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Kinetics and Mechanism of Electrode Reactions of Metal Complexes in Aqueous Electrolyte Solutions

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The kinetics and the mechanism of electrode reactions of metal complexes, which include rapid processes of reorganisation of outer and inner coordination spheres, are examined, and criteria for distinguishing between outer-sphere and inner-sphere mechanisms of the electrochemical stage are discussed. Published data provide the basis for a consideration of the mechanism of simple electrode reactions, uncomplicated by change in the composition of the inner coordination sphere of the reactant complexes, and of more complicated reactions, in which the composition of the inner coordination sphere of the complexes is partly or completely changed. Consideration is given mainly to electrode reactions of complexes containing electrochemically inactive ligands. A list of 258 references is included.

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I. INTRODUCTION

A central aspect of the kinetics of electrode processes, which is also the least studied, is the mechanism of the electrochemical stages, as well as the relation between the kinetic parameters of these stages and the properties of the reactant species, the electrode, and the medium. Discussion of the nature and the mechanism of the electrochemical and other stages of electrode reactions (in particular choice of a model for the transition state) must take into account available information on the kinetics and the mechanism of similar homogeneous reactions. The fruitfulness of such an approach has been noted several times [1-8] and has been confirmed experimentally [4,9-11] on several reactions of metal complexes. The relation between the rate constants of homogeneous and heterogeneous electron-transfer reactions of metal complexes has been discussed by several workers [5,12-17]. However, the vast quantity of data available on homogeneous reactions of metal complexes and their mechanism [18-30] are relatively little utilised in electrochemical kinetics. Nevertheless, such an approach is especially promising for studying the mechanism of electrode reactions of metal complexes, in particular for identifying the electrochemically active complexes directly involved in the electrochemical stage and the character of their interaction with the electrode [31]. One aim of the present Review is to illustrate this principle. The formal kinetics of the electrode reactions of metal complexes and diffusion hindrances have been discussed many times [4,32-34] and will not be considered in detail here. Nor will kinetic and catalytic currents be discussed, for they have been surveyed in monographs [33-36] and several reviews [4,32,37-39].

Attention will be paid mainly to electrode reactions of metal complexes complicated by outer-sphere association or by rapid reorganisation of the inner sphere, which may occur particularly in the adsorption of complexes on electrodes. Since it is important to compare the kinetic parameters of a cathodic process with those of the opposite anodic process in order to obtain sound conclusions as to the nature and mechanism of electrochemical stages of complicated electrode reactions [40-43], considerable attention will be paid to work on these lines. The Review discusses electrode reactions occurring in aqueous solutions and involving metal complexes formed by electrochemically inactive inorganic and simple organic ligands.

II. STATE OF METAL COMPLEXES IN ELECTROLYTE SOLUTIONS

Most investigations on homogeneous and heterogeneous reactions of metal complexes are conducted in the presence of foreign electrolytes. In concentrated solutions of so called "inert" salts the complexes exist as complicated aggregates [44-49], containing various numbers of ligands X, cations B and anions A of the supporting electrolyte, and water molecules. The total concentration of the frequently studied singly charged complexes MX_i, in which one central metal ion M^{Z+} is accompanied by i ligands X, can be expressed†

$$[MX_i] = \sum_x \sum_y \sum_z [MX_i(B)_x(A)_y(H_2O)_z], \qquad (1)$$

where the summation covers both inner-sphere and outer-sphere species. Published [50] concentration stability constants of complexes $\beta_i = [MX_i][M^{Z+}][X]^{-i}$ are effective quantities describing complicated equilibria between various associated forms and species from which they are produced [44-49]. The diversity and varying reactivity of the complexes present in solutions are responsible for the complicated character of their reactions. Study of the mechanism of the latter should utilise the greatest possible variety of methods for determination of thermodynamic and kinetic parameters of the processes. Outer-sphere association can be conveniently studied on highly charged

†The possible charge on the ligands and the metal complexes is omitted for simplicity. Henceforward water molecules forming part of the metal complexes will sometimes not be written out.

inert complexes of the type $Co(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$, in which substitution of outer-sphere ligands does not take place during a measurement[46-49].

Aggregates such as ion-pairs or outer-sphere complexes are formed by inner-sphere complexes with ions of the supporting electrolyte or with free ligands[45-51]. The term "ion-pairs" is applied to aggregates formed by the interaction of two oppositely charged ions, between which an interlayer of water molecules may be retained. If this is absent, so called "contact ion-pairs" are formed, whose stability may be determined not only electrostatically but also by specific donor–acceptor interactions. Contact ion-pairs in which a negatively charged inner-sphere complex is directly bound to a cation of the supporting electrolyte are essentially doubly charged complexes[47,48]. If a positively charged inner-sphere complex adds one or more anions of the supporting electrolyte or neutral ligands, outer-sphere complexes are formed, often characterised by specific interactions between outer and inner coordination spheres[45-49].

III. ELECTRODE REACTIONS OF METAL COMPLEXES AND THEIR STAGES

Electrode reactions occurring on electrodes are described by equations containing the initial species and the final products. Frequently only the inner sphere is taken into account in writing down the electrode reactions of metal complexes: i.e. electrochemical and inner-sphere chemical‡ stages are considered. This is partly due to insufficient study of outer-sphere association processes, which play an important part in many homogeneous[5,26-28] and heterogeneous[4,31] reactions, especially those involving highly charged species. Hence electrochemical kinetics must consider not only inner-sphere but also outer-sphere stages—the formation and break-down of ion-pairs and outer-sphere complexes, the rearrangement of outer-sphere solvent molecules, and other processes that may take place either in the bulk of the solution or at the electrode surface.

The isolation of electron-transfer stages from the overall reaction in the kinetic study of electrode and homogeneous redox reactions of metal complexes is based essentially on the Franck–Condon principle and Libby's principle of symmetry which follows from it[52,53]. According to the latter the electron-transfer stage involves complexes the structure of whose heavy particle (atomic nuclei) is intermediate between those of the ground states of oxidised and reduced reactant forms. Outer-sphere and inner-sphere electrochemical stages are distinguished by analogy with homogeneous electron-transfer reactions[4,5,7,31]. If surface atoms of the metal electrode are separated from inner-sphere ligands of electrochemically active complexes by one or more ligands (solvent molecules), an outer-sphere mechanism operates. If the surface metal atoms are directly bound to an inner-sphere ligand (ligands) of the electrochemically active complex or to its central ion, an inner-sphere mechanism operates[31] (e.g. in the ionisation of metal atoms).

‡Chemical stages of electrode reactions are those involving the rupture and formation of chemical bonds but not those involving charge transfer, which would entail interconversion of oxidised and reduced forms. The adsorption of ions and molecules on electrodes, involving partial transfer of charge, can be regarded as heterogeneous chemical stages.

Both inner-sphere and outer-sphere mechanisms may operate in the electrical reduction of complexes. With a slow electrochemical stage the rate of reduction of mononuclear complexes of a metal can in general be expressed

$$i = \sum_{j=1}^{n} k_j^0 [MX_j]_s \exp\left[-\frac{\alpha_j F(\varphi - \psi_1)}{RT}\right], \qquad (2)$$

where $[MX_j]_S$ is the concentration of electrochemically active complexes in the inner or outer Helmholtz planes, α_j is the apparent transfer coefficient, ψ_1 is the potential at the electrical centre of a reactant species in the transition state[54,55], φ the electrode potential relative to that of the reference electrode, and k_j^0 the rate constant. Under certain conditions, depending primarily on the nature of the reactant complexes, the material of the electrode and its potential, both inner-sphere and outer-sphere mechanisms may operate. If one type of complexes, e.g. the highest complexes MX_n, take part in the outer-sphere electrochemical stage, Eqn. (2) is converted into Frumkin's equation[54]

$$i = k[MX_n] \exp\left(-\frac{z_0 F \psi_1^0}{RT}\right) \exp\left[-\frac{\alpha F(\varphi - \psi_1^0)}{RT}\right], \qquad (3)$$

where $[MX_n]$ is the bulk concentration of the complex MX_n and z_0 is its charge, while ψ_1^0 is the potential in the outer Helmholtz layer. Diffusion hindrances are assumed to be absent.

