(Zn^{2+}/Zn^+) = -(2.0 \pm 0.4)$ V and $E^0(Cd^{2+}/Cd^+) = -(1.8 \pm 0.4)$ V. Systematic determinations of the potentials of metals in unusual oxidation states have been carried out by approximate theoretical methods as well as experimentally.

In order to calculate thermodynamically the redox potential of the $M^{n+}/M^{(n-1)+}$ couple we must evaluate the free energy ΔF of the reaction

$$M^{n+} + \frac{1}{2}H_2 \rightarrow M^{(n-1)+} + H^+. \qquad (19)$$

We therefore have to examine the constituent steps of the reaction, whose free energies are usually known [except that for the hydration of the $M^{(n-1)+}$ ion]. It has been assumed[122] that in a reaction such as (19), in which M^{n+} is a bivalent cation, the dependence of $\Delta G_{hydr}(M^+)$ on the ionic radius is the same as for the alkali metals. Furthermore, the M^+ radii were not known, and they had to be found by an approximate method. Thus, the radius of the Zn^+ ion was taken to be the mean of the Cu^+ and Zn^{2+} radii. In this way the $E^0(Zn^{2+}/Zn^+)$ potential was obtained from two values corresponding to the redox potentials of alkali metals having radii equal to those of Zn^{2+} and Cu^+. Similarly, for Cd^+, Pb^+, Mg^+, Ca^+, and Ba^+ the lower values of r_i were identified with those of the Cd^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, and Ba^{2+} ions, and the upper values with those of Ag^+, Tl^+, Na^+, K^+, and Cs^+ respectively. In the

case of Mn^+, Fe^+, Co^+, and Ni^+ the radii were assumed to be the same as for the same metals in the bivalent state.

Values of $E^0[M^{n+}/M^{(n-1)+}]$ obtained in this way are listed in Table 4. Obviously, these values are tentative, but nevertheless in many cases they agree well with experiment. For example, e^-_{aq} does reduce Zn^{2+}, Cd^{2+}, and Pb^{2+} but not Mg^{2+}, Ca^{2+}, or Ba^{2+}. On the other hand the E^0 values obtained for Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} are inconsistent with the observed, fast reactions of these ions with e^-_{aq}. Therefore this method is less attractive, on the whole, than the determination of the potentials by an approximate experimental method, consisting in studying the reactions with R radicals whose potentials (E) are known:

R	e^-_{aq}	H^-	CO_2^-	$(CH_3)_2COH$	CH_3CHOH	CH_2OH	OH	HO_2
E, V	−2.9	−2.3	−2.0	−1.8	−1.1	−0.97	2.8	1.7

Table 4. Redox potentials of metal ions in unstable states of oxidation.

M^{n+}	Calculation (Ref.122)			Experiment
	$r_{(M^{(n-1)+})}$, Å	Hydration energy of $M^{(n-1)+}$, kcal g-ion^{-1}	$E^0(M^{n+}/M^{(n-1)+})$, V	$E^0(M^{n+}/M^{(n-1)+})$, V
Zn^{2+}	0.74—0.96	112—98	−(2.5—3.2)	−(2.4±0.2) [70] *; −(2.0±0.4) [119]
Cd^{2+}	0.97—1.26	98—84	−(1.9—2.5)	−(1.9±0.1) [72]; −(1.8±0.4) [119]
Hg^{2+}	—	—	—	−(1.4±0.3) **
Ga^{3+}	—	—	—	~ −0.65 [123]
In^{3+}	—	—	—	~ −0.45 [123]
Tl^{3+}	—	—	—	+0.3 [86]
Sn^{4+}	—	—	—	+0.7 [124]
Pb^{2+}	1.20—1.40	78—69	−(1.1—1.5)	−(1.0±0.1) [90]
Pb^{4+}	—	—	—	+(1.8±0.3) **
Mn^{2+}	0.8	108	−3.1	~ −2.0 [63, 93] *
Fe^{2+}	0.76	110	−3.1	−(2.7)±2.3) [63, 125] *
Co^{2+}	0.74	112	−3.1	⩾−2.7 [63, 68, 69] *
Ni^{2+}	0.72	113	−2.7	−2.7 [94]
Mg^{2+}	0.65—0.95	118—98	−(4.0—4.8)	<−2.7 [53, 67] *
Ca^{2+}	0.99—1.33	97—81	−(4.8—5.5)	<−2.7 [53, 67] *
Ba^{2+}	1.35—1.69	80—68	−(4.6—5.1)	<−2.7 [53, 67] *

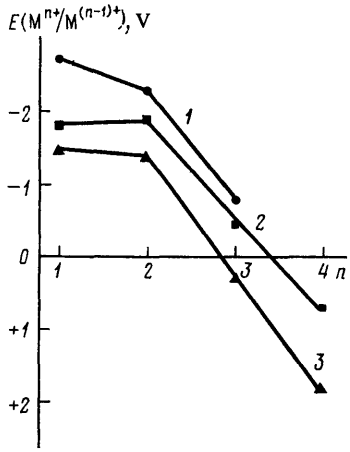
*Obtained from published data on the reactions of M^{n+} with e^-_{aq}, H, and organic radicals.

**Obtained from the dependence of E^0 on the ionic charge in a period and in a group (see Figure).

A study by pulse radiolysis of aqueous solutions of Zn^{2+} has shown[70] that e^-_{aq} reacts with Zn^{2+} to give Zn^+. On the other hand, H atoms reduce Zn^{2+} either very slowly or not at all. Hence we may assume that $E^0(Zn^{2+}/Zn^+)$ is smaller than −2.9 V in absolute value, and close to −2.3 V. There is some justification for assuming a value of −(2.4 ± 0.2 V), which is consistent with that calculated by Navon[119] [−(2.0 ± 0.4) V].

The Cd^{2+} ion is reduced by H and by the CO_2^- radical as well as by e^-_{aq}, but not by alcohol radicals, which have been shown to oxidise Cd^{2+}. It was concluded[72] that $E^0(Cd^{2+}/Cd^+) \cong$ 1.9 V. Potentials determined by this method for metals in aqueous solutions are listed in Table 4.

