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Electrochemistry of Iodine

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The results of studies of redox processes in systems which include iodine are generalised. The adsorption of iodine on metals is discussed, and the relationship between the type of adsorption and the electrode reactions of the iodine is examined. 190 references.

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I. SPECIFIC ADSORPTION OF IODIDE IONS

The adsorption of iodide ions on different electrodes from different media has been fully investigated[1-72]. The main aim of that work was to determine the structure of the electrical double layer (EDL) and, in particular, the effect of the specific adsorption of the ions on various electrode processes (metal dissolution, hydrogen evolution, etc.). In this Section we shall attempt to generalise (qualitatively) data on the adsorption of iodide ions on metals in order to explain the general features of the adsorption: this is an essential preliminary to any discussion of the kinetics and mechanism of the redox reactions of iodine.

The rate of an electrochemical process is strongly dependent on the structure of the EDL, which is determined by the nature of the adsorption of the reacting ions on the electrode surface. The adsorption type (especially in the case of specific adsorption) depends on the one hand on the stability of the complexes (or chemical compounds) formed by the adatoms (or ions) with the surface atoms of the metal electrode at the ψ' potential[1], and on the other hand it depends on the primary hydration (or solvation) number[2] of the ion in the bulk of the solution. The adsorption of iodide ions from different media and on different electrodes is determined by these factors.

On mercury electrodes[3-7] the adsorption of iodide ions causes an increase in the capacity of the EDL,[3] an anomalous change in zero-charge potential with the logarithm of the concentration of I^- (the Esin–Markov effect),[5] a lowering of the electrocapillarity maximum (accompanied by a negative shift)[1,3], a decrease in hydrogen evolution overvoltage (η_{H_2}) in acid solutions[4,7] a linear decrease in heat of adsorption with increase in surface coverage[6], and a shift of the ψ' potential towards more negative values[4,7]. If the formation of the surface compound results in a full (or partial) loss of charge by the iodide ions the EDL capacity should decrease, and conversely if as a result of the low stability of the surface complex the iodide ions accumulate in the fixed part of the EDL the capacity should increase.

The negative shift of ψ' (which lowers η_{H_2}) and the increase in capacity suggest a weak chemical interaction between Hg and I^-. In this case the I^- anions are adsorbed in the ionic "condenser plate" of the EDL, where they generate a negative ψ' potential and (according to the slow discharge theory) they increase the rate of evolution of hydrogen. However, it has been shown experimentally[8] that the negative shift of ψ' is not accompanied by an accumulation of H^+ ions on the mercury surface: this suggests[8] that the influence of I^- and other anions on this electrode is not primarily the ψ' effect but a substantial lowering of the activity coefficient of the activated complex. Another important factor on the mercury electrode is the mutual repulsion of the I^- ions chemisorbed on the surface, i.e. the high mobility of these ions on the uniform mercury surface[6].

There can be no doubt that the number of ions in the EDL depends on their degree of solvation (hydration) in the solution. Hence the observed sequence of specific adsorbability ($Cl^- < Br^- < I^-$) from water solutions, which applies to almost all metals, is invariably ascribed to decreasing hydration. In contrast to their behaviour in protonic solvents (water, methanol, acetic acid, etc.), iodide ions are easily solvated in dipolar aprotic solvents such as dimethylformamide (DMF), dimethylsulphoxide (DMSO), acetone, and acetonitrile[9]. This difference is sharply reflected in the specific adsorption of I^- at the mercury–electrolyte interface with non-aqueous solvents. For example, the surface activity of iodide anions at the mercury–DMF interface is lower than at the mercury–water interface[10,11,14], and the lowering of surface tension caused by the adsorption of I^- on an uncharged mercury surface in water is greater than in DMF.[10] The difference is even more marked if we compare water with formamide[10].

Damaskin and coworkers[10,11] ascribe this effect to competition between the adsorption of I^- anions and the adsorption of solvent molecules. Obviously, we must again allow for the strong solvation of I^- in aprotic solvents, since the difference in solvation energy of the anions decreases in the series from Cl^- to I^- in water, but increases in DMF.[11] The free energy of adsorption of I^- on an uncharged mercury surface from aqueous solutions is 37.1 kcal mole^{-1}, as compared with 29 kcal mole^{-1} for solutions in DMF under the same conditions. In comparison with the mercury–water interface, the mutual repulsion of specifically adsorbed anions is stronger at the mercury/DMF,[11] mercury–*N*-methylformamide (MFA),[12] mercury/formamide[15], and mercury/DMSO interface[13,16]: this is shown by the decrease in the second virial coefficient (B) when DMF is replaced by water.

Under certain conditions even organic surface-active ions have very little effect on the adsorption of I^- on mercury[7,17].

On iron, cobalt, and nickel. In contrast to its adsorption on mercury, the adsorption of I^- on solid metals (especially Fe,[18-24] Co,[25,26] and Ni [27-29]) is due to the formation of a strong M–I^- chemical bond. Iodide ions chemisorbed on an iron surface[18,19,21] have a passivating effect on the metal: η_{H_2} is increased[19,22], and the ionisation reaction is suppressed[20]. The capacity of the iron electrode decreases more

than two-fold in the presence of even very small amounts of KI (0.002 *N*), the additional decrease caused by increasing the KI concentration to 0.2 *N* being almost negligible[21]. The decrease in capacity increases with the concentration of H_2SO_4 (from 1 to 8 *N*).[21]

The maximum number of iodide ions adsorbed on Fe has been shown by a radioactive tracer method to be 4×10^{-10} g-atom cm^{-2}, corresponding to 50% coverage of the iron surface. Therefore it is generally thought that the passivating effect of I^- on Fe cannot be due to the formation of a surface compound. However, the lowering of the double layer capacitance of Fe from 33–35 μF cm^{-2} (in 1 *N* H_2SO_4) to 10–15 μF cm^{-2} by the addition of 0.001 mole $litre^{-1}$ of KI conclusively proves that iodide ions are chemisorbed[21]. It is interesting to note that the capacity of iron in sulphuric acid is unaffected by the presence in solution of an organic surface-active ion (the tetrabutylammonium cation), whereas addition of iodide ions to the same solution causes a marked decrease (to 7–10 μF cm^{-2}) in the capacity of the electrode[19]. This is explained by the formation of dipolar Fe–I^- molecules with their negative end pointing towards the solution, which assists the adsorption of positively charged species. The Fe–I^- surface complex is stable only in acid solutions[24].

It has also been shown that halogens adsorbed on Fe retain some excess negative charge, though not to the same extent as in the adsorption on mercury[22]. Oshe even suggests[23] that the halide ions can penetrate into the surface layer of the the iron and perturb the crystal structure.

Halide ions adsorbed on cobalt[25,26], as on iron, increase the overvoltage of both the cathodic process (discharge of hydrogen ions) and the anodic process (cobalt ionisation reaction). Increasing i_a and ϕ_a accelerates the removal of the adsorbed ions (together with the ionised surface atoms of the cobalt electrode[26]).

Iodide ions weaken the Ni–H bond: they displace adsorbed hydrogen atoms from the surface and they raise η_{H_2}, the magnitude of the effect increasing with the concentration of I^- in solution[27,28]. At low concentrations of I^- ($\lg c_{I^-} < -4$) the differential capacity of nickel decreases as the concentration of I^- increases due to increasing chemisorption of I^-. Further increase in the concentration of I^- brings less strongly bound I^- ions into the surface layer, and the capacity begins to rise[29].

On lead and tin. The adsorption of iodide ions on lead[30–34] takes place in two steps. Kolotyrkin and coworkers[30] have shown that the first step consist in the (fast) penetration of the anions into the EDL, accompanied by an increase in capacity. In the second (slow) step a strengthening of the bond between the anions and the surface metal atoms takes place, and the capacity decreases. In acid solutions an increase in the concentration of KI from 1×10^{-5} to 1×10^{-3} *N* increases the coverage of the lead electrode surface with iodide ions from 0.37 to 38.5% of a monolayer. At low coverages (0–15%) and increase in the number of adsorbed iodide ions lowers η_{H_2}, whereas at coverages greater than 15% the effect is the opposite: in this case an increase in adsorption produces a marked increase in η_{H_2}, to a level higher than the overvoltage in pure acid solutions when the coverage exceeds 30% of a monolayer.

The surface excess of specifically adsorbed I^- for the same total density of charge is lower on lead than on mercury[32]; the shift in the zero-charge potential caused by iodide anions is greater on mercury than on lead[31,33]; the minimum on the $c-\phi$ curve occurs at 10^{-5} *N* KI concentration on mercury[3], whereas on lead[31] (and on tin[37]) it occurs at 10^{-3} *N* KI. Thus it appears that the specific adsorption of I^- is weaker on lead than on mercury. A generalised model of the EDL [34] can be used to calculate the change in η_{H_2} on lead caused by the adsorption of I^-.

On cadmium and thallium. On a cadmium and a thallium electrode[30,35], as on a lead electrode, the positive swing in potential caused by I^- ions produces first a lowering and then a rise in η_{H_2}. The adsorption of water dipoles with their negative end towards the electrode surface is more marked on a cadmium than on a lead electrode[36]. The relative values of the energy of adsorption of the iodide ion on cadmium ($\Delta G^0_{I^-} = -22.0$ kcal $mole^{-1}$) and on mercury (−37.1 kcal $mole^{-1}$) are consistent with the surface excesses of iodide ions on the two metals, and show that the iodide ion is adsorbed less strongly on cadmium than on mercury[36].