It is advisable to use the following criteria to distinguish between outer-sphere and inner-sphere mechanisms of the electrochemical stage[7,31]: (i) the effect of the structure of the double layer on the kinetics of the electrochemical reaction[54] is based on the use of Eqn. (3), which is valid for an outer-sphere mechanism and is widely employed in electrochemical kinetics[35,55]; (ii) a low rate of substitution of inner-sphere ligands in the complex and of species directly adsorbed on the electrode§ (in comparison with the rate of the electrochemical stage) indicates an outer-sphere mechanism; (iii) the kinetic parameters of the electrochemical stage should be more greatly dependent on the electrode material with an inner-sphere than with an outer-sphere mechanism, for specific interaction of reactant complexes with the electrode takes place with the former mechanism; and (iv) larger negative entropies of activation should be observed with an outer-sphere than with an inner-sphere mechanism (for similar reactions).

The last three criteria resemble those used in studying the mechanism of homogeneous electron-transfer reactions[6]. However, it must be stressed that conditions of formation of the transition state differ significantly between homogeneous and heterogeneous electron-transfer reactions involving inert complexes. If rapid electron transfer occurs between two inert complexes in solution, an outer-sphere mechanism is functioning[5,28,57]. With fast electrochemical reactions of inert complexes, however, both outer-sphere and inner-sphere mechanisms may operate, because of the lability of most ions and molecules (including solvent molecules) adsorbed directly on metal electrodes. Such a conclusion may be drawn from the generally sharp increase in mobility of inner-sphere ligands with decrease in degree of oxidation of the central metal ion, especially with singly charged cations[19,28]. Yet the formal charge per metal atom on the surface of a metal

§Ions and molecules directly adsorbed on the electrode surface can be regarded as the "inner coordination sphere of the electrode"[56], and adsorbed species as inner-sphere ligands.

electrode, at the usual departures from the zero-charge point, is a small fraction of unity. A very low mobility has been established for oxygen adsorbed on platinum in the first and second monolayers in the range of potentials of the oxygen portion of the charging curve[58,59].

Two groups of electrode reactions can be distinguished: (i) in simple reactions the composition of the inner sphere of the complexes remains unchanged; (ii) complicated reactions involve change in the composition of the inner sphere. Assignment of an electrode reaction to a particular group may be based on the dependence of the equilibrium potential of the system on the concentration of an inner-sphere ligand (ligands) or on chemical analysis. If the equilibrium potential can be measured, its dependence on the concentration of inner-sphere and outer-sphere species can be used to establish the composition of the complexes present in solution and also the optimum conditions for kinetic measurements[60].

The usual division of electrode reactions of metal complexes into those involving and not involving chemical stages[4,33,34] is less convenient for the discussion of experimental results, since it requires a knowledge of the reaction mechanisms, which are often dubious and may vary with the experimental conditions.

IV. ELECTRODE REACTIONS UNACCOMPANIED BY CHANGE IN THE COMPOSITION OF THE INNER SPHERE

The change in the charge of an inner-sphere complex resulting from an electrode reaction leads to rearrangement of the outer coordination sphere. Hence the rates of the electrode reactions may be determined by the rearrangement of outer-sphere aggregates[7,31] and the structure of the surrounding solvent[12-15,61], by the structure of the electrical double layer, and by adsorption phenomena[35,55], as well as in certain cases by rearrangement of the structure of the inner sphere of the complex[4]. As a consequence of the high rates of outer-sphere processes[62,63] rearrangement of the outer sphere takes place under reversible conditions.

The composition and the stability of outer-sphere aggregates present in solution must be known in studies of the reaction mechanism of charged complexes. Such information is obtained by investigating the equilibria of the corresponding bulk processes, in particular by electrochemical methods[46-49,64-67]. The study of bulk outer-sphere processes is important not only for establishing the stoichiometry of the overall electrode reaction but also for assessing possible similar outer-sphere interactions, which may take place in the double layer and precede the electrochemical stage.

The reactivity of outer-sphere aggregates often differs significantly from that of the unassociated species[68-70]. One reason is provided by the different conditions of solvation (hydration) of the reactant species. In non-contact ion-pairs, which appear e.g. on the interaction of trebly and less strongly charged anionic complexes with hydrated cations of alkali and alkaline-earth metals[46], the electric field of the ion-pair probably[70] exerts an ordering influence on the water molecules surrounding the inner-sphere complex. This leads to inhibition of the activation of complexes such as $IrCl_6^{3-}$ [71-74] and $IrBr_6^{3-}$ [75,76] by hydrogen ions and ions of alkali and alkaline-earth metals, the effect increasing with the atomic mass and the cationic charge.

Similarly, outer-sphere ions may also influence the rates of electrochemical stages[70]. If the charge on an inner-sphere complex increases as a result of an electrochemical reaction, prior association of the initial complex with an oppositely charged ion should increase the rate of the electrochemical stage, since the structure of the solvent in the ion-pair will approach that of the solvent surrounding the reaction product. The cathodic reduction of anions on negatively charged electrode surfaces provides an example of such reactions, the rate increasing in the sequence $Li^+ < Na^+ < K^+ < Cs^+$ and with increase in the cationic charge of the supporting electrolyte[77-85,33-35,55].

If the charge on an inner-sphere complex ion decreases as a result of an electrochemical reaction, prior association of the initial complex with an oppositely charged ion should inhibit the electrochemical stage, since the structure of the solvent surrounding the "free" complex is closer to the structure of the reaction product (in comparison with the ion-pair). An example of this type of reaction is the cathodic reduction of inner complexes such as $Co(NH_3)_6^{3+}$, whose reactivity diminishes when they form ion-pairs with anions of the supporting electrolyte[4,86-89]. The need to allow for orientation of water molecules surrounding ion-pairs in the transition state of an electrochemical reaction, and the influence of this factor on its activation energy, have been noted previously[90]. The structure of the electrical double layer greatly affects the rate of the cathodic reduction of negatively charged complexes and other anions[55,77-85]. Several recent publications[91-94] have discussed the influence of this structure on the kinetics of electrode reactions complicated by the formation of ion-pairs in solution.

Iron(III)–Iron(II) System

With sufficiently large negative surface charges, at which anions are electrostatically repelled by the electrode, the polarograms for the reduction of $Fe(CN)_6^{3-}$ at a dropping mercury electrode in solutions containing alkali-metal cations obey Eqn. (3) and the corrected Tafel relation which follows from it[95,96]. The linear sections of these corrected relations yielded transfer coefficients α of 0.16, 0.17, and 0.19 for lithium, potassium, and caesium ions respectively[95]. The corrected Tafel relations for the reduction of $Fe(CN)_6^{3-}$, as for that of $S_2O_8^{2-}$, are independent of the nature of the negatively charged electrode[85,97]. It has recently been shown[98] that the corrected relations for the cathodic reduction of $Fe(CN)_6^{3-}$ coincide on negatively charged bismuth, cadmium, lead, and indium. Together with earlier results[85] this demonstrates the absence of specific adsorption of the reactant complexes, i.e. an outer-sphere mechanism of the electrochemical stage.