The variation of these potentials with the charge on the ion is shown in the Figure for the iso-electronic series of ions of metals in periods 4, 5, and 6. The first members of these series are copper, silver, and gold respectively. The redox potentials usually quoted for these metals[123] apply to reactions on a metallic electrode. In the case of metal atoms produced in the volume of the solution the potential must be corrected for the free energy of sublimation at room temperature ΔG^0_{sub}. By subtracting $\Delta G^0_{sub}/e$ (where e is the charge) from $E^0(M^+/M_{sol})$ we obtain the following values of $E^0(M^+/M_{at})$ for copper, silver, and gold respectively: −2.7, −1.8, and −1.5 V.



Redox potential of the $M^{n+}/M^{(n-1)+}$ couple against charge n for ions of metals in the 4th period (Cu, Zn, Ga, curve *1*), the 5th period (Ag, Cd, In, Sn, curve *2*), and the 6th period (Au, Hg, Tl, Pb, curve *3*); see also text.

We note from the Figure that within each subgroup (i.e. for equally charged ions) the quantity $E^0[M^{n+}/M^{(n-1)+}]$ increases regularly with the period number. Furthermore, within any one period (i.e. for iso-electronic ions) the $E^0[M^{n+}/M^{(n-1)+}]$ value increases strongly with the charge on the cation. For example, the metal ions in the electronic $^2S_{1/2}$ state with an unpaired electron in the s orbital which occur in the second subgroup (Zn^+, Cd^+, and Hg^+) are strong reducing agents, whereas those in the fourth subgroup (Sn^{3+} and Pb^{3+}) act as effective oxidising agents.

Having established the dependence of E^0 on the position of the element in its period and subgroup we are able to predict values of the potential. Thus $E^0(Hg^{2+}/Hg^+)$ should be −(1.4 ± 0.3) V, and $E^0(Pb^{4+}/Pb^{3+})$ should be +(1.8 ± 0.3) V. Since $E^0(Pb^{4+}/Pb^{2+}) = 1.7$ V,[123] we can calculate the potential $E^0(Pb^{3+}/Pb^{2+})$: +(1.6 ± 0.3) V. This value is consistent with the earlier conclusion that the potential must lie between 1.5 and 2.6 V, since at pH ~4 the Pb^{2+} ions are oxidised by OH radicals but they are oxidised extremely slowly (if at all) by HO_2 radicals[91].

Thus the postulated formation of metal ions in unusual and unstable states of oxidation (Zn^+, In^{2+}, Cd^+, Ga^{2+}, Sn^+, Tl^{2+}, Pb^{3+}, and many others) during the intermediate steps of electrochemical processes is confirmed by radiation-chemical experiments.

IV. REACTIONS OF METAL IONS IN UNUSUAL AND UNSTABLE STATES OF OXIDATION

Special features of the chemical reactions of metal ions in intermediate states of oxidation with each other or with other species present in solution may determine the kinetics

of the electrode process. Reactions of this type taking place in the volume of the solution have been studied by pulse radiolysis in recent years.

1. Disproportionation and Dimerisation Reactions

As for any other chemical reaction, the condition for the spontaneous occurrence of a disproportionation reaction is a gain in energy, i.e. ΔG must be negative. We shall consider two variants of the change in redox potential accompanying an increase in the degree of oxidation of the metal. In the first variant successive increases in the degree of oxidation require increasingly large amounts of energy, i.e. the removal of each electron requires a greater expenditure of energy than that of the previous electron. Under these conditions the redox potential increases monotonically. It is easy to see that in this case the disproportionation reaction

$$2M^{(n-1)+} \rightarrow M^{n+} + M^{(n-2)+} \qquad (20)$$

is impossible: the transition of $M^{(n-1)+}$ to the more highly oxidised state M^{n+} is impossible because it is less exothermic than the transition $M^{(n-1)+} \rightarrow M^{(n-2)+}$ is endothermic. In the second variant the transition $M^{n+} \rightarrow M^{(n-1)+}$ requires a greater expenditure of energy than the transition $M^{(n-1)+} \rightarrow M^{(n-2)+}$, i.e. $E^0[M^{n+}/M^{(n-1)+}] > E^0[M^{(n-1)+}/M^{(n-2)+}]$. In this case the disproportionation reaction is possible, since it leads to a gain of energy in the system ($\Delta G < 0$).

Table 5. Rate constants (litre mole^{-1} s^{-1}) of the recombination of metal ions in unstable states in aqueous solutions.