On silver. The adsorption of I^- anions on the (100) face of silver single crystals is stronger than on any other solid electrode[38]. This is explained by the extremely low solubility in water of the silver halides[39,40], which causes a substantial (2–3-fold) decrease in the differential capacity of the EDL,[40] as in the case of iron. Unlike the adsorption on Pb, the adsorption of I^- on Ag causes only an increase in η_{H_2} over a wide range of KI concentrations (from 10^{-9} to 10^{-3} g-equiv $litre^{-1}$).[40]

The potential corresponding to full adsorption varies substantially with the pH of the solution. An increase in pH at constant potential always produces a marked decrease in adsorption: the effect is strongest in acid solutions (pH < 6), whereas in strongly alkaline solutions the effect of pH on the adsorption is much weaker[40].†

Because of the very low coverage of the silver surface by adsorbed ions (~10% of a monolayer[39]) the penetration of I^- into the metal lattice is thought[40] to be unlikely. However it has been shown[42,43] that the adsorption of I^- on Ag is accompanied by penetration into the metal lattice as a result of the relatively fast exchange with surface atoms of silver.

On bismuth. The adsorption of I^- on bismuth[44–47,50] is lower than on mercury, but somewhat higher than on Pb [31] and Cd.[35] However, the surface activity of the iodide ions, i.e. the magnitude of the negative shift of the minimum in the ε,ϕ curve, is lower for Bi and In than for Pb and Tl.[51]

At low concentrations of KI (<10^{-2} M) the shift in the zero-charge potential for the (111) face of a bismuth single crystal is smaller than for the surface of a cast bismuth ingot, but at higher concentrations of KI (>10^{-2} M) the shift becomes greater for the monocrystalline than for the polycrystalline surface. The repulsion between specifically adsorbed I^- anions on a (111) face with $\varepsilon < 0$ is substantially higher than on the polycrystalline face, but with $\varepsilon > 0$ the opposite is true. On a cast bismuth electrode the enhanced specific adsorption is accompanied by closer approach of the inner Helmholtz plane to the electrode surface[44].

The adsorption of I^- on Bi is stronger from aqueous than from methanolic solutions[48,49], increasing more rapidly with the concentration of I^- in water than in methanol solutions. Changing from water to methanol solutions of I^- causes the planes of the EDL on Bi to move apart[48]. The increase in the distance from the outer Helmholtz plane to the surface (x_2) in methanol is accompanied by a strong (2–3-fold) enhancement of the repulsion between adsorbed ions, caused by the closer approach of the inner Helmholtz plane (x_1) to

†A similar pH effect is observed in the adsorption of I^- on Cu, Au, Pt, Ni, and stainless steel. On the other hand on glass the adsorption of I^- increases significantly with pH.[41]

the electrode surface with increasing adsorption of the iodide ion[49]. The standard free energy of adsorption $\Delta G^0_{I^-}$ on Bi is -23.9 kcal mole^{-1} from aqueous solutions and -25.6 kcal mole^{-1} from methanolic solutions[48]. The increase in $\Delta G^0_{I^-}$ on changing the solvent from water to methanol is due essentially to the lower solvation of the anions in the latter medium, but there is also an effect from the change in interaction energy of the solvent molecules adsorbed on the Bi.[48,49]

The adsorption of I^- is weaker on Bi than on Hg even when ethylene glycol is used as the solvent[52]. However, and in contrast to aqueous, methanolic, and ethylene glycol solutions, in DMF [53] and DMSO [54] solutions the surface concentrations of specifically adsorbed anions are almost identical on Bi and Hg. The orientation polarisation of the DMF dipoles increases in the series $Cl^- < Br^- < I^-$, as does also the solvation energy of the halide ions in DMF.[53] The specific interaction of the solvents with the uncharged bismuth surface decreases in the sequence DMF > DMSO > $H_2O \geq CH_3OH \geq$ acetonitrile, and the ratio $(x_2 - x_1)/x_2$ which characterises the approach of the inner Helmholtz plane to the electrode surface increases as follows when I^- is adsorbed on Bi from different solvents: $H_2O <$ acetonitrile < DMSO = ethanol < methanol < DMF.[53]

On gallium the adsorption of I^- is also less than on mercury, but the M–I^- bond is stronger on gallium than on mercury[55]. The increase in η_{H_2} due to the presence of I^- is more marked on a solid than on a liquid gallium electrode[56]. When gallium is melted in solutions of sulphuric or perchloric acid containing iodides the overvoltage η_{H_2} immediately falls to the level for a liquid electrode in the same solution. If the gallium is re-frozen in the same solution η_{H_2} increases (more slowly) to the limiting value η_{lim}. Solidification of the gallium strengthens the bond between the halide ions and the metal, and the effect increases with time, suggesting a continuing expansion of the crystal lattice in solid gallium[56].

The increase in EDL capacity accompanied by a shift of ϕ towards less negative values was explained by Frumkin[55] not in terms of anion adsorption, though it must play a part (even if only minor), especially in the case of I^- ion, but in terms of the adsorption of water molecules on the gallium. It is interesting to note that on high-purity gallium (99.9998–99.9999%) the addition of halide anions raises η_{H_2},[57] whereas on gallium of 99.996% purity halide ions lower η_{H_2}.[58]

On platinum. On smooth platinum the adsorption of I^- from a 1 *N* H_2SO_4 + 0.01 *N* KI solution is 1.5×10^{-9} g-ion cm^{-2} of apparent surface, i.e. close to the number needed to form a complete monolayer[59]. Incomplete coverage of the platinum surface has been reported[60,61]. The maximum adsorption of iodide ions on platinised platinum (at $\phi = 0.4$ V) is 3.7×10^{-9} g-equiv cm^{-2}; for smooth platinum under the same conditions an adsorption of 6.5×10^{-8} g-equiv cm^{-2} was obtained (i.e. ~20 times greater than on platinised platinum when calculated for a uniform surface)[61]. However, 2–2.5 times more hydrogen is desorbed from smooth than from platinised platinum.

The difference in adsorption capacity between smooth and platinised platinum is ascribed[61] to faults in the lattice of smooth platinum resulting from its technological surface treatment. The increased irreversibility of the adsorption of iodide on platinum, and the decreased adsorption and increased desorption at higher temperatures, are ascribed[61] to the penetration of the adsorbed particles into the underlying layers of the metal. Hydroxyl ions suppress the adsorption of iodide on platinum at all potentials more negative than 1.0 V with respect to the NHE.[59] At high anodic potentials (the oxygen evolution potential) in alkaline solutions, however, the adsorption of iodine is substantial and well in excess of several monolayers of I^-. This is explained by the formation of a stable chemical compound between iodine and the platinum oxides produced under those conditions. The surface compounds are easily soluble in acids, but they are stable in alkaline solutions even under cathodic polarisation[59]. However, it is pointed out[62–64] that I^- (unlike I_2 [62]) is not adsorbed on an oxide-covered platinum surface.

It has been reported[65,66] that in the iodide–iodine–iodide/iodine complex system the species adsorbed on platinum is not I_3^- but I_2 (or iodine atoms), and that the adsorption of I_2 is far greater than that of I^-. The double mechanism (reversible, or irreversible) of the adsorption of I_2 and I^- on platinum[65,66] should also be noted: I_2 is adsorbed irreversibly on the part of the platinum surface which is free from adsorbed iodide, whereas on the regions covered with I^- or with irreversibly adsorbed I_2 the further adsorption of I_2 is reversible. Thus the irreversibly adsorbed state includes I_2 as well as I^-.[63,65] Of the various oxidised forms of iodine the most strongly adsorbed is I^-, even to the extent of displacing other adsorbed ions or molecules[63,64]. This explains the steep drop in the EDL capacity of platinum and in the electrical conductance of the platinum–solution interface, the decrease in the amount of adsorbed hydrogen, and the decrease in the energy of its bond to the platinum surface in the presence of I^-.[59,60,67,68]

On palladium, rhodium, and iridium. The main features of the adsorption of I^- on Pd,[69,70] Rh,[71] and Ir [72] are described by the logarithmic Temkin isotherm and Roginskii–Zel'dovich equation. The adsorption of I^- on palladium[69] produces a new phase of the compound PdI_2. In the ϕ region where the formation of compounds between I^- and the metal is inhibited the I^- ion exists at Pd–I^- dipoles. Pd and Rh surfaces, like Pt surfaces, acquire a greater positive charge in NaI solutions than in NaBr. On Rh, as on Pt, the coverage of the surface by iodide increases rapidly at first and then more slowly[71]. On rhodium the I^- cannot compete with oxygen for surface sites[71]. As on Pt,[61] and on Pd,[69] partial charge transfer from I^- to the electrode takes place on Ir.[72]

The metals of the platinum group can be arranged in the following order of decreasing displacement of adsorbed hydrogen by iodide ions: Rh > Ir > Pt > Pd. The slope of the I^- adsorption isotherms for metals of the platnium group is thought[71] to be determined by the simultaneous effect of two distinct factors: the nature of the surface non-uniformity and the mutual repulsion forces between anions.

Thus the adsorption of iodide ions on different electrodes is essentially chemical in nature. However, a number of features are inconsistent with this statement: a) full coverage of the metal surface by adsorbed ions is only exceptionally observed; b) the adsorption of I^- on Cd, Pb, Ga, and Bi is smaller than on Hg, and the adsorption on Ag and Pt is greater than on Hg, in spite of the fact that the energy of formation (in kcal mole^{-1}) of the compounds PbI_2 (41.85), CdI_2 (48), and GaI_3 (51.2) is much higher, and that of AgI (14.91) and PtI_4 (21.6) is much lower, than the energy of formation of HgI_2 (25) or Hg_2I_2 (29);[73,74] c) the radius of the Pt atom (1.38 Å) or of the Pt^{2+} ion (0.93 Å) is almost one-half the radius of the I^- ion (2.2 Å),[75] and therefore the formation of compounds of the PtI_2 (and especially the PtI_4) type on the surface of Pt seems unlikely.