The effect of the nature of cations of the supporting electrolyte on the rate of cathodic reduction of anions is attributed[78-82] to specific adsorption of the cations on the electrode. The adsorbed cations attract the reducible anions: i.e. they act as "bridges", diminishing the electrostatic repulsion of the anions by the negatively charged electrode surface and thereby accelerating the process.

Alkali-metal cations exert a similar accelerating effect[99] in 1 M solutions of their chlorides when hexacyanoferrate complexes undergo charge transfer on a positively charged platinum electrode. The exchange current density i_0 of the complex system increases by factors of ~3 and 15 in passing from 1 M lithium chloride to 1 M sodium chloride and from the latter to 1 M potassium chloride respectively: i.e. effects are observed analogous to those occurring on negatively charged electrode surfaces (at cation concentrations of $\sim 10^{-3}$ M).[95,96]

The great effect of the nature of the alkali-metal cation in 1 M solution on the rate of charge transfer between negatively charged iron complexes on platinum (Table 1) is probably due mainly to differences in the nature of the outer-sphere aggregates of oxidised and reduced forms present in solution. According to published results [46,100,101] the association of hexacyanoferrate(II) complexes with alkali-metal cations is accompanied by breakdown of the hydrate sheath of the cation, which does not occur with the oxidised complex. Thus among alkali-metal ions lithium ions form the most stable aggregates with hexacyanoferrate(II) ions, and the least stable with hexacyanoferrate(III) ions, since the radius of the hydrated cation increases on passing from caesium to lithium [102]. In accordance with this the concentration of electrochemically active iron hexacyanide complexes, which according to the Franck–Condon principle should have the same structure of inner and outer coordination spheres, will increase from lithium to sodium and then to potassium ions. This is obviously responsible also for the increase in rate constant k_S (in exchange current density) in the hexacyanoferrate system on passing from 1 M lithium chloride to 1 M potassium chloride (Table 1). This explanation is consistent also with the smaller effect of the nature of the alkali-metal cation on the rate of charge transfer between $Fe(CN)_5X^{2-}$ and $Fe(CN)_5X^{3-}$ complexes ($X = NH_3$, H_2O) [99] (Table 1), which, like other doubly and trebly charged complexes, probably associate with hydrated alkali-metal ions. The stability of the resulting ion-pairs increases in the sequence $Li^+ < Na^+ < K^+$. [46]

Table 1. Standard heterogeneous charge-transfer rate constants k_S for iron complexes* at 25°C.

System	Supporting electrolyte, M	k_S, cm s^{-1}	Ref.
$Pt/Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	1KCl	0.24	103
	1LiCl	0.0032	99
	1NaCl	0.01	99
	1KCl	0.15	99
$Pt/Fe(CN)_5NH_3^{2-}$, $Fe(CN)_5NH_3^{3-}$	1LiCl	0.024	99
	1NaCl	0.032	99
	1KCl	0.08	99
$Pt/Fe(CN)_5H_2O^{2-}$, $Fe(CN)_5H_2O^{3-}$	1LiCl	0.0032	99
	1KCl	0.012	99
a—Ag/; *b*—Au/; *c*—$Pt/Fe(C_2O_4)_3^{3-}$, $Fe(C_2O_4)_3^{4-}$	$0.5K_2C_2O_4$ (20° C)	*a*—0.001; *b*—0.005; *c*—0.009	104
$Hg/Fe(C_2O_4)_3^{3-}$, $Fe(C_2O_4)_3^{4-}$	$1K_2C_2O_4$; $0.5H_2C_2O_4$	1.29	105

*Rate constants k_S for certain systems [99] were calculated from the exchange current density on the assumption that the sum of the transfer coefficients of cathodic and anodic processes is unity (transfer coefficients of the cathodic process α for the first and last systems above are respectively 0.50 [103] and 0.84 [105]).

Study of charge transfer in hexacyanoferrate and similar complexes of iron in 1 M solutions of foreign salts has revealed [99] a breakdown of the linear dependence of the exchange current density

$$\lg i_{ex} = \lg zFk_s + \beta \lg c_{ox} + \alpha \lg c_{red} \qquad (4)$$

on the concentrations of oxidised and reduced forms c_{ox} and c_{red} that follows from the slow-discharge theory. This is attributed [99] to the involvement of dimers—polymerisation products of iron(III) and iron(II) complexes—present in solution, in the charge-transfer processes. However, this conclusion is inconsistent with results [103] establishing the validity of Eqn. (4) over wide concentration ranges of hexacyano-complexes of iron(III) and iron(II). Values of k_S and α obtained in this work [103] agree with those of other investigators¶. The absence of appreciable quantities of dimers in hexacyanoferrate(III and II) solutions is indicated also by results for their homogeneous electron-transfer reactions [106], whose rates, however, are sensitive to the pH of neutral and nearly neutral solutions. A similar effect can probably occur on charge transfer in hexacyanoferrate complexes on electrodes. At a rotating graphite electrode [107] in the region of Tafel behaviour kinetic orders less than unity with respect to the reactant complexes are found, and apparent transfer coefficients of cathodic (0.2) and anodic (0.2) processes whose sum is significantly less than unity. In the vicinity of the equilibrium potential the apparent transfer coefficients are 0.5 on graphite [107] and platinum [103] electrodes. This indicates that the electrode potential has a significant influence on the conditions of charge transfer in relatively simple electrode reactions, uncomplicated by change in the composition of the inner sphere. It is concluded [107] that charge transfer in hexacyanoferrate complexes on graphite takes place in the adsorbed state.

The considerable dependence of the constant k_S on the electrode material found for charge transfer in trioxalatoiron complexes [104,105] indicates an inner-sphere mechanism of the electrochemical stage.

Cobalt(III)–Cobalt(II) System

Exchange current densities observed in charge transfer on a platinum electrode between higher complexes of cobalt(III) and cobalt(II) with ammonia [86,88,89], ethylenediamine (en) [87], diethylenetriamine (dien) [108,109], cyclohexanediamine (chn) [110,111], and phenanthroline (phen) [112] conform to Eqn. (4) provided that c_{ox} and c_{red} are the concentrations respectively of oxidised and reduced forms with the same composition of inner and outer coordination spheres and that the process suffers no retardation caused by adsorption of ligands, complexes, and their hydrolysis products. With increase in the concentration of a ligand X the exchange current increases initially owing to the formation in solution of higher complexes from lower complexes of the reduced form (e.g. of $Co\,en_3^{2+}$ from $Co\,en_2^{2+}$), and then either ceases to depend on [X] or decreases (with increase in the concentration of diethylenetriamine, cyclohexanediamine, or phenanthroline). This is attributed to adsorption of the organic diamines, which block part of the electrode surface. The adsorption of hydrolysis products of cobalt(III) complexes has a similar effect. Other workers have also established [113,114] the electrochemical inactivity of $Co\,en_i^{2+}$ complexes in which $i < 3$ in an electrode reaction involving $Co\,en_3^{3+}$ and $Co\,en_3^{2+}$ complexes.

Table 2 shows that k_S decreases on passing from a chloride to a sulphate supporting electrolyte, and with trisethylenediaminecobalt complexes in the sequence $Cl^- > Br^-$, $SO_4^{2-} > S_2O_3^{2-}$. This sequence applies to the increase in stability of the outer-sphere complexes formed by the interaction of $Co\,en_3^{3+}$ with anions of the supporting electrolyte [117,118], which according to what has been stated

¶Table 1 gives values of k_S and α obtained [103] for the reduced surface of a platinum electrode. The values found for oxidised platinum are $k_S = 0.028$ cm s^{-1} and $\alpha = 0.46$.

earlier in this Section are electrochemically less active than are the free $Co\,en_3^{3+}$ complexes.