Reaction	pH	$2k \cdot 10^{9}2k$	References
$2Zn^{+} \rightarrow Zn^{0} + Zn^{2+}$	5—7	0.3	[70]
$2Cd^{+} \rightarrow Cd_2^{2+}$	5—7	3.0	[72]
$2Hg(I) \rightarrow Hg_2^{2+}$	1.9	8.0	[73]
ditto	2.0	4.5	[74]
»	4.3	5.2	[74]
»	2.4	4.2	[80]
»	4.8	3.5	[80]
»	9.8	8.6	[80]
»	10.2—10.8	11.5	[80]
$2HgOH \rightarrow Hg_2(OH)_2$	5—7	4.4	[76]
$2HgCl \rightarrow Hg_2Cl_2$	~7	8.0	[75]
$2HgBr \rightarrow Hg_2Br_2$	5—7	8.0	[78]
$2HgI \rightarrow Hg_2I_2$	5—7	5.0	[79]
$2HgCNS \rightarrow Hg_2(CNS)_2$	~7	6.0	[82]
$2HgCN \rightarrow Hg_2(CN)_2$	5—7	12	[77]
$2Ga(II) \rightarrow Ga(I) + Ga(III)$	2.4—3.0	8.1	[83,84]
$2In(II) \rightarrow In(I) + In(III)$	2.0—2.4	18	[83]
$2Tl^{2+} \rightarrow Tl^{+} + Tl^{3+}$	1 *M* $HClO_4$	0.12	[85]
ditto	»	0.19	[86]
$2TlOH^{+} \rightarrow Tl(I) + Tl(III)$	>5	5.0	[88]
ditto	»	3.7	[89]
$2Tl(OH)_2 \rightarrow Tl(I) + Tl(III)$	>8	6.3	[89]
$2Pb^{+} \rightarrow Pb^{0} + Pb^{2+}$	~5	0.17	[90]
$2PbH^{+} \rightarrow H_2 + Pb^{2+} + Pb$	~5	0.4	[90]
$Ag^{0} + Ag^{+} \rightarrow Ag_2^{+}$	5—7	k=5.9	[97]
$2Ag^{2+} \rightarrow Ag^{+} + Ag^{3+}$	5—7	3.8	[97]
$Tl^{0} + Tl^{+} \rightarrow Tl_2^{+}$	1 *M* $HClO_4$	k>100	[85]
$2Au^{0} \rightarrow Au_2$	1—2	5.0	[100]
$2AuCl_2 \rightarrow Au(I) + Au(III)$	1—2	1.4	[101]
$2Au(Cl_3)^{-} \rightarrow Au(I) + Au(III)$	1—2	0.86	[101]
$2Au(Cl_4)^{2-} \rightarrow Au(I) + Au(III)$	1—2	0.025	[101]
$2Pt(I) \rightarrow Pt^{0} + Pt(II)$	5—7	4.1	[102]
ditto	1—2	2.5	[102]
$2PtCl_4^{-} + Cl^{-} \rightarrow PtCl_4^{2-} + PtCl_6^{2-}$	~2	~1	[103]

Thus the condition for the disproportionation reaction is inversion of the potential energy levels of the system. By comparing the data in Table 4 with the potentials of the same metals in stable valence forms[123] we find level inversion for most of the metals in intermediate states of oxidation, i.e. we find conditions favourable to the fast disappearance of these ions by disproportionation reactions. Studies by the pulse radiolysis method of the disappearance of metal ions in unusual states of oxidation have shown that in most cases recombination is accompanied by disproportionation (Table 5).

An obvious exception to this rule are the metal ions having one unpaired electron in an *s* or *p* orbital and a low charge (0 or 1), such as Ag^0, Cd^+, and Hg^+ (whose electronic shell has the $(N-1)d^{10}Ns^1$ configuration), or Tl^0 and Pb^+ [$(N-1)d^{10}Ns^2Np^1$ shell]. These particles tend to form dimers in which the unpaired electrons are shared in σ_s or σ_{p_z} bonds. Thus, Cd^+ and Hg^+ ions undergo fast recombination, forming Cd_2^{2+} and Hg_2^{2+} ions. More surprisingly, Cd^+, Hg^+, and other ions of this type can also form unstable dimeric particles of the type of Cd_2^{3+}, Hg_2^{3+}, etc. in which the two atoms are joined by a one-electron bond (half a covalent bond). Thus it has been shown that Ag^0 atoms[97-99] and Tl^0 atoms[85-89] formed by the reduction of Hg^+ and Tl^+ ions (at concentration $>10^{-5}$ M) by hydrated electrons disappear by the pseudo-first order reaction

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ ,$$
$$Tl^0 + Tl^+ \rightarrow Tl_2^+ .$$

Direct evidence of the existence of the Ag_2^+ ion has been obtained[126-128] by ESR during the low-temperature (77 K) radiolysis of aqueous solutions of Ag^+. The effect of the initial concentration of Cd^{2+} ions on the disappearance of Cd^+ ions in aqueous solutions containing methanol has been studied[69] by pulse radiolysis. In 0.1 M solutions of Cd^{2+} the Cd^+ ions disappear by a pseudo-first order reaction, and a relatively long-lived absorption at 280 nm is observed after the absorption corresponding to Cd^+ ions has completely disappeared. No suggestion has been put forward[69] as to the nature of this absorption. One possibility is the reaction of Cd^+ with Cd^{2+} ions:

$$Cd^+ + Cd^{2+} \rightarrow Cd_2^{3+} . \qquad (21)$$

The formation of paramagnetic dimeric Cd_2^{3+} ions has been detected by ESR and optical spectroscopy methods in glassy aqueous solutions containing 0.1 M $CdSO_4$ gamma-irradiated at 77 K.[129,130]. The maximum optical absorption of Cd_2^{3+} in the solid matrix also occurs at ~280 nm. This ion is stabilised, apparently, by the collectivisation of one unpaired electron on the Cd—Cd σ bond. The rate constant of reaction (21) is much lower than that of the recombination of Cd^+ ions, and therefore reaction (21) is predominant only at high concentrations of Cd^{2+} ions. The existence of Hg_2^{3+} particles also has been established by ESR and optical spectroscopy methods in the low-temperature gamma-radiolysis of aqueous solutions of Ag^{2+}.[129,130].

Pb^+ ions are structurally iso-electronic with Tl^0, and therefore we can expect them to decay by the following reaction at high concentrations of Pb^{2+} ions in solution:

$$Pb^+ + Pb^{2+} \rightarrow Pb_2^{3+} .$$

There are no data on this reaction for liquid aqueous solutions, but the formation of Pb_2^{3+} particles during the low-temperature gamma-radiolysis of acidic or alkaline solutions of Pb^{2+} has been observed by optical spectroscopy[131,132].