The metals can be arranged in the following sequence of increasing adsorption of I^-: Cd (−0.402) ≅ Tl (−0.336) < Sn (−0.140) ≅ Pb (−0.126) < Ga (−0.520) < Bi (+0.200) < Hg (+0.788) < Co(−0.277) ≅ Ni (−0.25) < Fe (−0.036) < Ag (+0.799) ≅ Rh (~+0.8) ≅ Pd (+0.987) ≅ Ir (+1.00) < Pt (~+1.200). The numbers in brackets are the standard redox potentials (in volts) of the metals in aqueous solutions[75]. The adsorption of I^- increases as the standard potential becomes more positive, with gallium and the elements of the iron family as the only exceptions. Hence we may assume that the adsorption of I^- on metals is not purely chemical, but physicochemical in nature, i.e. dependent on the charge of the metal surface. This hypothesis is consistent with the finding[76] that the standard free energy of adsorption of I^- on mercury is linearly related to the positive charge on the electrode.

The sharp drop in EDL capacity caused by the adsorption of I^- on solid metals and the associated (partial, or full) charge transfer from the I^- to the metal[77] (especially on metals with a strongly positive surface charge) can be explained by the distortion of the outer electron clouds of the adsorbed ions, resulting in a deviation from a discrete distribution in the case of a solid electrode (in contrast to the mercury electrode).

II. STANDARD AND EQUILIBRIUM POTENTIALS IN SYSTEMS WHICH INCLUDE IODINE

The equilibrium potentials of the I_2/I^- system, for the overall electrode reaction

$$2I^- - 2e \rightleftarrows I_2 , \qquad (1)$$

and of the I_3^-/I^- system, for the overall electrode reaction

$$3I^- - 2e \rightleftarrows I_3^- , \qquad (2)$$

are given by the Nernst equation[78–80]

$$\varphi_{(1)} = \varphi^0_{(1)} + (RT/nF)\ln([I_2]/[I^-]^2) , \qquad (3)$$

$$\varphi_{(2)} = \varphi^0_{(2)} + (RT/nF)\ln([I_3^-]/[I^-]^3) . \qquad (4)$$

In these expressions n is the number of electrons in the overall electrode reaction, and F is the Faraday. The standard electrode potentials (in V) of the I_2/I^- system in aqueous solutions are 0.621 [81–83] or 0.628 [82,84] with I_2(aq), and 0.535 [83,85] or 0.536 [82] with I_2(s), whereas those for the I_3^-/I^- system are 0.536 [81–83,85] or 0.545.[82,84]

In Eqns.(3) and (4) the pre-logarithmic factor is the same for reactions (1) and (2), since $n = 2$ in both cases, and is a function of temperature only: $\partial\phi_p/\partial \ln([I_2]/[I^-]^2) = \partial\phi_p/\partial \ln([I_3^-]/[I^-]^3) = 0.02958$ at 25 °C.[79]

Increasing the concentration of I^- in solution converts the iodine into the iodine–iodide complex (I_3^-), and the equilibrium potential depends not only on the activity of I^- but also on the activity of I_3^-. At constant concentration of I_3^- the equilibrium potential of the I_3^-/I^- system decreases exponentially with the concentration of I^-:

$$\varphi_p = \varphi_0' - (RT/nF)\ln[I^-]^3 = \varphi_0' - (3RT/2F)\ln[I^-] . \qquad (5)$$

Assuming that the electrode reaction is described by Eqn.(1), at constant I_2 concentration the rate of decrease of the electrode potential with increasing I^- concentration is described by the equation

$$\partial\varphi_p/\partial \ln[I^-] = -(RT/F) .$$

At low and constant concentration of iodine[78], or when no iodine is present in the initial solution[80], the experimentally observed decrease in ϕ_p with increase in I^- concentration corresponds to Eqn.(5), i.e. the equilibrium in the system is described by Eqn.(2). This assumption is confirmed by the temperature dependence of the equilibrium potential, i.e.[80]

$$\partial\varphi_p/\partial T = -3R(\ln[I^-])/2F .$$

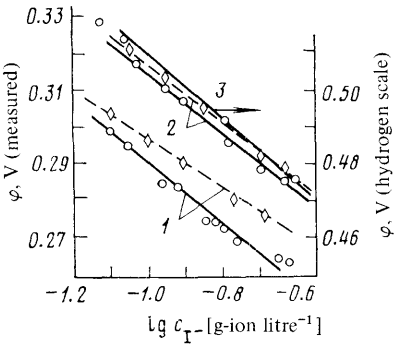


Figure 1. Equilibrium potential ϕ_p against logarithm of the concentration of iodide ions on platinum (*1*, *2*) and on graphite (*3*) in the presence (broken lines) and in the absence (full lines) of naphthenic acids[80]: *1*) and *3*) without supporting electrolyte, *2*) in the presence of 1 *N* Na_2SO_4.

At all concentrations of I^- the platinum[78,80] and the graphite[80] electrode have a positive potential (Fig.1), due to the dipole in the Pt–I^- bond[59], and the potential changes are caused not only by changes in surface coverage but also by changes in the electrode–adsorbate interaction energy[51] and changes in the dipole moment of the platinum–iodide bond brought about by the increased strength of the bond[59].

The equilibrium potential of platinum becomes more positive in the presence of 1 *N* Na_2SO_4 (Fig.1), evidently as a result of a change in state of the I^- in the outer Helmholtz plane (i.e. of a change in the ψ' potential)[80]. Naphthenic acids also cause a positive shift in the potential of platinum in iodide solutions (Fig.1).

On a tellurium[86] and a zinc[87] electrode in aqueous solutions the equilibrium potential corresponding to the following reactions is rapidly established:

$$TeI_6^{2-} + 4e \rightleftarrows Te + 6I^-$$

$$ZnI_3^- + 2e \rightleftarrows Zn + 3I^- .$$

The standard I_2/I^- potentials decrease as the concentration of acetic acid increases in $CH_3COOH + H_2O$ mixtures: the effect amounts to 200 mV for a change in concentration from 0 to 80% CH_3COOH.[88] This dependence of the standard potential of the I_2/I^- system on the concentration of acetic acid cannot be explained by an increase in the stability of I_3^-, since this complex raises the potential of the system [see Eqn.(4)].

The standard redox potentials (in V) are:

Solvent	Nitromethane	Acetone	Acetonitrile	DMF	CH_3COOH
I_3^-/I^-	0.11 [82,90]	0.11 [82,90]	0.06 [82,90]	−0.37 [82]	−0.112 [82]
I_2/I_3^-	0.36 [82] 0.71 (90]	0.86 [82,90]	0.396 [82] 0.65 [90]	0.27 [82]	0.344 [82]
I_2/I^-	0.31 [82,90]	0.36 [82,90]	0.26 [82,90]	—	0.273 [82,89]

The normal potentials (in V) are:

Medium	Neutral	Alkaline
I^-/IO^-	0.99 [82,85]; 1.313 [81]	0.49 [82,85]; 0485 [83]
I^-/IO_3^-	1.195 [84,85]; 1.085 [81,82]	0.26 [82—85]

In solutions containing chlorides $\phi^0_{I_2/ICl} = 1.19$ V [82,83,85] and $\phi^0_{I_2/ICl_2^-} = 1.06$ V [82,85] or 1.056 V.[83]

For the I_3^-/IO_3^- system $\phi^0 = 1.154$,[81] and for I_2/IO_3^- the following values of ϕ^0 have been reported:

t, °C	25	37.5	50
φ°, V	1.1942 [91]; 1.195 [82,83]; 1.178 [81]	1.1903 [91]	1.1863 [91]

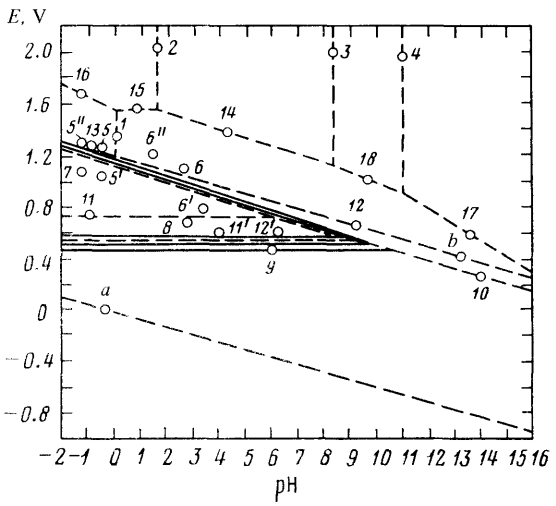


Figure 2. Potential–pH diagram for iodine[81] in the following systems: *a*) H_2/H^+, *b*) O_2/O_2^-, *1*) HIO_3/IO_3^-, *2*) HIO_4/IO_4^-, *3*) IO_4^-/HIO_5^{2-}, *4*) HIO_5^{2-}/IO_5^{3-}, *5*) I_2/HIO_3, *5'*) I_2/HIO_3 and I_2(s), *5''*) I_2(s)/HIO_3, *6*) I_2/IO_3^-, *6'*) I_2/IO_3^- and I_2(s), *6''*) I_2(s)/IO_3^-, *7*) I_2/I^+ and I_2(s), *8*) I^-/I_3^-, *9*) I^-/I_2, *10*) I^-/IO_3^-, *11*) I_3^-/I_2 and I_2(s), *11'*) I_3^-/I_2(s), *12*) I_3^-/IO_3^-, *12'*) I_3^-/IO_3^- and I_2(s), *13*) I^+/HIO_3 and I_2(s), *14*) IO_3^-/IO_4^-, *15*) IO_3^-/HIO_4, *16*) HIO_3/HIO_4, *17*) IO_3^-/IO_5^{3-}, *18*) IO_3^-/HIO_5^{2-}.