Information on the interaction of electrochemically active complexes of bi- and ter-valent cobalt with the electrode material is very limited. From an analysis of the Faraday impedance of the system comprising the complexes $Co\,en_3^{3+}$ and $Co\,en_3^{2+}$ with a mercury electrode Laitinen and Randles concluded [115] that both adsorbed and unadsorbed cobalt complexes take part in the reaction. From this it may be assumed that two mechanisms—inner-sphere and outer-sphere—operate in the electrochemical stage in this system. The close similarity in the values of k_S determined for trisethylenediaminecobalt and bisdiethylenetriaminecobalt complexes at mercury and platinum electrodes (Table 2) is consistent with the hypothesis that the electrochemical stage takes place either entirely or largely by an outer-sphere mechanism.

Table 2. Charge-transfer rate constants k_S and transfer coefficients of the cathodic process α for cobalt complexes at 25°C.

System	Supporting electrolyte, N	$10^2 k_S$, cm s^{-1}	α	Ref.
$Pt/Co(NH_3)_6^{3+}$, $Co(NH_3)_6^{2+}$	$1NH_4Cl+7NH_3$	0.0525	0.58	86
	$1(NH_4)_2SO_4+7NH_3$	0.021	0.59	88
$Hg/Co(en)_3^{3+}$, $Co(en)_3^{2+}$	$1NaClO_4+0.1$ en	9 (19° C)	—	115
$Pt/Co(en)_3^{3+}$, $Co(en)_3^{2+}$	$1NaClO_4+0.1$ en	2.9	—	87
	$1KCl+0.1$ en	2.1	0.24	87
	$1Br^-+0.1$ en	0.62	—	87
	$1SO_4^{2-}+0.1$ en	1.64	—	87
	$1S_2O_3^{2-}+0.1$ en	0.46	—	87
$Hg/Co(dien)_2^{3+}$, $Co(dien)_2^{2+}$	$NaClO_4$	14.7–43		116
$Pt/Co(dien)_2^{3+}$, $Co(dien)_2^{2+}$	$1KCl+0.1$ dien	7.7	0.23	108
$Pt/Co(chn)_3^{3+}$, $Co(chn)_3^{2+}$	$1KCl+0.1$ chn	0.075	0.23	110, 111
$Pt/Co(phen)_3^{3+}$, $Co(phen)_3^{2+}$	$1KCl+4\cdot10^{-3}$ phen	4.8	0.23	112

Values of k_S obtained for hexammine- and triphenanthroline-cobalt complexes (Table 2) and the rate constants of the corresponding homogeneous electron transfers conform [89,112] to the Marcus relation [12], which should hold for an outer-sphere mechanism. With the trisethylenediamine complexes, however, this relation is not satisfied, which is attributed [87] to a possible complicating influence on the electrochemical stage by either hydrolysis products or the electrode surface, which may change for instance [89] the spin multiplicity of the complexes. The high-spin and low-spin configurations respectively of the cobalt(II) and cobalt(III) complexes that predominate in solution ($t_{2g}^5 e_g^2$ and t_{2g}^6) compel rearrangement of the electronic configuration of the reactant complexes, which is responsible† for the slow transfer of electrons between cobalt(III) and cobalt(II) complexes having inner spheres of the same composition in homogeneous [20,28,121,122] and perhaps heterogeneous [4] electron-transfer reactions.

†The slow exchange of electrons between cobalt(III) and cobalt(II) complexes of similar composition had earlier been attributed [119] to a considerable change in the cobalt–ligand bond length with change in the valency state of the cobalt. However, it was later established [120] that the difference in bond lengths between the hexammines is 0.15 Å, which differs little from other similar systems.

As the Marcus relation [12] between the rate constants of homogeneous and heterogeneous electron-transfer reactions is not obeyed in the $Cr\,bipy_3$–$Cr\,bipy_3^+$ system, other available data on the relation between electron-transfer rate constants have been discussed [123].

Other Systems

The heterogeneous rate constants k_S for the MnO_4^{2-}–MnO_4^- system at platinum, palladium, gold, and graphite electrodes (0.012, 0.0064, 0.008, and 0.02 cm s^{-1} respectively) and the corresponding transfer coefficients for the cathodic process (0.30, 0.30, 0.35, and 0.25), determined [124] with rotating disc electrodes in 1 M potassium hydroxide (at 20°C), are little affected by the electrode material. In view of this, the high k_S values, and the inertness of the complexes and oxygen atoms adsorbed in the region of the equilibrium potential of the redox system [0.610 V (n.h.e.) in 1 M sodium hydroxide [125]], at least in the case of a platinum electrode, it may be concluded that the electrochemical stage has an outer-sphere mechanism. Analysis of cathodic and anodic polarisation curves obtained for different concentrations of manganate and permanganate ions (in 1 M sodium hydroxide) indicated [125,126] that the electrochemically active complexes were in an adsorbed state, their adsorption on the electrode being accompanied by partial transfer of charge [55,127–137]. An outer-sphere mechanism of the electrochemical stage does not exclude specific interaction between electrode and species reacting on it (by analogy with outer-sphere complex formation in the bulk of the solution).

It is a complicated problem to establish the mechanism of electrochemical stages in the potential range corresponding to high rates of exchange with the solution of species directly adsorbed on the electrode. In such cases systematic investigations of the influence of the structure of the double layer, the material of the electrode, the nature of foreign electrolytes, and other parameters on the kinetics of the electrode reaction are necessary. Kinetic investigation of charge transfer between aquo-complexes of europium(III) and europium(II) at a mercury electrode in 1 M potassium chloride and iodide solutions, allowing for the effect of the structure of the double layer, indicates that electrochemically active complexes are localised in the region of the outer Helmholtz plane [138], i.e. that the electrochemical stage has an outer-sphere mechanism.

Comparison of the kinetic parameters of similar homogeneous and heterogeneous electron-transfer reactions may sometimes indicate the mechanism of the electrochemical stage. Thus the rate of reduction at a mercury cathode of the inert complexes $CoX(NH_3)_5^{2+}$ (where X is a singly charged anion) and other similar cobalt(III) complexes depends on the nature of the inner-sphere ligand X in the same way as does the rate of their reduction by the inert complexes $Ru(NH_3)_6^{2+}$. Since an outer-sphere mechanism operates in the latter case, a similar mechanism was deduced [10] for the reduction of cobalt(III) complexes at a mercury electrode. An outer-sphere mechanism for such electrochemical reactions had been suggested previously [4].

V. ELECTRODE REACTIONS ACCOMPANIED BY CHANGE IN THE COMPOSITION OF THE INNER SPHERE

The sequence of chemical and electrochemical stages in complicated electrode reactions depends primarily on the nature of the reactant complexes and may vary with

the experimental conditions, e.g. with change in the electrode potential. Thus nitrilotriacetate complexes of cadmium[139,140] and other metals[32] are directly reduced on a dropping mercury electrode at sufficiently negative potentials, but at more positive potentials the electrochemical stage of the cathodic process is preceded by detachment of an anion of nitrilotriacetic acid.