For the Ga^{2+}, In^{2+}, Tl^+ and other ions the formation of dimers by recombination is not typical, possibly owing to the predominance of electrostatic repulsion. We have shown[83,84] that the loss of Ga^{2+} and In^{2+} is by a second-order reaction, involving disproportionation or interaction with OH radicals. The reactions of Tl(II) have been studied by pulse radiolysis of deaerated aqueous solutions containing Tl(I) and Tl(III).[85-89] Under these conditions the reactions between

e^-_{aq} and Tl(III), and between OH and Tl(I), yield only Tl(II). The latter have been shown to disappear by the reaction

$$Tl(II) + Tl(II) \rightarrow Tl(I) + Tl(III)$$

whose rate constant is strongly influenced by the presence of Cl^- ions in the solution[87], and also by the pH.[88,89] Pb^+ ions disproportionate with formation of Pb^0, which gives an absorption with $\lambda_{max} < 250$ nm.[90]

In the absence of acceptors of OH radicals the disappearance of transition metal ions in unstable states of oxidation (Mn^+, Co^+, Ni^+, etc.) is by a second-order reaction[62-67,93,94], evidently through interaction of the ions with each other and with the OH radicals. In the presence of organic compounds (acceptors of OH radicals) the univalent ions disappear by more complex reactions with formation of metal–organic intermediates.

2. Reactions with Inorganic Compounds

The effect of various additives on the kinetics of electrode processes, and in particular on metal corrosion, may be related to the reactions of these additives with metal ions in unstable states. The mechanism of the reactions of Zn^+, Cd^+, and Ni^+, and of many other metal ions, with various inorganic compounds (O_2, H_2O_2, N_2O, NO_2^-, NO_3^-, BrO_3^-, IO_3^-, etc.) has been studied by the pulse radiolysis method[65,69,70,133-138]. The metal ions have been shown to reduce these compounds at fairly high rates. The rate constants of the reactions of Zn^+, Cd^+, Ni^+, and Co^+ ions with some inorganic compounds in aqueous solutions are compared in Table 6 with the corresponding rate constants for the strongly reducing agents e^-_{aq} and H.

The ions can be arranged in the following series in order of decreasing reactivity towards inorganic oxidising ions: $Zn^+ \geq Cd^+ > Co^+ > Pb^+ > Ni^+ > Hg^+ \geq Cr^{2+} > Cu^+$. However, there are many exceptions: for example, with molecular O_2 the Ni^+ ion reacts almost as fast as Zn^+ and Cd^+, and Co^+ reacts even faster. The reactivity is determined by the electronic structure of the ions, by the nature of the acceptor, and by the specific mechanism of the oxidation–reduction reaction. In the Zn^+ and Cd^+ ions the electron is localised on the outer *s* orbital, with a substantial shift into the outer sphere. As a result, these ions are strong reducing agents. However, even between Zn^+ and Cd^+ we observe a decrease in reactivity towards several oxidising agents (see Table 6).

This decrease is even more marked in Hg^+. Thus the rate constant of the reaction between Hg^+ and O_2 was found[80] to be 4×10^8 litre mole^{-1} s^{-1}, i.e. almost an order of magnitude smaller than the values for Zn^+ and Cd^+. This decrease in reactivity in the Zn–Cd–Hg group is easily explained by noting that the stability of the lower states of oxidation for this group of metals increases in the same sequence, and that the Hg^+ ion is a fairly stable species (for example, in the dimeric form). In the transition metals an additional electron is accommodated in an inner *d* orbital, and as a result the ions are less active as reducing agents than the Zn^+ or Cd^+ ions.

We should stress that the reactivity sequence of the $M^{(n-1)+}$ ions is not the inverse of the reactivity sequence of M^{n+} towards e^-_{aq}. No definite correlation has been noted between the relative rate constants for the reactions of e^-_{aq}, H, and the $M^{(n-1)+}$ ions, suggesting that different mechanisms may apply to the redox reactions of these particles. For example, $M^{(n-1)+}$ (unlike e^-_{aq}) reacts very slowly with H_3O^+, or not at all. A possible explanation is that the redox potential of the $M^{(n-1)+}$ ions is too low, in general, to allow these ions to reduce H_3O^+.

Because of their technological importance we shall examine in somewhat greater detail the reactions between the lower-valency forms of metals and molecular oxygen in corrosion processes, and we shall discuss their mechanism. The reactions of Ag^0, Hg^0, Zn^+, Cd^+, Pb^+, Cu^+, Co^+, Ni^+, and Cr^{2+} with molecular O_2 have been studied by pulse radiolysis, and their rate constants have been measured (Table 7). With the exception of Cu^+, Ni^+, and Cr^{2+} these ions were found to be oxidised with formation of the O_2^- ion radical:

$$M^{(n-1)+} + O_2 \rightarrow M^{n+} + O_2^- \quad . \qquad (22)$$

Table 7. Rate constants for the oxidation of metals in unstable states by O_2 in aqueous solutions (litre mole^{-1} s^{-1}).

Species*	$10^{-8}\,k$	Species	$10^{-8}\,k$
Ag_2^+	3.8 [133]	Hg_2 (I)	11 [82]
Au^0	36 [100]	HgCl	10 [75]
Cd^+	30 [138]	Ni^+	18 [65,133]
Co^+	60 [138]	Pb^+	39 [65]
Cr^{2+}	1.6 [137]	$Pt(CN)_4^{3-}$	0.18 [102]
Hg^+	4.0 [80]	Zn^+	28 [65,133]

*For Cu^+ we have $k \leq 10^{-6}$ litre mole^{-1} s^{-1}.[133]

Table 6. Rate constants of the reactions of e^-_{aq}, H, and $M^{(n-1)+}_{aq}$ with inorganic compounds in aqueous solutions (litre mole^{-1} s^{-1}).