The pH dependence of the redox potential for various iodine compounds is shown in Fig.2.

III. REDOX PROCESSES IN I^-/I_2 AND I^-/I_3^- SYSTEMS

1. Electrolytic Oxidation of Iodide Ions

a) Studies by Faradaic impedance and rectification methods. The study of anodic and cathodic reaction kinetics in I_2/I^- and I_3^-/I^- systems is complicated by the strong diffusion control of the reactions[92]. Further difficulties arise from the adsorption of reactants and products in both anodic and cathodic reactions, and from the large number of independent paths available to the reactions.

Vetter[92] showed that the overall electrode reaction (2) takes place though the following steps:

$$I^- \rightarrow I\,(ads) + e \qquad (6)$$

$$2I\,(ads) \rightleftarrows I_2 \qquad (7)$$

$$I_2 + I^- \rightleftarrows I_3^-, \qquad (8)$$

reaction (6) being rate-determining. The kinetic order of the anodic reaction (p_a) with respect to I^- is 1, that of the cathodic reaction (p_c) with respect to I_2 is 1/2. This mechanism has been used[93,94] with a transfer coefficient $\alpha = 0.6$, but it was shown that at low concentrations of I^- the adsorption of I^- becomes rate-determining, and that electron transfer through a very thin adsorbed layer is slow.

Dane and coworkers[95] believe that Vetter's equations[92] are not generally applicable because they do not allow for changes in the coverage of the surface by I_2 and I^-, and they conclude that the impedance of the I_2/I^- system on a Pt electrode is unaffected by the adsorption of I^- and I_3^-, the rate-determining step being the Heyrovsky (electrochemical desorption) reaction

$$I^- + I\,(ads) \rightarrow I_2 + e\,. \qquad (9)$$

However, Tyagai's calculations[96] from Faradaic rectification data of the kinetic equations of the elementary steps [discharge–recombination, reactions (6) and (7), discharge–electrochemical desorption, reactions (6) and (9), and recombination–electrochemical desorption, reactions (7) and (9)], using the Langmuir, Temkin, and Frumkin adsorption isotherms, have clearly established that the electrode reaction mechanism for the Pt–I_3^-/I^- system consists of a series of discharge–recombination reactions with a slow discharge step, corresponding to the Langmuir isotherm.

The effect of surface non-uniformity on the kinetics of the electrode processes was studied by measuring the Faradaic impedance of an iridium electrode in the iodine–iodide system[97]. The electrode reaction on iridium was shown to take place only on active surface sites, whose size is smaller than the thickness of the diffusion layer. The extent of blocking of the Ir electrode increases with temperature.

b) Studies by voltammetry and oscillographic polarography. The anodic current–voltage curves for the oxidation of I^- in 3 and 6 M solutions of H_2SO_4 show one wave corresponding to the reversible oxidation [reaction (1)] of iodide to iodine[98]. In every case, irrespective of the composition and pH of the supporting electrolyte, this process begins at a potential of 0.55 V. A decrease in the anodic oxidation current of I^- has been observed[99] at 0.68–0.70 V (against the NHE). Changes in pH from approximately 0 to 12 have no effect on the potential at which the fall in current begins. This effect must be due to a retardation of reaction (2) [99] or (especially at the higher potentials, 1.6–1.7 V) to an oxide covering of the platinum surface[98].

The oscillographic polarograms for the oxidation of I^- obtained at 51 °C with a potential sweep rate of $\nu = 0.09$ V s^{-1} show a steep current rise followed by a fall[100], preceded by another clearly visible portion which becomes longer at high temperatures and disappears at low temperatures (20 °C). This additional feature of the polarogram is explained[100] by the evolution of liquid iodine on the electrode: the subsequent freezing of the iodine is responsible for the fall in current. The surface layer of iodine consists[101] of a dense part (next to the electrode) and a porous outer layer, and partial dissolution of the outer layer occurs while the dense inner layer becomes thicker. The decrease in current is due simply to the high resistance of the anodic film of iodine (0.18×10^5–7.0×10^5 Ohm cm).

A combination of oscillographic polarography and measurements of light intensity against time (ρ–τ) led to the conclusion[102] that the deposition of liquid iodine on the anode causes ρ to decrease, and the subsequent freezing of the layer results in a further increase in ρ. The maximum, and the final decrease in ρ, are ascribed to the consolidation of the iodine film.

In aqueous solutions reaction (1) is reversible on a Pt electrode[63,103], and in $HClO_4$ reaction (2) also takes place[103], the potential of reaction (1) being more positive than that of reaction (2). The second wave could correspond to the formation of I^+ [103,104] or of an oxide film[105,106].

The I^- ion has been studied by voltammetry also in other solvents; acetic acid[107–110], acetonitrile[90,111–117], DMF,[117–119] DMSO,[120] fluorosulphuric acid[121], nitromethane[90,122], pyridine[104,123,124], methanol[119,125], propanol[126], ethylene carbonate[127], propene carbonate[128], sulpholane[129], and acetone[90,113].

Changing from water to an organic solvent does not significantly alter the mechanism of the reactions in the I_2/I^- system: the oxidation of I^- in different solvents may involve either one or two steps. As Krishtalik points out[130], a change in the solvation energy of the electrically active ion is not directly reflected by the overvoltage of the electrode reaction. The indirect effect may be quite large, and lead to an increase in the concentration of non-solvated ions and in the stability of the I_3^- complex ion in different (protonic, or aprotic) solvents. The following values have been reported for the constant of the equilibrium (8): in water 10^3,[92,113] in t-butanol $10^{3.73}$,[131] in methanol $10^{4.2}$ (or $10^{4.94}$),[125,129,131] in isopropanol $10^{4.36}$,[131] in DMSO $10^{4.9}$,[131] in acetic acid $10^{5.0}$ (or $10^{5.24}$),[107,132] in acetonitrile $10^{6.6}$ (or $10^{6.75}$, $10^{4.0}$),[90,111,113,131] in nitromethane $10^{6.7}$,[90] in DMF $10^{7.35}$,[133] in sulpholane $10^{7.4}$,[129] and in acetone $10^{8.3}$.[90]

One-step oxidation of I^- is observed mainly in protonic solvents (water, methanol, acetic acid, etc.), the rate of the anodic reaction decreasing steeply (almost two-fold) from water to methanol and only slightly from methanol to CH_3COOH while the activation energy remains almost unaffected[119]. In aprotic solvents (acetonitrile, DMF, DMSO, nitromethane, etc.) the oxidation takes place in two steps: in the first the I_3^- complex is formed by reaction (2), and in the second it is discharged by the reaction

$$2I_3^- - 2e \rightarrow 3I_2 , \qquad (10)$$

because of the greater stability of I_3^- in these solvents.

In dilute (up to 10^{-3} M) methanolic solutions the I^- ion shows only one oxidation wave[125] to I_2 by Eqn.(1), whereas in more concentrated solutions the oxidation occurs in two steps through the formation of I_3^-. In acid methanolic solutions (pH 4.0) only one wave is observed [Eqn.(1)]. In weakly alkaline solutions (pH 8.5) two waves of approximately equal height are observed:

$$I_2 - 2e \rightarrow 2I^+ .$$

The I_2/I^- system in acetonitrile has been studied on pyrolytic graphite[112] by non-stationary and cyclic voltammetry, and three oxidation waves of I^- have been detected. The first has been assigned[113,114] to the irreversible reaction (2). The second wave is assigned to reaction (10), which is reversible according to the cyclic voltammetry method[112,127]. When an excess of iodine is added to a solution of KI in acetonitrile the I^- is converted into I_3^-, and the polarisation curve shows only the second wave with a height equal to the sum of the heights of the two I^- oxidation waves obtained in the absence of I_2.[114] Cyclic voltammetry has shown that the height of the cathodic peak is double the height of the anodic peak: this is explained[112] by the substantial adsorption of the electrically active I_2 species on the surface, as pointed out in Refs.63 and 65. The second wave shows a well developed anodic peak and a relatively small cathodic peak at low sweep rates (v) of the potential. This is explained by the instability of the product corresponding to the second peak. The cyclic voltammetry plots for the third wave do not show a cathodic wave in neutral or acid media[112]. Oxidation of I^- by reactions (2) and (10) is reported also in Ref.129.

In acidified pyridine four stable forms have been identified[124]: I^-, I_2, I_2^-, and I^+. The concentration of pyridine (even above 3 M) has no effect on the height of the first or the second wave in aqueous solutions, though the half-wave potential of the second wave is shifted towards more negative values[113]. The current decreases in the sequence pyridine > 2-picoline ≫ 2,6-lutidine (dimethylpyridine), which is the same as the order of decreasing basicity of these molecules.

At low concentrations of I^- (0.06 g-ion litre^{-1}) and especially in the presence of H_2SO_4 the potentiodynamic current–voltage curves[134] show two Tefel regions, corresponding to reactions (2) and (1), with the limiting current associated with the first step and the current peak with the second. The linear portions of the ϕ,lg i curves for the first step are parallel for different concentrations of KI, giving the order of the anodic reaction as $p_a = 2$.