The occurrence of preceding chemical stages and their reversibility are usually assessed from the effect of the ligand concentration on the rate of the electrode reaction[4,32-35]. In order to diminish (or eliminate) the complicating influence of the diffuse structure of the electrical double layer such investigations are usually made at a high and constant solution concentration (ionic strength μ). In interpreting the order of the electrode reaction with respect to the ligand it is usually assumed that the equilibrium constants of the chemical stages remain unchanged over the range of ligand concentrations studied, but with a variable ionic strength or a considerable change in solution composition this requires special proof.

We shall first discuss reactions involving oxidised and reduced forms dissolved in the electrolyte, i.e. so called redox systems, and then the electrodeposition and the anodic dissolution of metals.

1. Redox Systems

Titanium(IV)–titanium(III) system

Irreversible cathodic and anodic waves are observed on charge transfer between titanium ions at a dropping mercury electrode in acid chloride[141-144], bromide[144,145], and sulphate[146] solutions. The dependence of the half-wave potential on the concentrations of hydrogen and chloride ions with $\mu = 1$ suggests[141-144] the electrochemical stage

$$Ti(OH)Cl^{2+} + e \rightleftarrows Ti(OH)Cl^{+}, \quad (5)$$

the electrochemically active complexes in which are formed in preceding reversible chemical stages from the oxidised and reduced forms $Ti(OH)_2Cl_2$, $TiOCl^+$ and Ti^{3+} that predominate in solution. The sum of the transfer coefficients $\alpha' + \beta' = 1.00 \pm 0.05$ (where α' varies from 0.34 to 0.45). Charge transfer between titanium ions was studied[144,145] in 1 M HBr + KBr and in 0.06 M HBr + xM KBr (where $x = 0.02-0.80$), i.e. with a variable ionic strength in the latter case. It was concluded that the electrochemical stage involved the complexes $TiBr^{3+}$ and $TiBr^{2+}$, produced reversibly from the respective forms $Ti(OH)Br_2^+$ and Ti^{3+} that predominate in solution. The apparent transfer coefficients vary slightly with the solution composition, their sum being $\alpha' + \beta' \simeq 1.1-1.2$. In acid sulphate and sulphate–perchlorate electrolytes ($\mu = 1$)[146] the electrochemical stage involves the complexes $TiHSO_4^{3+}$ and $TiHSO_4^{2+}$, which are in equilibrium with the complexes $Ti(OH)HSO_4^{2+}$ and Ti^{3+} that predominate in solution.

Chromium(III)–chromium(II) system

The oxidation of labile hydrated Cr^{2+} ions at a mercury electrode is catalysed by halide and other anions, the catalytic effect diminishing in the sequence $I^- > Br^- > Cl^-$ [147,148], i.e. the sequence in which the specific adsorption of halide ions on mercury decreases. In the presence of sufficiently high chloride-ion concentrations the oxidation product is the inert complex $CrCl^{2+}$ [147-149]. In the presence of bromide ions inert complexes of Cr^{3+} and $CrBr^{2+}$ are formed, their concentration ratio depending on the electrode potential[148]. The composition of the reaction products, together with chronopotentiometric and other measurements, show that chloride and bromide ions adsorbed on mercury act as bridging ligands in the electrochemically active complexes $Hg...X...Cr^{II}$. The latter arise directly on the surface of the mercury electrode, not by the adsorption of CrX^+ complexes formed by a preceding homogeneous chemical reaction, as might be supposed[6]. The results show[148] that, in the oxidation of Cr^{2+}, chloride and bromide ions are non-bridging ligands which have a great influence on the kinetics of homogeneous electron-transfer reactions[150-158], in particular in the chromium(III)–(II) system[151,152,154-158]. Non-bridging ligands may influence the rate of electrochemical reactions[157].

An inner-sphere mechanism operates in the oxidation of Cr^{2+} on mercury in the presence of thiocyanate ions[159]. The inert $Cr(NCS)_i^{3-i}$ complexes contain 1–5 thiocyanate ions, the number increasing as the potential becomes more positive and with increase in the thiocyanate-ion concentration. The products *cis*-$Cr(NCS)_2^+$ and $Cr(NCS)_3$, formed when $CrNCS^+$ complexes are almost completely absent from the solution, indicate that polybridging electrochemically active complexes take part in the electrochemical stage. Here chromium ions are attached to nitrogen atoms in two or three thiocyanate ions, which in turn are attached to mercury through the sulphur atom. The chromium(III) complexes formed are adsorbed more strongly on the positively charged mercury surface than are thiocyanate ions. A detailed kinetic investigation of the electrochemical reduction on mercury of the inert complexes $Cr(NCS)_3.(H_2O)_3$ [160] and other similar chromium(III) complexes[161] included an independent study of the adsorption of the reactant complexes. Activity coefficients both of the predominant adsorbed complexes and of the transition state of the electrochemical stage must be taken into account in the kinetic equations[160].

Many processes involving the cathodic reduction of inert chromium(III) complexes have been studied[4,65], including subsequent chemical stages resulting in change in the composition of the inner sphere of the labile chromium(II) complexes formed[162-170].

Europium(III)–europium(II) system

Kinetic examination of the reduction of europium(III) at a mercury electrode in solutions of different concentrations of thiocyanate ions (mainly $\mu = 1$ with sodium perchlorate), allowing for the ψ_1 effect[54], indicates[8] comparable participation of Eu^{3+} and $EuNCS^{2+}$ ions in the cathodic process when present in comparable quantities in the solution. The $EuNCS^{2+}$ complex has a considerably larger standard heterogeneous rate constant than does the hydrated Eu^{3+} ion (respectively 8×10^{-4} and 4×10^{-5} cm s^{-1}). On passing from the bulk of the solution to that adjacent to the negatively charged electrode, however, the ratio $[Eu^{3+}]/[EuNCS^{2+}]$ increases. This is responsible for the comparable contributions by the two ions to the cathodic process, which had been disregarded hitherto[171]. Results[8,171] indicate an outer-sphere mechanism of the reduction of Eu^{3+} and $EuNCS^{2+}$. The latter complex loses the NCS^- ligand, probably after the electrochemical stage.

In the presence of excess of ethylenediaminetetra-acetic acid at pH 9.5 monoligand complexes $Eu^{III}L$ and $Eu^{II}L$ take part in the electrochemical stage, while $Eu^{III}L_2$ and $Eu^{II}L_2$ predominate in solution (where L is the anion of the complexone)[172].

Platinum(IV)–platinum(II) system

Steady-state polarisation and other measurements[173-185] indicate slowness of the electrochemical stage of charge transfer in PtX_6^{2-} and PtX_4^{2-} complexes (X = Cl, Br, I)[173-183,185] and other structurally similar complexes[181-184] at a platinum electrode. Study of the process in chloride complexes of platinum at platinum, rhodium, and iridium electrodes (0.4–1 M NaCl, 3 M H_2SO_4) suggested[176,180] that the electrochemical stage involved adsorbed complexes of the type $M...Cl_{ads}...PtCl_5^{3-}$ and $M...Cl_{ads}...PtCl_5^{-}$ (anodic and cathodic processes respectively), where M represents a metal atom on the electrode surface. It was assumed that the planar $PtCl_4^{2-}$ complex associates reversibly with a chloride ion adsorbed on the electrode and a free chloride ion, which bring its configuration to an octahedron[176,180]. An analogous mechanism was suggested[181] for the anodic oxidation of $Pt(NH_3)_4^{2+}$ in the presence of chloride and bromide ions, as well as for other platinum(II) complexes[177, 182-184]. It is consistent with the approximately first order of the oxidation of PtX_4^{2-} with respect to the ligand (Cl^-, Br^-) observed at high concentrations (~0.3–1 M) of chloride and bromide ions[174-177,180]. At low concentrations halide ions are subject to competition by water molecules, which is more successful with negatively charged platinum(II) complexes than with positively charged and neutral complexes of the type $PtX_{4-i}(NH_3)_i^{i-2}$, where X = Cl, NO_2 and $i = 2,4$.[181,182]