Compound	e^-_{aq}*	H*	Zn+	Cd+	Ni+	Co+
N_2O	$5.6 \cdot 10^9$	$1.2 \cdot 10^4$	$1.3 \cdot 10^7$ [133]	$2 \cdot 10^6$ [133]	$6.3 \cdot 10^6$ [133]	$1.0 \cdot 10^9$ [138]
	—	—	$3.7 \cdot 10^8$ [138]	$3.5 \cdot 10^8$ [138]	$9.1 \cdot 10^8$ [138]	—
H_2O_2	$1.23 \cdot 10^9$	$1.6 \cdot 10^8$	$1.8 \cdot 10^9$ [133]	$1.55 \cdot 10^9$ [133]	$4.3 \cdot 10^7$ [133]	$1.6 \cdot 10^9$ [138]
	—	—	$2.3 \cdot 10^9$ [138]	$2.2 \cdot 10^9$ [138]	$3.2 \cdot 10^7$ [138]	—
NO_2^-	$4.6 \cdot 10^9$	$6 \cdot 10^8$	$2.2 \cdot 10^9$ [133]	$2.0 \cdot 10^9$ [133]	$1.5 \cdot 10^8$ [133]	—
NO_3^-	$1.1 \cdot 10^{10}$	$1.7 \cdot 10^7$	$2.1 \cdot 10^9$ [133]	$3.5 \cdot 10^8$ [111]	$1.4 \cdot 10^6$ [133]	$1.8 \cdot 10^9$ [138]
ClO_3^-	$4 \cdot 10^8$	—	$\leqslant 3 \cdot 10^8$ [133]	—	—	—
BrO_3^-	$2.1 \cdot 10^9$	$1.95 \cdot 10^7$	$2.1 \cdot 10^9$ [133]	$1.25 \cdot 10^8$ [133]	$8.4 \cdot 10^6$ [133]	$7.1 \cdot 10^8$ [138]
IO_3^-	$7.7 \cdot 10^9$	$5.9 \cdot 10^7$	$3.6 \cdot 10^9$ [133]	$2.3 \cdot 10^9$ [133]	$2.2 \cdot 10^8$ [133]	$4.3 \cdot 10^9$ [138]
$S_2O_8^{2-}$	$1.1 \cdot 10^{10}$	$2.4 \cdot 10^7$	$1.3 \cdot 10^9$ [138]	$2.4 \cdot 10^9$ [138]	$1.5 \cdot 10^8$ [138]	$2.8 \cdot 10^9$ [138]
CrO_4^{2-}	$1.8 \cdot 10^{10}$	$1.6 \cdot 10^{10}$	$1.6 \cdot 10^{10}$ [138]	$1.6 \cdot 10^{10}$ [138]	—	—
MnO_4^-	$2.6 \cdot 10^{10}$	$2.8 \cdot 10^{10}$	—	$1.3 \cdot 10^{10}$ [65]	$7.5 \cdot 10^8$ [65]	$1.06 \cdot 10^{10}$ [65]
Cu^{2+}	$3.3 \cdot 10^{10}$	$6 \cdot 10^8$	$2.5 \cdot 10^8$ [133]	$1.2 \cdot 10^8$ [133]	$2.4 \cdot 10^7$ [133]	$4.1 \cdot 10^8$ [133]

*Rate constants given in Ref. 53.

For Ni^+ and Cr^{2+} the relatively stable complexes NiO_2^+ and CrO_2^{2+} were identified. The NiO_2^+ complex can be protonated (pK_a = 3.2), and both forms disappear by an intramolecular dissociation reaction giving Ni^{2+} and O_2^- or HO_2.[137-140] The interaction of Cu^+ with O_2 was found[137] to be either very slow or reversible (with a forward reaction much slower than the reverse reaction). The tabulated results show that the formation of stable complexes such as $MO_2^{(n-1)+}$ is characteristic of the transition metals with an unfilled inner *d* orbital. Complex formation involves the transfer of the unshared electron pair of the O_2 molecule to these levels.

The reaction of metals in unstable states of oxidation with H_2O_2 produces OH radicals[133,138]:

$$M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + OH + OH^- . \quad (23)$$

From the standpoint of corrosion processes reactions (22) and (23) can be interpreted as intermediate steps in the anodic dissolution of the metal. The O_2 and H_2O_2 are often treated as cathodic depolarisers. These species can be actively involved in the intermediate steps, and determine the rate of dissolution of the metal if the reactions take place directly on the anode.

The pulse radiolysis method has been used to prepare and investigate several metal ions in unstable states of oxidation showing strongly oxidising properties. One of these is the Cu(III) ion, which can oxidise the Br^- and NO_2^- ions, alcohols, and H_2O_2.[66,95] It has also been shown[95] that the Cu(III) ion can decompose water with formation of OH radicals by the reversible reaction

$$Cu(III) + H_2O \rightleftarrows Cu(II) + OH + H^+ .$$

The equilibrium constant calculated for this reaction at pH 3.65 (9.0×10^5 mole^{-1} litre) assumes that the redox potential of the Cu^{3+}/Cu^{2+} couple is only 0.2 V lower than the potential of the OH/H_2O couple.

3. Reactions with Organic Compounds

The effect of organic compounds on the kinetics of electrode (metal discharge and ionisation) reactions is usually ascribed to adsorption of these compounds on the electrode, formation of colloidal solutions, etc. Obviously, the participation of organic compounds in the intermediate steps by reaction with metal ions in unusual and unstable states of oxidation cannot be excluded. Reactions of this type have been studied by the pulse radiolysis method far less fully than reactions with inorganic compounds. It has been shown[141] that $M^{(n-1)+}$ is an effective reducing agent (by the one-electron mechanism) for aromatic dyes Ar:

$$M^{(n-1)+} + Ar \rightarrow M^{n+} + Ar^- .$$

The rate constants for the reaction of some ions with *p*-benzoquinone, menaquinone, and benzophenone in aqueous solutions at pH 5–6 are given in Table 8.

The mechanism of the interaction of metals with halogenated aliphatic acids has been shown[142] to include transfer of the halogen atom,

$$M^{(n-1)+} + XCH_2COOH \rightarrow [MXCH_2COOH]^{(n-1)+} ,$$

rather than electron transfer, i.e. the mechanism is the same as for the reaction with the H atom (but not for the reaction with e_{aq}^-).[143]

The Tl^{2+} and Ag^{2+} ions behave as "mild" oxidising agents, and they react with benzoic acid (BA) and methoxybenzoic acid (MBA) with very high rate constants (~10^9 litre mole^{-1} s^{-1}), forming short-lived anion radicals[144,145]:

$$BA(MBA) + Tl^{2+} (or\ Ag^{2+}) \rightarrow BA^{\cdot}(MBA^{\cdot}) + Tl^+ (or\ Ag^+).$$

Derivatives of benzoic acid are widely used as corrosion inhibitors: their effect on the corrosion process may be due at least in part to reactions of this type.