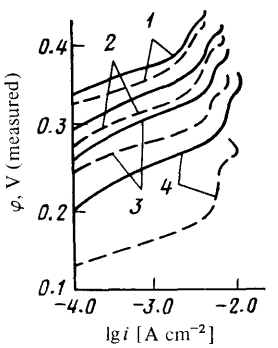


Figure 3. Anodic potentiodynamic curves in a solution (c_{KI} = 0.09 mole litre^{-1}) containing sulphuric acid (pH 0.62) in the presence (broken lines) and in the absence (full lines) of naphthenic acids for different potential sweep rates[136]: *1*) 0.04, *2*) 0.2, *3*) 0.4, *4*) 1.0 V min^{-1}.

The slope of the ϕ,lg i straight lines for the first step varies with the supporting electrolyte: in a solution without supporting electrolyte the slope is 0.042 V (α = 0.7), whereas in 1 *N* Na_2SO_4 it is 0.034 V (α = 0.87).[135,136] In the presence of an excess of supporting electrolyte the hydration of the I^- ions is suppressed, and this facilitates the discharge. Thus, in the presence of 1 *N* Na_2SO_4 the temperature coefficient of the overvoltage $(d\eta/dT)_i$ decreases from 3.5×10^{-3} to 0.85×10^{-3} V K^{-1}. Also, the activation energy of the process in 1 *N* Na_2SO_4 is much lower than in the absence of supporting electrolyte[135]. Even naphthenic acids (usually thought to be surface-active) lower the overvoltage for the oxidation of I^- (Fig.3), and when both the naphthenic acids and 1 *N* Na_2SO_4 are present together in solution the oxidation of iodide on platinum becomes almost barrierless (α = 0.97).[136] However, on a graphite electrode[137], and especially on a lead dioxide anode[138], the oxidation of I^- is strongly suppressed by naphthenic acids (Fig.4).

c) Studies by the rotating disk electrode method. The rates of the anodic and of the cathodic process are differently affected by the speed of rotation of a disk electrode ω:[139] a) the i,ϕ curves for the anodic and the cathodic process are asymmetric for different values of ω: b) the anodic reaction is ~10 times faster than the cathodic reaction; c) the rates of both processes are strongly influenced by stirring, but the effect is even more marked on the cathodic than on the anodic process.

At polarisation potentials <30 mV the rate of the anodic process is almost independent of ω, but for $\phi > 30$ mV the rate initially increases very rapidly with $\omega^{1/2}$ and reaches a constant level[140] for $\omega^{1/2} = 115-130$ min$^{-1/2}$. For fixed values of the potential and of ν the current increases with ω: the fall in current becomes sharp, and a large number of crystallisation centres appears on the electrode[141]. In a more concentrated solution (0.5 *N* KI + 0.01 *N* I_2) with $\omega = 580$ min^{-1} the fall in current no longer occurs, suggesting[141] a passivating role for the iodine film in the electrode process.

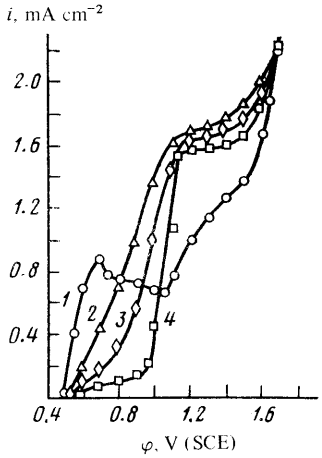


Figure 4. Anodic polarisation curves for the oxidation of iodide ions in an artificial concentrate on a lead dioxide electrode for different concentrations of naphthenic acids[138]: *1*) 0, *2*) 0.65, *3*) 1.02, *4*) 1.30 g litre^{-1}.

At low speeds of rotation of the electrode the overvoltage in the initial portion of the i, ϕ curve is close to that calculated by the Nernst equation (3).[97,142] However, as ω increases, the contribution to the polarisation from the slow electrochemical reaction also increases. Therefore in order to determine the kinetic currents (i_{kin}) for the oxidation of I^- we must extrapolate[142] the current at a given potential to an infinitely large value of ω by Frumkin and Tedoradze's method[143], since under these conditions linear (Tafel) regions are not found in the $\lg i-\phi$ curves. Extrapolation of the linear portions of the $\lg i_{kin}, \eta$ curves to $\eta = 0$ gave the exchange currents (i^0), which were shown[142] not to be equal for corresponding anodic and cathodic processes ($i_a^0 > i_c^0$, always).

The α_a and α_c values calculated from the slopes of the linear portions of the $\lg i_{kin}, \eta$ curves (i.e. the transfer coefficients for the anodic and the cathodic reaction) do not add up to 1. In solutions with $c_{I^-} \gg c_{I_2}$ we always find $\alpha_a + \alpha_c > 1$ (as high as 2 in some cases), whereas in solutions with similar concentrations of I^- and I_2 the sum is $\alpha_a + \alpha_c \leqslant 1$.[142] The order p_a is 1 with respect to I^- and 0 with respect to I_3^-. From these results it is concluded[142] that in the I^-/I_3^- system the overall electrode reaction (2) involves the two consecutive reactions (6) and (9), and the exchange current of the former reaction is greater than that of the latter.

The anodic oxidation of I^- becomes to a large extent irreversible when the solution pH is increased (pH > 1),[104] and it becomes reversible when the ratio $c_{I_3^-}/c_{I^-}$ decreases (with $c_{I^-} \leqslant 2.5 \times 10^{-4}$).[144] In very dilute solutions adequate kinetic currents are not obtained[145].

The order of the anodic reaction (1) with respect to I^- depends (though only slightly) on the supporting electrolyte present in solution[142]: without a supporting electrolyte $(\partial \lg i_{kin}/\partial \lg c_{I^-})_\phi = 1.3$, and in 1 *N* Na_2SO_4 $(\partial \lg i_{kin}/\partial \lg c_{I^-})_\phi = 1.0$. This effect is explained, according to Frumkin's theory[146], by the existence of a ψ' effect in the I_2/I^- system. Since in the presence of iodide ions the SO_4^{2-} ions are not specifically adsorbed, and the I^- ions irreversibly chemisorbed on Pt are not electrically active[63], we may assume[142] that the reacting species are mostly found on the outer Helmholtz plane of the diffusion layer, whose potential (ψ') varies with the concentration of the supporting electrolyte. Also, an increase in i^0 with concentration of the supporting electrolyte is possible only if ψ' is negative.

According to the present writer it is incorrect to ignore the decrease in hydration of I^- with increase in concentration of the supporting electrolyte. In the presence of electrolyte the concentration of non-hydrated I^- near the electrode surface increases, and this assists the discharge act. Hence in the presence of supporting electrolyte not only i^0 but also α should increase. In the absence of molecular iodine and under equilibrium conditions the inner Helmholtz plane consists of irreversibly adsorbed I^-(ads) species, and the outer plane of non-hydrated (or partially hydrated) I^- ions which are in equilibrium with the fully hydrated I′ ions:

$$I^-(ads) \leftarrow I^- \rightleftarrows I' . \qquad (11)$$

When the oxidised form I_2 is also present in the solution (and adsorbed on the surface) the system becomes more complex:

$$\begin{array}{l} I^-(ads) \leftarrow \\ I_2(ads) \rightleftarrows I^- + I_2 \rightleftarrows I_3^- \rightleftarrows I' + I_2(aq) \rightleftarrows I_3' \end{array} \qquad (12)$$

Obviously the exchange current will increase with the concentration of I^- in both cases, but the dependence of the rate of the anodic process on $[I^-]$ will be more marked for (11) than for (12) because of the absence of I_3^- ions. Increasing the concentration of I_2 shifts the equilibria (12) towards the formation of I_3^-, which lowers the concentration of I_3^-, and should lower the limiting current of the anodic curve (as is found experimentally[139]). In the absence of the oxidsed form or with an excess of supporting electrolyte the equilibrium (11) is strongly displaced towards the left and the rate of the anodic process increases and becomes almost proportional to the square of the concentration of iodide ions[134,137].

It is interesting to consider whether adsorbed iodide can be oxidised. If a chemical compound of the MI_2 type is formed on the surface of the metal electrode this question cannot be answered meaningfully, but if physico-chemical adsorption (depending on the charge on the surface) is assumed, easy discharge of the adsorbed iodide can be expected.

After being immersed in a solution of KI for some time a platinum electrode gave a sharp current rise (at $\phi = 0.53$ V) followed by a slight fall. Even a second oxidation wave (iodine to iodate) has been observed at $\phi = 1.19$ V, and ascribed[148] to oxidation of adsorbed iodide. However, it is strongly argued[65] that oxidation of iodide does not take place on a Pt electrode previously immersed in an I^- solution: the adsorbed iodide is stated to be electrically inactive since the adsorption is irreversible and the exchange reaction $I^-(ads) \rightleftharpoons I^-(sol)$ is slow. These views are inconsistent with many published results[92,94,144,147]. It has been suggested[149] that the absence of an anodic oxidation wave for I^- on an electrode previously immersed in a solution of KI [65] could

be due to the influence of oxygen atoms resulting from the treatment of the platinum surface. Lukovtsev and coworkers[142,150,151] stress the lack of electrical activity of adsorbed iodine.

Various additives (ClO_4^-, CH_3COO^-, SO_4^{2-}, PO_4^{3-}, citrate ion) in I^- solutions lower the effective activation energy E_{eff} of the anodic process, the magnitude of the effect increasing with the concentration of the additive[152]. The dehydrating action of the added ions was suggested[152] as an explanation. At the higher additive concentrations the rate of the anodic process falls due to the adsorption of the added ions on the platinum surface[153]. Cationic additives (Hg_2^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}) lower the limiting current of both the anodic and the cathodic process[151] by being adsorbed on the electrode or by forming stable compounds with the iodide.