The oxidation of $PtCl_4^{2-}$ complexes on platinum has different mechanisms in the double-layer region of the charging curve and at more positive potentials, at which oxygen is adsorbed (1 M NaCl, 3 M H_2SO_4[185,186]). On passing from potentials of 0.7–0.85 V (n.h.e.), at which chloride ions act as bridging ligands, to ~1.1–1.3 V the apparent transfer coefficient of the anodic process decreases from 0.9 to 0.48.[185] This is attributed[186] to a decrease in the effective negative charge of the adsorbed chloride ions, which stabilises electrons in d_{z_2} orbitals in adsorbed platinum(II) complexes, and these are transferred in the electrochemical stage. At ~1.1–1.3 V oxygen atoms (hydroxide ions) having a considerable negative charge appear owing to deprotonation of adsorbed water molecules on the platinum. This is probably responsible for their preferential involvement as inner-sphere bridges in the anodic oxidation of $PtCl_4^{2-}$ complexes. Hence the complexes $PtCl_4(H_2O)_2$ and $PtCl_6^{2-}$ (70% and 30%) have been detected by thin-layer voltammetry[179] among the products of the oxidation of $PtCl_4^{2-}$ complexes in 1 M hydrochloric acid at ~0.8–1.0 V. The change in state of water molecules adsorbed on platinum, on passing from the double-layer range to a more positive potential, is probably responsible for the similar change in mechanism of the anodic process in the $SbCl_6^{-}$–$SbCl_4^{-}$[187] and arsenic(V)–(III)[188] systems.

The inhibiting effect of the ligand X on the cathodic reduction of PtX_6^{2-} complexes (X = Cl, Br) on platinum is attributed[176,185] to a preceding reversible heterogeneous chemical reaction

$$M-X + PtX_6^{2-} \rightleftarrows M...X...PtX_5^{-} + X^-, \qquad (6)$$

which may occur by an exchange type of mechanism. The surface complex formed by reaction (6) takes part in a slow electrochemical stage. The closely similar transfer coefficients for cathodic and anodic processes in the $PtCl_6^{2-}$–$PtCl_4^{2-}$[174-176] and $PtBr_6^{2-}$–$PtBr_4^{2-}$[177] systems, whose sum in the double-layer potential range of the platinum electrode is ~2, indicate simultaneous or almost simultaneous transfer of two electrons in the electrochemical stage. A similar mechanism had been suggested earlier[189-193] for the transfer of electrons between octahedral platinum(IV) and planar platinum(II) complexes in the bulk of the solution.

The great instability of platinum(III) complexes is indicated by the simultaneous transfer of two electrons from chromium to platinum via a bridging inner-sphere chloride ion when quadrivalent platinum complexes $PtCl(NH_3)_5^{3+}$ are reduced by Cr^{2+} ions[194,195]. The unstable quadrivalent chromium complex formed, $CrCl^{3+}$, is then reduced by bivalent chromium. The hypothesis of a successive transfer of electrons in electrode reactions of platinum(IV) and platinum(II) complexes[173,183,184] therefore requires further support. The lack of influence of chloride ions (at concentrations of 0.3–1 M) on the rate of electrochemical reduction of $PtCl_6^{2-}$ and the small apparent transfer coefficient of the cathodic process (0.44) suggest that the mechanism of the reduction of $PtCl_6^{2-}$ complexes[183] differed from that suggested[176,180], perhaps owing to different surface states of the platinum electrodes. The effect of the chemisorption of foreign species on the kinetics of electrode reactions of platinum complexes has been investigated[184].

Other systems

The cathodic reduction of inert cobalt(III) and rhodium(III) complexes[4,64-66,169,196,197], like that of chromium(III) complexes, usually involves subsequent chemical stages leading to rearrangement of the resulting labile complexes of the reduced forms. Reversible chemical stages have recently been established[198], as a result of which the forms of bi- and tervalent iron predominating in acetate solution are converted into their acetate complexes, and these take part directly in the slow electrochemical stage on a platinum electrode. During charge transfer between ferrous and ferric ions at a platinum electrode in the presence of salicylate ions (0.01–0.1 M) and an acetate buffer the electrochemical stage involves $FeSal^+$ and FeSal complexes formed by preceding reversible chemical reactions from the oxidised and reduced species $FeSal_2^-$ and Fe^{2+}, which predominate in solution[199].

2. Electrodeposition and Anodic Dissolution of Metals

The electrodeposition and the anodic dissolution of metals in complexing solutions, as in non-complex media[40-43,200], may involve successive electrochemical stages. We shall consider initially the simpler one- and two-electron electrode reactions, which include a single electrochemical stage uncomplicated by crystal growth or disintegration. Gerischer[60] regarded such processes, occurring on the surface of metal amalgams, as macromolecular reactions of the type

$$M^{(z)}X_k + ze \rightleftarrows M + kX, \qquad (7)$$

where $M^{(z)}X_k$ is a complex directly involved in the electrochemical stage. With $k > 1$, however, a single-stage mechanism is improbable for reaction (7)[32,33]. A similar structure must be expected for the activated complexes of the single electrochemical stage of cathodic and anodic processes[52]. In view of this and the fact that the stage of ionisation of metal atoms is preceded by formation of their complexes on the electrode surface (adsorption of

ligands)[201-203] the anodic reaction occurring on the electrode can be represented[204] by the sequence of stages

$$E{-}M^{(0)} + k\,X \rightleftarrows E{-}M^{(0)}X_k, \qquad (8.1)$$

$$E{-}M^{(0)}X_k \rightleftarrows E{-}M^{(z)}X_k + ze, \qquad (8.2)$$

$$E{-}M^{(z)}X_k + (n-k)\,X \rightleftarrows E + M^{(z)}X_n, \qquad (8.3)$$

where E is the electrode to which are directly bound the ionising, formally "zero-charged" metal atoms and their complexes $M^{(0)}$ and $M^{(0)}X_K$. The adsorption of ligands and complexes is accompanied by displacement of water molecules or other species adsorbed on the electrode, which for simplicity is ignored in Eqns. (8.1)–(8.3). The concentration of the metal complex $M^{(Z)}X_n$ predominating in the solution will be regarded as identical with the total concentration of metal ions in the solution.

If anodic and cathodic processes involve the same stages (8.1)–(8.3), slow occurrence of the electrochemical stage (8.2) and reversibility of the chemical stages (8.1) and (8.3) should lead to satisfaction of the equation[204]

$$\left|\partial \lg \frac{i}{i_{d,c}-i}/\partial \lg [X]\right|_{(\varphi-\varphi_0)<0} + \left|\partial \lg \frac{i}{i_{d,a}-i}/\partial \lg [X]\right|_{(\varphi-\varphi_0)>0} = n, \qquad (9)$$

where i is the polarising current density at the electrode potential φ, with $i_{d,c}$ and $i_{d,a}$ the limiting diffusion currents of cathodic and anodic processes respectively, and φ_0 is the equilibrium potential of the $M/M^{(Z)}X_n$ system. It is assumed that $[X] \gg [M^{(Z)}X_n]$ and that the coverage of the electrode surface by electrochemically active complexes is insignificant. Relation (9) should be satisfied independently of whether the equilibrium constants β_{0k} and β_{kn} of the heterogeneous chemical stages (8.1) and (8.3) are functions of the electrode potential. If the dependence of these constants on φ can be neglected, the relation

$$\left|\partial \lg \frac{i}{i_{d,c}-i}/\partial \varphi\right|_{(\varphi-\varphi_0)<0} + \left|\partial \lg \frac{i}{i_{d,a}-i}/\partial \varphi\right|_{(\varphi-\varphi_0)>0} = \frac{zF}{2{,}3RT} \qquad (10)$$

should also be satisfied, since with a single electrochemical stage the sum of the apparent transfer coefficients is equal to the total number of electrons transferred[40-42].