Table 8. Rate constants (10^{-9} *k*, litre mole^{-1} s^{-1}) of the reactions of metal ions with organic compounds in aqueous solutions at pH ~5–6.[141]

Compounds	Cd+	Co+	Ni+	Pb+	Zn+
Benzoquinone	4.8	5.1	0.23	4.1	4.8
Menaquinone	4.6	4.0	2.4	3.7	3.8
Benzophenone	1.0	2.5	—	—	2.5

Note. For the reaction of 2-methoxybenzoic acid (pH ~3) with Ag^{2+} and Tl^{2+} the *k* values are 1.2×10^9 and 6.8×10^8 litre mole^{-1} s^{-1} respectively[144,145].

4. Formation of Intermediate Complexes

Metal ions tend to form unstable complexes in one-electron redox reactions with radicals (H, OH, alcohol radicals, etc.) or with molecular compounds. For example, in the fast oxidation of Fe^{2+} by OH radicals the $FeOH^{2+}$ ion is formed[146]. The reaction of Fe^{2+} with HO_2 radicals, and the reaction of Fe^{3+} with H_2O_2, yield the $Fe^{3+}...HO_2^-$ complex[125], which is unstable and dissociates by a first-order reaction whose rate constant is independent of the pH (in the range pH 0–2.1) and of the concentration of O_2 and Fe^{3+}, but increases slightly with the concentration of Fe^{2+}. The latter effect shows that the decomposition of the complex is catalysed by Fe^{2+} ions, whose participation in the intermediate step of the reaction yields the bridging compounds

$$[Fe^{3+} \ldots HO_2^-] + Fe^{2+} \rightarrow [Fe^{3+} \ldots HO_2^- \ldots Fe^{2+}] \rightarrow Fe^{2+} + Fe^{3+} + HO_2^- .$$

Other transition metal ions (M^{n+}) in aqueous solution react with O_2^- ion radicals to give $MO_2^{(n-1)+}$ complexes. For example, the species MnO_2^+ has been detected[93] by the pulse radiolysis method in aerated aqueous solutions of $Mn(ClO_4)_2$. The equilibrium constant of the reaction

$$MnO_2^+ \rightleftarrows Mn^{2+} + O_2^-$$

was found to be $(1.5 \pm 0.6) \times 10^4$ M^{-1}. As stated above, Ni^+ and Cr^{2+} also interact with molecular oxygen to form the intermediate complexes NiO_2^+ [137,138] and CrO_2^{2+}.[139,140] We must assume that these same complexes are formed by the reaction of Ni^{2+} and Cr^{3+} with the O_2^- ion radical.

Hydrogen atoms react with Fe^{2+} with formation of the unstable hydride FeH^{2+} which disappears by the reaction

$$H^+ + FeH^{2+} \rightarrow Fe^{3+} + H_2$$

with a rate constant of ~1×10^4 litre mole^{-1} s^{-1}.[125] Apparently hydride formation is characteristic also of other transition metals (Co^{2+}, Ni^{2+}, etc.) reacting with H atoms. These metals have an unfilled inner *d* shell. On the other hand, if the metal has a filled inner *d* shell (Hg, Cd, Zn, etc.) these reactions are not observed.

Our results are consistent with the traditional classification of metals into two groups with respect to their electrochemical properties[147,148]. The first group (metals of the platinum group and iron) has a high heat of adsorption of hydrogen atoms, and the rate of evolution of molecular hydrogen from these metals is limited by the chemical

dimerisation reaction of the hydrogen atoms. A likely explanation of these properties is the formation of fairly strong chemical bonds with the metal atoms on the surface of the electrode. The second group of metals (Hg, Cd, Zn, etc.) is characterised by weaker adsorption bonds with hydrogen atoms. The rate-limiting step in the evolution of hydrogen is a slow discharge process. We may assume that the hydrogenation of metals produced by various electrode processes is due to the step mechanism of the discharge (ionisation) reaction, involving the formation of hydride complexes during the intermediate steps.

Metals in unusual states of oxidation react with organic (e.g., alcohol) radicals to form unstable metal–organic compounds[69,72,77,94,149]:

$$M^{(n-1)+} + R \rightarrow MR^{(n-1)+} .$$

These compounds usually show characteristic optical absorption bands in the u.v. region of the spectrum. The life time of the intermediate complexes is determined by the rate of hydrolysis. For example, the cadmium-organic compounds CdR^+ decompose by the reaction

$$CdR^+ + H^+ \rightarrow Cd^{2+} + RH$$

with rate constants 161 s^{-1} for R = $(CH_3)_2COH$ and 257 s^{-1} for R = CH_3CHOH.[72] Nickel–organic compounds are more stable. Their lifetime is ~1 s when R is a methanol or ethanol radical, and even longer for more complex radicals[94]. Nickel compounds are easily oxidised in the presence of H_2O_2. In experiments with aqueous solutions of 2-methyl-2-propanol it was shown[94] that the resulting organic radicals react with Ni^+ to form isobutene:

$$Ni^+ + CH_2C(CH_3)_2OH \rightarrow Ni^{2+} + CH_2{=}C(CH_3)_2 + OH^- .$$

The rate constant of this reaction is 3×10^9 litre $mole^{-1}$ s^{-1}.