In DMF solutions the order of reaction (2) with respect to I^- is 1, and the adsorption of I^- on the electrode has been suggested[117] as the slow step of reaction (2), since DMF is adsorbed on platinum more strongly than water and thus inhibits the adsorption of I^-. The fall of the current in the i,η curves is also explained[117] by the slow desorption of iodine from the electrode surface rather than by the formation of a new phase (iodine film) postulated for water solutions.

As the concentration of DMF in a water + DMF mixture increases, the overvoltage of the anodic reaction increases gradually, reaching its highest value in pure DMF.[118] On the anodic curves for the oxidation of I^- in a medium containing relatively small additions of water to DMF (2.2 and 11 M H_2O in DMF) two I^- oxidation waves are observed, as in pure DMF.[117] As the water content of the mixed solvent is increased, the first wave becomes indistinct, and at the potentials of the second wave we observe a sharp rise in current with an associated fall, as in the case (water solution) of the formation of a surface film on the electrode[101,114]. When the concentration of DMF in the mixture is increased, i^0 decreases and the sum of α_a and α_c changes from 2 (in pure water) to 1 (in pure DMF). It has been suggested[118] that in DMF and its mixtures with water (as in pure water) the overall electrode reaction involves two consecutive steps: discharge and electrochemical desorption [reactions (6) and (9)], with comparable exchange currents. The same mechanism# is proposed for DMSO [120] and acetonitrile[111].

d) Studies by chronopotentiometry. The kinetics of electrode reactions in the I^-/I_2 system have been studied[64] by the application of very short galvanostatic pulses, assuming the mechanism of the anodic and the cathodic reaction proposed by Vetter[92].

The chronopotentiograms for the electrolytic oxidation of I^- in water, methanol, 1-butanol, 2-propanol, and acetic acid indicate the formation of I_2 by a single one-electron step[104,110]. Two-step oxidation of I^- to I_2 was observed[110] in ethylene glycol, acetonitrile, acetone, 1,2-dimethyloxyethane, nitromethane[154], DMSO, and acetic anhydride. In pyridine (Py) the anodic reactions $I^- \to I$ and $I \to I^+$ take place[110,113] in spite of the fact that I_3^- is more stable than PyI_2.[155] The addition of NaI to a solution of I_2 in pyridine produces three steps on the chronopotentiogram, with $E_{1/4}$ values of 0.35, 0.5, and 0.9 V respectively, corresponding to reactions (2) and (10), followed by the oxidation of I_2 to I^+ [110] as a result of the dissociation of the iodine molecule in pyridine[123]:

$$2I_2 + Py = PyI^+ + I_3^- .$$

#At high positive potentials and low surface coverages the rate-determining step of the second wave in DMSO is thought to be the reaction[120] $I_3^- + M \rightleftharpoons M(I_3) + e$.

In the presence of chloride ions the oxidation of I^- in nitromethane[154] takes place by the reaction

$$I^- + Cl^- - 2e \to ICl . \qquad (13)$$

2. Electrolytic Reduction of Iodine and of the Iodine–Iodide Complex

a) Studies by Faradaic impedance and rectification methods. Vetter's Faradaic impedance method[92] has established the value of p_c for the electrochemical reduction of iodine on platinum by the overall reaction

$$I_3^- + 2e \to 3I^- \qquad (14)$$

and has led to the following mechanism for the process:

$$I_3^- \to I_2 + I^- \qquad (15)$$

$$I_2 \to 2I \qquad (16)$$

$$I + e \to I^- , \qquad (17)$$

in which the discharge is the slow step. The same mechanism has been proposed[156] for the electrolytic reduction of I_3^- on a porous graphite electrode in acid or neutral protonic solvents, with the following kinetic parameters:

α_c	α_a	p_c (for I_3^-)	p_a	p_c (for I^-)	p_a
0.5	0.5	0.5	0	−0.5	1

Simultaneous measurements of the Faradaic impedance and of rectification[157] have confirmed the scheme involving reactions (16) and (17). The transfer coefficient of the discharge step is given[157] as 0.47 (±0.04), but other workers[144, 150,151] report an α value varying regularly with the concentration of iodine in solution. The rate constant of the cathodic reduction of I_3^- is $(1-5) \times 10^{-2}$ cm s^{-1},[157] and it is assumed that at low coverages by adsorbed iodine ($\theta \to 0$) $p_c(I_2) = p_c(I_3^-) = \alpha = 1$, and the cathodic reduction of iodine on CdS and CdSe electrodes takes place by the discharge–electrochemical adsorption mechanism[157]

$$I_2 + e = I^- + I\,(ads) , \qquad (18)$$

with simultaneous rate limitation by the two electrochemical steps.

b) Studies by voltammetry and oscillographic polarography. The shape of the cathodic wave on the voltammetric curves measured on a platinum electrode is independent of the direction of the potential sweep[104]. The diffusion current is proportional to the concentration of I_2, and the ratio i_d/c_{I_2} is 190 μA mM^{-1}. In the absence of Cl^- ions the iodine is reduced by the reaction

$$I_2(aq) + 2e \rightleftarrows 2I^- , \qquad (19)$$

but in 4 M HCl the iodine exists mainly as the iodine–chloride complex (I_2Cl^-), and the electrode process corresponds to the reaction

$$I_2Cl^- + 2e \to 2I^- + Cl^- . \qquad (20)$$

In 0.1 M perchloric acid and in the presence of 0.05 M sodium cyanide the cathodic iodine reduction wave is not observed. Iodine cyanide, formed by the reaction

$$HCN + I_2 \rightleftarrows H^+ + I^- + ICN , \qquad (21)$$

is not reduced on platinum, and no free iodine is present[104].

On a Pd electrode the reduction of iodine is irreversible up to an overvoltage of ~500 mV, beyond which a steep current rise is observed, associated[158] with the reduction of the

film of iodine on the electrode surface. When this film has been removed the electrolytic reduction of iodine becomes much faster, reaching the limit set by the diffusion current. The existence of a "pre-wave" on the polarisation curve for the electrolytic reduction of iodine on Pd is explained by the partial blocking of the electrode at η values up to 0.5 V, so that the observed limiting currents are lower than those for an electrode with a uniform surface.

Since I_3^- is much more stable in DMF than in aqueous solutions, the species which is reduced in DMF is not I_2 but I_3^-.[118] The potentiodynamic curve for the reduction of I_3^- in DMF includes a limiting current plateau followed (beginning at $\eta = 0.8$ V) by a decrease in current arising from the negative charge of the reacting species[159]. This explanation implies that in the presence of an excess of I_2 (and in contrast to the case of high concentrations of I^-) no current fall should occur at potentials up to −2.0 V. During the reduction of I_3^- the curves plotted in the reverse direction always lie below the forward plots. Furthermore, the depth of the current minimum (beyond the current fall) decreases as the potential sweep rate increases, and disappears completely at the highest rates ($v \geq 40$ mV s^{-1}). According to Povarov and coworkers[159], at potentials close to the equilibrium value I_2 is reduced to I_3^-:

$$3I_2 + 2e \rightarrow 2I_3^- , \qquad (22)$$

and in the presence of high concentrations of KI the iodine–iodide ion is further reduced to I^- by reaction (14). These processes take place through the adsorption of I_2 and I_3^- on the electrode. At sufficiently high negative potentials the iodine is desorbed from the surface, and subsequent reduction takes place without adsorption. "Stretched" irreversible waves are observed in the reduction of iodine, and inhibition of the reaction in the case of I_3^- reduction: thus the process appears to be determined by the rate of penetration of I_3^- into the EDL.

Two-step reduction of iodine by reactions (22) and (14) has been observed also in acetic anhydride[107].

c) Studies by the rotating disk electrode method. A diffusion-limited current is observed[104,144,151,160] in the reduction of I_3^- on a Pt electrode. Under both turbulent and laminar stirring regimes a well defined plateau is observed on the cathodic i, ϕ curves for a 0.1 M I_2 + 1 M KI solution at different values of ω, and the limiting diffusion current varies linearly[160] with $\omega^{1/2}$, the activation energy of the cathodic process under laminar stirring being almost one-half the value for turbulent stirring. The activation energy of the process (E_{eff}) is also a function of the rate of rotation of the electrode: at first E_{eff} increases with $\omega^{1/2}$, but at the higher values of ω (beyond $\omega^{1/2} = 110$ $s^{-1/2}$) E_{eff} becomes constant[139]. The rate of the cathodic process also increases in proportion to the concentration of I_2.[139]

These results confirm that the rate-limiting process (as in the anodic process) is the diffusion of the reacting ion towards the electrode. But since the products of the anodic and the cathodic process are removed from the electrode at different rates, i.e. fairly slowly in the case of the anodic process (iodine–iodide complex) and rapidly in the case of the cathodic process (iodide ion), the oxidation and the reduction processes in the I_2/I^- system are affected by ω to different extents. For $\omega = 3000$ min^{-1} the rate of the cathodic process increases by a factor of 22.4 (as compared to the rate for $\omega = 0$), whereas the rate of the anodic process increases only by 9.6.[139] However, in a solution containing ~10 times more I_2 than I^- the rate of the cathodic process is ~10 times higher than the rate of the anodic process[140]. At high speeds of rotation the parameter ω no longer affects the rate of cathodic reaction[139,140], indicating electrochemical rate control.