Formulae (9) and (10) can conveniently be used as criteria in study of the mechanism of the electrodeposition and the anodic dissolution of metals in complex electrolytes. Since the electrochemically active complexes in the ionisation of metal atoms contain metal–metal bonds, the opposite cathodic process should correspond to a transition state of similar structure, in conformity with the mechanism (8.1)–(8.3). Examination of published data shows that relation (9) is satisfied more often than is (10). A probable reason is the dependence of the equilibrium constants of reactions (8.1) and (8.3) on the electrode potential[204], which may be due in particular to variation in the ψ_1 potential.

Table 3 lists parameters of electrode reactions in which, in conformity with the mechanism (8.1–8.3), integral or nearly integral orders‡ are observed with respect to the ligand in cathodic and anodic processes, and formula (9) holds.

The satisfaction of relations (9) and (10) in the first four systems in Table 3 supports the mechanism (8.1)–(8.3), which includes the inner-sphere electrochemical stage (8.2). Variation of the electrode potential either has no effect on the concentration of electrochemically active complexes or has opposite effects on the slopes of cathodic and anodic Tafel lines in these systems, and such effects balance out.

Table 3. Parameters (at 25°C) of electrode reactions for which Eqn. (9) is satisfied*

System	Complexes in soln.	k	α'	β'	Ref.
Zn(Hg)/Zn(II), $P_2O_7^{4-}$	$Zn(P_2O_7)_2^{6-}$	1	0.62	1.26	205
Zn(Hg)/Zn(II), NH_3; $\Delta\varphi \lesssim 50$ mV	$Zn(NH_3)_i^{2+}$, $i=3,4$	2	1.10	0.80	206
Pb(Hg)/Pb(II), $P_2O_7^{4-}$	$Pb(P_2O_7)_2^{6-}$	1	0.80	1.18–1.28	207
Au/Au(I), CN^-	$Au(CN)_2^-$	1	0.50	0.45	210, 211
Pd/Pd(II), Cl^-	$PdCl_4^{2-}$	2	0.84	0.84	208
Pd/Pd(II), Br^-	$PdBr_4^{2-}$	2	0.82	0.82	209

*k = number of ligands in electrochemically active complex; α' and β' are the apparent transfer coefficients of cathodic and anodic processes.

The dependence of the exchange current density measured near the equilibrium potential of amalgams of zinc[60], cadmium, and other metals[33,34] on the concentration of the complexes and the species forming them is also consistent with the mechanism (8.1)–(8.3).

The proportionality between the rate of cathodic reduction of the complexes $PdCl_4^{2-}$ [208,212-214] and $PdBr_4^{2-}$ [209,212,215] and their concentration, established with palladium[208,209,214] and dropping mercury§ electrodes[212,213,215], indicates that the electrode surface is only slightly covered by the reducible complexes.

A second order with respect to the chloride ion had been observed earlier for the anodic ionisation of palladium[216,217]. Nearly integral values (−2) of the order with respect to the ligand are observed for the cathodic reduction of PdX_4^{2-} (where X = Cl [208,213], Br [209,215,218]) at palladium and dropping mercury electrodes. Complexes of $PdCl_2$ are considered[219,220] to undergo direct reduction in the electrodeposition of palladium.

The sum of the apparent transfer coefficients $\alpha' + \beta'$ for the Pd/Pd^{II} system is slightly <2 (Table 3), which, on the hypothesis of the simultaneous involvement of two electrons in the slow electrochemical stage, can be attributed to a decrease in the concentration of electrochemically active complexes with increase in the polarisation of the electrode. Thus increase in the positive potential of a palladium anode may be accompanied by a decrease in the concentration of surface PdX_2^{2-} complexes owing to displacement of their X^- ligands by water molecules[204]. The coefficient α' determined from the Tafel relationship may be underestimated because of a breakdown of equilibrium in the preceding chemical stage.

‡The kinetic order departs considerably from an integral value for the ionisation of zinc from its amalgam in a pyrophosphate electrolyte (the order of the anodic process with respect to $P_2O_7^{4-}$ is 0.76 at −1.28 V s.c.e.). The corresponding value $\beta' = 1.26$ (Table 3) was obtained with $[P_2O_7^{4-}] = 0.025$ M.[205]

§At $PdCl_4^{2-}$ and $PdBr_4^{2-}$ concentrations $\geqslant 2 \times 10^{-4}$ M their reduction at a dropping mercury electrode is inhibited by the reduction products, which accumulate on the mercury drop during its lifetime[212,213,215].

The slow occurrence of this stage in the cathodic reduction of $PdCl_4^{2-}$ complexes on a palladium electrode with a high concentration of chloride ions is indicated by a decrease in the product $i\tau^{\frac{1}{2}}$ with increase in the polarising current density i (where τ is the transition time)[221]. Detachment of a chloride ion from the complex $PdCl_4^{2-}$ is the slow stage, for which application of a galvanostatic method[221] gave the rate constant as 500 s^{-1} (for 0.06–1 M HCl and 3 M H_2SO_4 at 25°C). Smaller values of k^- (in s^{-1} at 25°C)—8.9 ± 0.8 (in 0.5 M $HClO_4$ by a spectrophotometric method) [222] and 5.6 ± 0.5 [in 0.3 M (Li, H)ClO_4 by the temperature-jump method] [251]—have been found for the homogeneous aquation

$$PdCl_4^{2-} + H_2O \xrightarrow{k} PdCl_3H_2O^- + Cl^-. \qquad (11)$$

This discrepancy may be due to a catalytic effect of the surface of the palladium electrode on the rate of dissociation of chloride complexes of palladium. Since it has been concluded[221] that the preceding chemical stage has a homogeneous character, this problem requires further investigation.

The diffusion nature of the limiting currents observed in the reduction of $PdCl_4^{2-}$ complexes at a dropping mercury electrode suggests[213] that the preceding chemical reaction may be catalysed by mercury ions or atoms. The rate of cathodic reduction of $PdCl_4^{2-}$ and $PdBr_4^{2-}$ complexes increases sharply on passing to a palladium electrode, which indicates an inner-sphere mechanism of the electrochemical stage. It probably involves complexes, adsorbed on the electrode surface, which contain two halide ions and palladium atoms directly attached to metal atoms on the electrode surface[213,215], which is consistent with the mechanism (8.1)–(8.3).

The participation of two electrons in the slow electrochemical stage of the reduction of $Pd\,py_4^{2+}$, $Pd(NH_3)_4^{2+}$, and $Pd\,en_2^{2+}$ complexes (py = pyridine) was deduced from an analysis of non-stationary galvanostatic curves[223]. The apparent transfer coefficient of the cathodic process was determined[223] to be respectively 0.91, 0.85, and 1.46 for these complexes, and the absence of preceding slow chemical stages was established. Oscillopolarographic oxidation of the reduction products of $Pd(CN)_4^{2-}$ complexes at a mercury cathode reveals intermediate complexes of univalent and zerovalent palladium[224], probably stabilised by cyanide ions. A similar situation is found in the cathodic reduction of cyanide complexes of cobalt(II) [225] and nickel(II) [226], as well as other similar complexes formed by strong-field ligands[4]. Yet the Tafel slopes corresponding to the reduction on mercury of ammine (ammonia is a weak-field ligand) nickel(II) complexes (42 mV [227] and 60 mV [228]) indicate the simultaneous transfer of two electrons in the electrochemical stage. The latter involves $Ni(NH_3)_2^{2+}$ complexes formed by a rapid chemical reaction from higher ammine complexes, which supports the mechanism (8.1)–(8.3).