The formation of unstable metal–organic compounds has been demonstrated by pulse radiolysis for the reaction of alcohol radicals with Zn^+,[69] HgCN,[77] and the Cr^{2+} ion[149]. Chromium–organic compounds are more stable to hydrolysis than nickel–organic compounds. For example, the compound $CrCH_2OH^{2+}$ decomposes in water with a rate constant of ~7×10^5 s^{-1}.[149]

5. Reduction to Metals

The chemical reduction to a metal from aqueous solutions of its salts must occur through a number of intermediate steps in which the metal displays unusual valency forms. Radiation-chemical methods (and, in particular, the pulse radiolysis method) have proved very useful in studies of the reduction mechanism of the cations and of the nucleation of the metal in aqueous solutions. The chemical steps in the reduction are fairly specific for the individual cations (Ag^+, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pt^{2+}, etc.) and are usually complex. For example, the Ag^0 atoms produced by a 2 μs pulse of electrons on a 10^{-5} M solution of Ag^+ saturated with argon and containing 0.1 M CH_3OH disappear in a few tens of microseconds by reacting with the Ag^+ ions to form Ag_2^+. The disappearance of the latter is accompanied by the formation of two new particles:

$$Ag_2^+ + Ag^+ \rightarrow Ag^{2+} + Ag_2 .$$

The relatively slow removal of Ag_2 by a pseudo-first order reaction is markedly influenced by the concentration of Ag^+. The reaction is assumed to be

$$Ag_2 + Ag^+ \rightarrow Ag_3^+ .$$

After a few milliseconds we observe a long-lived optical absorption at 390 nm, assigned[97] to the association of Ag_3^+ particles to form agglomerates of metallic silver:

$$Ag_3^+ \rightarrow \text{metal}.$$

These results show that even an apparently simple process such as the nucleation of atomic silver in an aqueous solution of Ag^+ can be complex and involve a number of steps. The reduction of a cation to the metal includes a large number of intermediate steps: one-electron reduction of the cation, disproportionation or dimerisation of the reduction product, cluster formation and growth of the clusters to give massive metal particles. The radiation-chemical reduction of the cations and formation of a metallic deposit is most effective in deaerated, neutral aqueous solutions of the salts containing organic additives such as formate ions, alcohols, etc. The latter act as acceptors of OH radicals, thus preventing back oxidation of the metal ions reduced by solvated electrons or by H atoms.

The formation of metal granules by pulsed irradiation of aqueous salt solutions has been studied in more detail for the cadmium deposition system. It was found[71] that the optical absorption due to the short-lived Cd^+ and Cd_2^{2+} ions (which are the precursors of the metal atoms) disappears ~10^{-4} s after the application of the electron pulse, and the solution becomes fully transparent. The transparent state persists for ~0.1 s, after which a new absorption occurs over the whole of the optical region, increasing to a constant value in ~10 s. The optical density D increases with the fourth power of the wavelength in the u.v. region, a characteristic property of media containing suspended matter which scatters rather than absorbs light.

The effect of the ionic strength of the solution on the rate of formation of finely divided metallic cadmium suggests[72] that the metal is being deposited from complex cadmium clusters having an effective charge of +5.5. The time for nucleation and growth of the metal grains decreases as the supersaturation of the solution increases (i.e. in proportion to the dose of radiation per pulse). A few minutes after the appearance of turbidity in the solution, precipitation of the metal begins, accompanied by a decrease in absorption in the u.v. region of the spectrum and increased absorption at longer wavelengths[72], caused by the increase in size of the metallic agglomerates. The precipitation curves are accurately described by a pseudo-first order equation with respect to Cd^0 concentration, with a rate constant of $(5 \pm 2) \times 10^4$ s^{-1}.[71]

Similar effects have been observed in the formation and deposition of metal by the pulse radiolysis of aqueous solutions of Ag^+ and its ammine complex[97,98], and also of Ni^{2+}.[94] It has been shown[71] that under identical pulsed irradiation conditions the induction period t_0 (time of nucleation) of many salt solutions calculated from the experimentally observed delay in the appearance of turbidity depends on the nature of the cation and decreases in the sequence $Pb^{2+} \cong Cd^{2+} \gg Zn^{2+} > Ni^{2+} > Co^{2+}$.

6. Metal Dissolution

The stability of a metal and its rate of dissolution in aqueous or other solutions is determined by its electrode potential. The rate of dissolution decreases if the potential is shifted towards more negative values, and becomes zero when a definite value of the potential is reached. Alkali and alkaline-earth metals dissolve in water at approximately constant rates. Since their redox potential

is more negative than −2.9 V we can expect hydrated electrons to be formed during their dissolution.

The possibility of forming hydrated electrons by the reaction between sodium amalgam and water has been demonstrated[150,151] by the acceptor competition method:

$$Na\,(Hg) + H_2O \rightarrow Na^+ + e^-_{aq} \quad .$$

This conclusion was based on the detection of N_2 as the main reaction product in an aqueous solution containing N_2O and CH_3OH, by the reaction

$$N_2O + e^-_{aq} \rightarrow N_2 + O^-$$

rather than H_2, expected to be formed by the reaction

$$CH_3OH + H \rightarrow H_2 + CH_2OH$$

if the H atom had been a primary product of the dissolution of sodium amalgam. On the other hand, experiments with pure sodium suggest that several mechanisms contribute to the dissolution of this metal in water (see Ref.53).

It has been suggested[152,153] that the generation of e^-_{aq} can be induced by cathodic polarisation of an electrode. The same conclusion was reached from the observation of a substantial decrease (by ~35%) in the yield of H_2 from a smooth platinum electrode on adding N_2O to a neutral solution. On the other hand the presence of CH_3OH had no effect on the relative yields of N_2 and H_2. These results convincingly demonstrate the participation of an electron in the formation of N_2. However, there is reason to believe that the reaction involving the electron takes place directly on the cathode (with adsorbed N_2O), and not in the bulk of the solution (as it would if the hydrated electron was involved).

The important role of the e^-_{aq} species in the chemical dissolution of metals has been stressed[154], and used as a basis for discussing instability criteria. The first step in the dissolution was assumed to be the formation of an uncharged activated complex,

$$M + H_2O \rightarrow (MH_2O)^* \quad .$$

In the second step this complex dissociates into e^-_{aq} and the metal ion:

$$(MH_2O)^* \rightarrow M^{n+} + ne^-_{aq} \quad .$$

Neither of the steps is electrochemical, since no charge is transferred across the metal–solution interface, and therefore the rate of the overall process should be independent of the potential. However, the rate of dissolution can be expected to depend on the pH, on the nature of the surface, and on the overall current density, and these expectations have been confirmed experimentally.