Because iodine is reduced with a high overvoltage on a rotating Pd electrode[158] the order p_c with respect to I_2 can be determined from the kinetic currents obtained by extrapolation of the $i^{-1}, \omega^{-1/2}$ curves to $\omega \rightarrow \infty$: for $\eta = 100$–150 mV, $p_c = 1$.[158] On a Pt electrode the p_c value for I^- and I_2 could not be determined accurately[142,158], because the slope of the linear portions of the $\lg i_{kin} - \phi$ curves varies with the concentration of I^- and I_2. By using curves with similar slopes the parameter p_c was determined approximately for I^- and I_2: $p_c(I_2) = 1$ and $p_c(I^-) = -1$.[142] The negative order of p_c with respect to iodide suggests[142] that the kinetic unit in the cathodic process is I_2 rather than I_3^-. Thus, as the potential of the electrode is made more negative the bond between I^- and I_2 in the I_3^- complex should be weakened by the repulsion forces acting on the iodide, which favour the formation of adsorbed atoms or molecules of iodine on the electrode surface[64].

From the initial portions of the i, ϕ curves obtained in a study[144] of the electrolytic reduction of iodine on a rotating Pt electrode, which gave the kinetic parameters of the cathodic reaction, the order p_c was found to depend both on the concentrations of I_2 and I^- and on ω. This result was explained[144] in terms of the non-uniformity of the electrode surface. It was shown that electron transfer from the platinum to an adsorbed iodine atom is the slow step in this case. The height of the cathodic I_2 reduction waves on Pt is unaffected (within experimental error) by changes in the acidity of the solution[98], but the limiting current decreases if the time of immersion of the electrode in the solution is increased[151]. These changes in current on an activated electrode can be as high as 20–30% of the i_d value for the first wave in a solution containing an excess of supporting electrolyte (Na_2SO_4). In solutions containing only I_2 and I^- the time dependence of i_d is slighter, and decreases with the concentration of iodine. The changes in limiting current are ascribed[151] to non-uniformity of the platinum surface, produced by the irreversible adsorption of iodine on Pt.

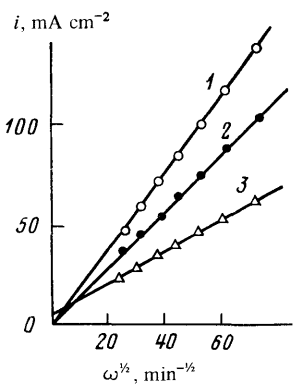


Figure 5. Cathodic limiting current against speed of rotation of the platinum electrode for a 0.2 M KI + 2 × 10^{-2} M I_2 solution at different temperatures[150]: *1*) 50, *2*) 25, *3*) 1 °C.

The surface non-uniformity of the platinum[139] and of the iridium electrode[97] causes anomalous variations of i_d with $\omega^{1/2}$: at low temperatures (1 °C) the extrapolation of the linear $i_d, \omega^{1/2}$ plots for the reduction of iodine does not pass

through the origin[150] (see Fig.5). A quantitative interpretation of this observation was proposed[150] by introducing into the Levich equation an additional term as required by Landsberg's theory[161], independent of ω and determined by the number of active sites on the electrode surface and on the distance between these sites:

$$1/i_d = 1.61\nu^{1/6}/nFD^{2/3}c\omega^{1/2} + \left|\sum A_n\right|/nFDc\,, \qquad (23)$$

where $|\Sigma A_n|$ is the non-uniformity function of the electrode surface, which increases with the non-uniformity, i.e. as the ratio of the radius (r_1) to the spacing (r_2) of the active sites decreases.

According to Landsberg[161] if $r_2 > \delta$ (where δ is the thickness of the diffusion layer) the current i_d is given by the equation

$$i_d = nFD^{2/3}\omega^{1/2}/1.61\nu^{1/6}\left(1 + \left|\sum A_n\right| r_n/r_2\right)\,, \qquad (24)$$

and if $r_2 \ll \delta$, i_d is given by Eqn.(23). It is pointed out[151] that at ordinary temperatures $r_2 > \delta$ on a platinum surface, and therefore i_d is given by Eqn.(24). At lower temperatures the size of the active sites decreases and we have $r_2 < \delta$, leading to a non-linear dependence of i_d on $\omega^{1/2}$ [Eqn.(23)]: a possible explanation of the decrease in radius of the active sites at low temperatures is the chemisorption of ions on the electrode surface[150]. The surface of the iridium electrode in the I_2/I^- system is partially blocked, and the active sites are small. Therefore the variation of i_d with $\omega^{1/2}$ is as predicted by Eqn.(23).[97] The surface of the palladium electrode is fairly uniform: a large number of small active sites is present on an active palladium surface. However, the number of active sites decreases with time, and the Pd electrode becomes similar to the iridium electrode, with relatively few, small active sites, so that for a partially poisoned Pd electrode we can write $r_2 \ll \delta$. When the electrode surface is uniform the E_{eff} value for the limiting diffusion current is determined by the activation energy for viscous flow, as in the case of the Pt electrode§. However, for the Ir electrode[97] the activation energy is lower, and it is a function of ω. The activity of the iridium surface decreases as the temperature rises: this effect is partially compensated by the increased rate of diffusion.

When zinc and mercury ions are present in solution the time dependence of i_d is even more marked[151]. At sufficiently negative potentials the surface is blocked by a film of zinc iodide, which causes a sharp fall in current, and the electrolytic reduction of I_2 and electrodeposition of zinc are suppressed. Mercury ions are adsorbed with the iodine, lowering the rate of both the anodic and the cathodic reaction. Zinc ions also increase the amount of iodine irreversibly adsorbed on the electrode surface, but the effect is less marked than with mercury. Cadmium ions have a smaller effect than Zn^{2+} ions on the cathodic reduction of iodine. They are adsorbed on Pt over a wide range of potential[162], and their effect on the cathodic process is negligibly small, but they lower the rate of the anodic process. A possible explanation[162] is the suppression of iodine adsorption, and hence of the rate of the electrochemical desorption (9), by the adsorbed Cd^{2+} ions. The adsorption of Cu^{2+} on Pt prevents the formation of Pt–I^- bonds but it has almost no effect on the amount of iodine reversibly adsorbed on the electrode surface[151]. Unlike mercury ions, which block the surface by forming iodine compounds, metallic mercury deposited on a Pt surface has very little effect on the current[151]. The presence of Cl^- ions does not affect the half-wave potential for the reduction of I_2 to I^-, or the reversibility of the process[164].

The fluctuation of the limiting reduction current of I_2 is also ascribed to surface non-uniformity[165]. On a platinised platinum electrode the mean amplitude of the oscillations of the limiting current is lower by almost a factor of two than on smooth platinum, and decreases faster than on smooth platinum with increase of ω.[165] Potential and current oscillations have been observed[84] in the I_2/I^- system, and ascribed to turbulence in the flow of electrolyte. The adsorption of Hg^{2+} on the electrode surface minimises the fluctuations in the limiting current[165], and the adsorption of DMF suppresses them completely. DMF solutions (unlike water solutions) show a fall in current (after the limiting current) accompanied by much stronger fluctuations[159].

In DMF two limiting currents for the cathodic reduction of iodine are observed, and both are free from oscillations. These waves correspond to reactions (22) and (19).[117]

Since the slopes of the $\Delta\phi$, $\lg(1 - i/i_d)$ plots for both these waves are substantially higher than their theoretical values the authors[159] conclude that the processes are irreversible, especially in the case of reaction (19), due to the absence of adsorbed iodine. When an excess of I^- is present in solution the cathodic curve consists of one wave, and the reaction is

$$I_2\ (ads) + I^- \rightleftarrows I_3^-. \qquad (25)$$

In solutions containing more I_2 than I^- the reduction of I_2 is kinetically of the first order, and the most likely slow step is the adsorption of iodine on the electrode surface[159]. In ethylene glycol[166] and acetonitrile[111] with $[I_2] > [I^-]$, I_2 and I_3^- are reduced successively by reactions (22) and (14). In acetonitrile both the first and the second cathodic process go through the rate-determining step (18).[111] In DMSO [120] the rate-determining step is the reaction

$$I_3^- + e \rightarrow I\ (ads) + 2I^-. \qquad (26)$$

In methanolic solutions[119] the iodine is reduced as in aqueous solutions, with more marked stirring effects on the cathodic than on the anodic process.

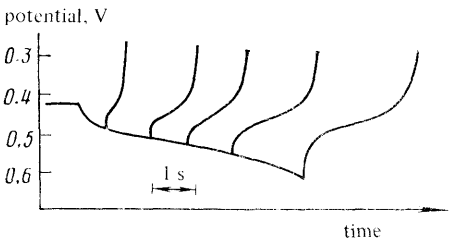


Figure 6. Effect of applying reverse current at various points of the chronopotentiogram for the oxidation of iodide ions[65].

d) Chronopotentiometric studies of the reduction of iodine in DMSO have given results consistent with those of the rotating disk electrode method: in particular, reaction (14) was shown to be irreversible. However, its rate constant determined chronopotentiometrically [$(1.12–2.86) \times 10^{-4}$ cm

§ An activation energy of 2.2 ± 0.1 kcal mole^{-1}, independent of ω, was obtained[97] from the slope of the $\lg i_d, T^{-1}$ straight lines. This is consistent with the published values[160,163] 2.08 and 1.88 kcal mole^{-1} respectively.

s^{-1}] is lower than the value obtained on a rotating disk electrode (6.8×10^{-4} cm s^{-1}).[120]

Contradictory conclusions as to the lack of electrical activity of adsorbed iodine have been drawn from chronopotentiograms. According to Hubbard and coworkers[63] only reversibly adsorbed iodine can be reduced cathodically, and the amount of electrically active iodine on the Pt surface is much less than the strongly bound iodine. However, Osteryoung and Anson[65] find that the reverse (cathodic) chronopotentiograms taken at different points of the anodic chronopotentiogram give transition times proportional to the amount of iodine evolved anodically and adsorbed on the electrode surface (Fig.6). According to Schuldiner and Presbrey[64] even α_c depends on the number of iodine atoms adsorbed on the Pt. The high rate of oxidation of I_2 chemisorbed on PbO_2 has been pointed out[62].