The kinetic parameters determined[207,229-231] in a study of irreversible cathodic and anodic processes for the $Zn(Hg)/Zn(OH)_4^{2-}$ system, in contrast to the systems listed in Table 3, conform neither to Eqn. (9) nor to (10). This is explained[229,230] by differences in the nature of the electrochemical stages of cathodic and anodic processes. The approximate orders of −2 and 1 with respect to hydroxide ions for the two processes suggest that the complexes $Zn(OH)_2$ and $ZnOH^-$ are involved in their slow electrochemical stages. Near the equilibrium potential of the system the anodic process is of second order with respect to hydroxide ions[60]. An approximate halving of the order for the ionisation of zinc atoms with respect to the ligand on passing from low to high anodic polarisations is observed also when zinc amalgam dissolves in the presence of ammonia molecules[206] and for zinc in a citrate electrolyte[232]. This is probably due to competition with the adsorbed ligands by water molecules, a considerable proportion of which, at the low negative surface charges on the electrode characteristic of high anodic polarisations, are oriented with the oxygen atoms towards the surface zinc atoms, which should decrease the concentration of electrochemically active complexes and the order of the anodic process with respect to the ligand. The approximate halving of the apparent transfer coefficient of the anodic process which accompanies[206,232] the decrease in order with respect to the ligand may be due to a transition from a slow two-electron stage to a one-electron stage. The apparent transfer coefficients of cathodic and anodic processes (0.82 and 0.34) found for the $Zn(Hg)/Zn(OH)_4^{2-}$ system in 4 M K(OH, F) solution¶ are attributed[231] to a stepwise transfer of electrons in cathodic and anodic processes. However, these values are consistent also with a two-electron electrochemical stage during cathodic polarisation and slow detachment of the first electron at high anodic polarisations. It has been concluded that intermediate univalent zinc species are adsorbed on zinc during its electrodeposition and anodic dissolution in the presence of malonate ions (pH 6–7)[233] and in alkaline solutions[234,235].

Consecutive transfer of electrons probably always occurs in three-electron reactions, whose stage-by-stage mechanism has been studied in detail on the $Bi(Hg)/Bi^{III}$ and $In(Hg)/In^{III}$ systems[41-43,200]. The kinetics and the mechanism of the anodic dissolution of indium in various media have been surveyed[200]. The cathodic reduction of indium(III) complexes is complicated by slow chemical stages and also by the dependence of the concentration of adsorbed complexes and ligands on the electrode potential (see reviews[38,200,236]), which adds to the difficulty of determining the kinetic parameters of the cathodic process and of subsequent analysis based on Eqns. (9) and (10).

The three-electron cathodic reduction of rhodium(III) complexes also involves one- or two-electron stages[223,237-241]. With $RhCl_6^{3-}$ and $RhCl_5H_2O^{2-}$ complexes on mercury[238,241] and rhodium[240] electrodes the slow electrochemical stage is preceded by reversible detachment of some of the chloride ions from the initial complexes. The rapid replacement of inner-sphere ligands in inert complexes may be due to catalysis by the electrode surface or intermediate products. Heterogeneous catalysis of the replacement of ligands in inert complexes has been studied[242] on cobalt(III) complexes.

The bond between electrochemically active complexes and the electrode may vary significantly in character for different electrochemical stages of the same many-electron reaction. According to the above considerations the last electrochemical stage of electrodeposition, with formation of metal atoms (their surface complexes), should have a non-bridging inner-sphere mechanism, which occurs e.g. in the sequence of stages (8.3), (8.2), and (8.1). In the case of the initial electrochemical stages of electrodeposition, as a result of which intermediate uni- or bi-valent metal complexes are formed from the initial complexes, an outer-sphere or a bridging inner-sphere

¶Apparent transfer coefficients $\alpha' = 0.80$ and $\beta' = 0.52$ were determined[207] by a potentiodynamic method for the $Zn(Hg)/Zn(OH)_4^{2-}$ system in 3 M (KOH + NaCl) solution.

mechanism may operate†. The presence of bridging ligands in bivalent zinc, cadmium, and lead complexes adsorbed on a mercury electrode[243-246] (see also references in Refs. 247 and 248) does not exclude a non-bridging inner-sphere mechanism of the electrochemical stage in the reduction of these complexes. Complexes adsorbed through the ligand, which predominate on the electrode surface, may be converted by a preceding rapid chemical reaction into electrochemically active complexes containing a metal–metal bond.

It follows from the above considerations that, with a slow electrochemical stage complicated by complex formation, the main features of the electrochemical kinetics are the same on liquid and solid electrodes. The kinetics of practically important processes of the electrodeposition of solid metals from complex electrolytes have been examined in a monograph[249]. A review has recently been published[250] on the electrodeposition of noble metals.

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A very important but little studied problem is the relation between the kinetic parameters of an electrode reaction and the electronic structure of the complexes. The electrode reactions discussed above involved the transfer of electrons from the electrode to orbitals localised mainly on the metal ion or in the reverse direction[4]. The transfer of t_{2g} electrons from or to low-lying orbitals of a metal occurs more rapidly than that of e_g electrons[252,253]. This is explained by the greater change in metal–ligand bond length in the latter case, and hence the greater energy of rearrangement of the inner coordination sphere (while its composition remains unchanged).

In the electrochemical reduction of complexes electrons may be transferred also to orbitals of inner-sphere ligands. In order to elucidate the reaction mechanism in such cases it is necessary to make a parallel kinetic study of the cathodic reduction of coordinated and free ligands[254-257].

The kinetic investigations on electrode reactions of trisbipyridyl and similar complexes of iron in water and dimethylformamide[258] and of trisbipyridyl complexes of ruthenium, osmium, chromium, titanium, vanadium, and molybdenum in dimethylformamide[254-256] have revealed two groups of electrode reactions. One group of complexes, with which a t_{2g} electron is transferred, have rate constants $k_S = 0.8-1.3$ cm s^{-1}. The other group of complexes, with which an electron localised on a π^* orbital of a ligand is transferred, correspond to $k_S = 0.1-0.3$ cm s^{-1}. The fact that k_S is relatively unaffected by the nature of the electrode (mercury, platinum), the solvent (water, dimethylformamide), the state of oxidation of the metal, or the charge on the complex indicates the decisive role of rearrangement of the inner coordination sphere in determining the rate of the electrochemical stage[256]. Electron transfer to orbitals of the ligand is suggested in the second group of complexes by the closeness of their k_S values to those found for the bipy/bipy$^-$ system (0.13 and 0.21 cm s^{-1} for mercury and platinum electrodes respectively). The redox properties of ligands coordinated by metal ions has recently been studied intensively. This topic is of intrinsic interest, and will not be considered here.

†With a bridging inner-sphere mechanism one or more inner-sphere ligands of the electrochemically active complex are attached directly to metal atoms on the electrode surface. In both heterogeneous and homogeneous electron-transfer reactions bridging ligands may fill various functions[5].

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