According to Antropov[154] the condition for self-dissolution of the metal is

$$S_M + \sum_1^n I_{n+} \leqslant A^{H_2O}_{M^{n+}(r)} + nA^{H_2O}_{e^-(r)}$$

where S_M is the free energy of sublimation of the metal, $\sum_1^n I_{n+}$ is the sum of the ionisation potentials (from 1 to n) of the metal, and $A^{H_2O}_{M^{n+}(r)}$ and $A^{H_2O}_{e^-(r)}$ are the real free energies of hydrated M^{n+} ions and electrons respectively. This criterion has been tested for alkali and alkaline-earth metals. However, direct experimental evidence of the formation of e^-_{aq} during cathodic polarisation of the electrode or during chemical dissolution of the metals in water has not yet been obtained.

A detailed critical analysis of these hypotheses is given in Refs.155 and 156. The probability of thermionic emission of an electron into the aqueous solution is believed, on theoretical grounds[157], to be very low, and the contribution from this mechanism to the cathodic currents is probably negligible, even at high negative potentials. On the other hand, the probability of ordinary cathodic reactions (electron transfer to adsorbed ions or molecules) is quite high at these potentials.

Nevertheless the possible formation of e^-_{aq} during the reaction of some metals (such as alkali or alkaline-earth metals) with water cannot be excluded: this is shown, for example, by the reported[158] formation of e^-_{aq} during the condensation of finely divided sodium and potassium with water vapour on a surface cooled to 77 K. We should also note that the cathodic generation of solvated electrons was detected experimentally in solvents which are stable at large negative potentials (hexamethylphosphotriamide, liquid ammonia, some amines, etc.; see review in Ref.159).

Dependence of the rate of corrosion of metals on the nature of the anions suggests that the anions are directly involved in the reaction. According to Kolotyrkin and coworkers[49–51] the anodic dissolution of metals takes place through the formation of a complex the metal (M) and a ligand (L):

$$M + L \rightleftarrows ML \quad .$$

The adsorption of ligands lowers the electronic work function and accelerates the corrosion of the metal:

$$ML \rightarrow ML^{n+} + n\,e^- \quad .$$

The dissolution of iron in acid solutions is now believed[51] to take place through the formation of the unstable intermediate FeOH, in which the iron displays the unusual state of oxidation +1. Evidently, the formation of unstable coordination compounds of the ML^{n+} type during the intermediate stages of the electrochemical or chemical dissolution of metals is a fairly common phenomenon. In the first section of this review we had discussed experimental evidence for the formation of metals in unusual states of oxidation during electrochemical reactions (for example, Zn^+, In^{2+}, Tl^{2+}, etc.). Evidently, in many cases the disproportionation (or dimerisation) of these species is energetically more favourable than further ionisation (see Section IV, Pt.1).

It is important to note that when $E^0[M^{n+}/M^{(n-1)+}] \lesssim E^0(e^-_{aq}/\frac{1}{2}H_2)$ the ionisation of $M^{(n-1)+}$ in aqueous solutions (especially at high pH values) can yield a hydrated electron:

$$M^{(n-1)+}_{aq} \rightarrow M^{n+}_{aq} + e^-_{aq} \quad .$$

The possibility of these reversible reactions has been examined[160] in the case of the interaction of e^-_{aq} with Zn(II) and Al(III) in aqueous solutions of alkalis. More recently it has been shown by the pulse radiolysis method[161,162] that the rate of disappearance of e^-_{aq} decreases (as expected) as the concentration of Zn(II) increases. This effect was explained by postulating the equilibrium reaction

$$e^-_{aq} + Zn\,(OH)_4^{2-} \rightleftarrows Zn\,(OH)_3^{2-} + OH^- \quad . \qquad (24)$$

The equilibrium constant of this reaction for a 3 M solution of LiOH is 0.1 M^{-1}, i.e. the E^0[Zn(II)/Zn(I)] value under these conditions is only ~0.09 V more positive than $E^0(H_2O/e^-_{aq})$.

The redox potentials of the Zn^{2+}/Zn^0 and Al^{3+}/Al^0 couples in acid solution are −0.76 and −1.66 V respectively[123]. In an alkaline medium these metals exist as hydroxo complexes, and the potentials of the $Zn(OH)_4^{2-}/Zn^0$ and $Al(OH)_4^-/Al^0$ couples are more negative (−1.22 and −2.35 V respectively[123]). It follows that the potential of the $Zn(OH)_4^{2-}/Zn(OH)_4^{2-}$ couple also suffers a negative shift [as compared with the potential of the Zn^+/Zn^{2+} couple, ~(−2.4 V)], and thus becomes comparable with $E^0(H_2O/e^-_{aq})$. These considerations allow us to predict reversible reactions of the type of (24) not only for hydroxo complexes of metals in alkaline media but also

for cyano and other complexes in neutral solutions. The latter complexes also experience a large negative shift of the potential[123], and the following condition may apply:

$$E^0(MX_{m-n}^{n-}/MX_{n-n}^{(n+1)-}) \lesssim E^0(e_{aq}^-/{}^1/_2H_2)$$

* *
*

Thus the advances in radiation-chemical (and, in particular, in pulse radiolysis) techniques made in the last 15 years have markedly influenced the new developments in the chemistry of metals in unusual and unstable states of oxidation. The discovery of these short-lived particles, the study of their properties, and the formulation of rules governing those properties will undoubtedly stimulate further developments in the chemistry of the intermediate steps of redox reactions, involving metals in unstable valence forms. Of course, the preparation of various ions in unusual states of oxidation by radiation-chemical methods cannot in any way be taken as evidence for the formation of those same ions during electrochemical reactions. However, the generation of data on the properties of these intermediate particles should greatly assist the study of the mechanism of multi-step electrochemical processes.

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