IV. REDOX REACTIONS IN I^-/IO_3^-, I_2/IO_3^-, AND I_2/I^+ SYSTEMS

1. Anodic Processes

Unlike the electrolytic oxidation of iodide to iodine, the deep oxidation of I^- to oxygenated compounds, in particular by the reaction

$$I^- + 3H_2O - 6e = IO_3^- + 6H^+, \quad (27)$$

depends on the pH of the electrolyte, as has been confirmed experimentally. Changing the pH between 5.85 and 1.72 produced a linear shift in potential towards more positive values[98] by 0.06 V for each pH unit, as required by Eqn.(27). Further increase in acidity did not affect the potential.

Since the "reverse" voltammetry curves (i.e. those plotted by decreasing the positive potential after the anodic wave corresponding to the formation of IO_3^-) do not reproduce the wave given by the oxidation of iodide to iodate[98,104], a mechanism involving the participation of oxygen from surface oxide layers of the platinum has been suggested[98]:

$$PtO[O]_n + I^- \rightarrow IO_3^- + PtO[O]_{n-3}. \quad (28)$$

The current fall observed on the polarisation curves is also ascribed to the formation of surface oxide layers on the platinum. It is suggested that reaction (27) takes place at 0.9–1.2 V, whereas at more positive potentials the oxidation of I^- involves the scheme (28). It has been established[148] that the second anodic oxidation wave of I^- corresponds to the deep oxidation of iodine:

$$I_2 + 6H_2O - 10e \rightarrow 2IO_3^- + 12H^+. \quad (29)$$

On an electrode consisting of a mixture of graphite and azobenzene[167] and on a pyrolytic graphite electrode[112,168] two iodide oxidation waves have been observed: to hypoiodite and to iodate. The height of these waves is proportional to the concentrations of I^- and I_2, and depends on ω. The total height of the waves is determined by the diffusion of OH^- to the electrode (for intermediate concentrations of OH^-). The electron transfer reaction for the iodate formation step is of the first order with respect to I^-; with respect to OH^- the order is 0.23 at pH 6–10.6 and zero at higher pH values. hence we may conclude that in alkaline solutions I^- is discharged on the surface sites where OH^- ions are adsorbed[167]:

$$I^- + OH^- \rightarrow HIO + 2e \quad (30)$$

$$I^- + 6OH^- \rightarrow IO_3^- + 3H_2O + 6e \quad (31)$$

or

$$M + OH^- \rightarrow M{-}OH + e \quad (31a)$$

$$x(M{-}OH) \rightarrow M{-}(O)_x + xH_2O \quad (31b)$$

$$M{-}(O)_x + I^- \rightarrow M{-}(O)_{x-3} + IO_3^-. \quad (31c)$$

In solutions of pH > 6.5–7 free iodine cannot take part in the anodic reaction because of its disproportionation

$$I_2 + OH^- \rightleftarrows IO^- + I^- + H^+ \quad (32)$$

$$3I_2 + 3OH^- \rightleftarrows IO_3^- + 5I^- + 3H^+. \quad (33)$$

In iodic acid solutions the $\lg i, \phi$ curve for Pt, Pb, and PbO_2 electrodes[169] has two linear portions, corresponding to two controlling steps for the oxidation of iodine to highly oxygenated compounds by the reactions (29) and (34):

$$HIO_3 + H_2O - 2e = HIO_4 + 2H^+, \quad (34)$$

the rate of the latter reaction determining the rate of the overall process. On a PbO_2 electrode (or on anodically oxidised lead) the iodine is oxidised by the oxidation products of water, and in particular by $OH^\cdot$ radicals according to the mechanism (31a)–(31c).

It has been shown[104] that in acid aqueous solutions of I^- two anodic waves [corresponding to reactions (1) and (35)] are obtained:

$$I_2 - 2e \rightarrow 2I^+. \quad (35)$$

The maximum current of the second wave is equal to twice the diffusion current of the first wave. At pH 8 the two waves merge, but the limiting current still corresponds to the quantitative oxidation of I^- to I^+. In a medium containing 0.05 M NaCN and 0.1 M $HClO_4$ the I^- ion gives an anodic wave with a height double that for an iodine solution of the same normality:

$$I^- + HCN \rightarrow ICN + H^+ + 2e. \quad (36)$$

These results[104] are not confirmed by chronopotentiometric data[170–172], which suggest that the second anodic wave in the oxidation of I^- is associated with reaction (29) rather than with the formation of I^+ by reaction (35), since this wave is completely suppressed when the electrode is polarised from an oxidation towards a reduction potential.

Measurements by the rotating disk electrode method with a guard ring have shown[164] that positively charged iodine ions (I^{n+}) are formed by the deep oxidation of I^- on a disk electrode and are transferred by convective diffusion to the ring electrode where they react with the I^- in solution as follows:

$$I^{n+} + nI^- = 1/2(n+1)I_2. \quad (37)$$

This explains the failure of positively charged forms of iodine to give a reverse electrolytic reduction wave. A mechanism involving reaction (27) was assumed[164], as in Ref.170, on the grounds that the ratio of the limiting currents for the first and the second I^- oxidation wave is six. However, it should be noted that the participation of the Cl^- ions in the electrode process was ignored in that work[170], though these ions are known to affect the mechanism of the deep oxidation of I^-. In the presence of a high enough concentration of Cl^- the first anodic wave corresponds to the oxidation of iodide to iodine [reaction (1)] followed by the formation of the iodine–chloride complex, and the second wave to the conversion of I_2Cl^- into iodine chloride[104,164,173–176]:

$$I_2Cl^- + 3Cl^- \rightarrow 2ICl_2^- + 2e. \quad (38)$$

The charge transfer processes in reactions (13) and (38) are polarographically reversible on smooth platinum[177].

In chloride solutions the I_2Cl^-, ICl, ICl_2^-, and I_3^- complexes are stable, with $[I_2Cl^-]/[ICl]\cdot[I^-] > [I_2Cl^-]/[I_2]\cdot[Cl^-] > [I_3^-]/[I_2]\cdot[I^-] > [ICl_2^-]/[ICl]\cdot[Cl^-]$.[177,178]

In methanolic solutions[125] and in acetic anhydride[107] iodine is oxidised to I^+, but the half-wave potentials for the oxidation of I_2 to I^+ and for the reduction of I^+ to I_2 are not the same at a given pH. In methanolic solutions the redox couple is thought[125] to be not I_2/I^+ but the iodine–iodonium methoxide couple:

$$I_2+2CH_3OH\rightarrow 2CH_3OI+2H^++2e\ . \qquad (39)$$

Iodonium methoxide is unstable and decomposes into iodates. The insolubility of iodates in methanol and the growth of an iodate layer cause passivation of the electrode.

In acetic anhydride[107] the iodine is initially oxidised to I^+, and then the I^+ reacts further with the acetic acid

$$I_2+2CH_3COOH-2e\rightarrow 2CH_2ICOOH+2H^+ \qquad (40)$$

to give monoiodoacetic acid which is decomposed in the next step by the Kolbe reaction

$$CH_2ICOOH-e\rightarrow (CH_2I)^\cdot+CO_2+H^+ \qquad (41a)$$

$$(CH_2I)^\cdot+H^+\rightarrow (CH_3)^\cdot+I^+\ . \qquad (41b)$$

2. Cathodic Processes

Iodine monochloride gives two scarcely distinguishable electrolytic reduction waves[104,179]:

$$2ICl_2^-+2e\rightarrow I_2Cl^-+3Cl^- \qquad (42)$$

$$I_2Cl^-+2e\rightarrow 2I^-+Cl^-\ . \qquad (43)$$

The reduction of ICl to I_2 is reversible, whereas the reduction to I^- is reversible only for $c_{H^+} < 0.3$ M.[164] The reversibility of the reduction of ICl_2^- to I_2 is influenced both by the concentration of HCl and by the state of the electrode surface. On smooth platinum the reduction of ICl_2^- to I_2Cl^- is quasi-reversible for $c_{HCl} \leq 1$ M, and becomes fully reversible for $c_{HCl} = 4$ M.[82]

On the dropping mercury electrode the reduction potential of IO_3^- in alkaline solutions is independent of pH, but in acid solutions it becomes less negative as the pH decreases[82].

The electrolytic reduction of iodates in aqueous, ethylene glycol, and propylene glycol solutions is essentially a catalytic reaction, different organic or inorganic additives affecting its rate in different ways[180]. Increasing the concentration of $NaClO_4$ lowers the reduction potential of IO_3^-; additions of $N(C_4H_9)_4^+$ in small amounts increase the rate of reduction, but in large amounts they inhibit the reduction by being adsorbed on the electrode. It is clear from the polarograms for the electrolytic reduction of IO_3^- [181] that gelatin, tylose, X-100 Triton, cetylpyridinium bromide, and cetyltrimethylammonium bromide behave as inhibitors towards this process, whereas *N,N*-dimethyl-*p*-phenylenediamine, hexamine, hydrazine, and polyethyleneimine catalyse it. It is suggested[181] that in acid and in neutral solutions the rate-determining step is a one-electron process, and in alkaline solutions a two-electron process, the slow step being the transfer of the second electron (involving breaking of the first bond between iodine and oxygen atoms).

Chronopotentiometric curves have been used[182] to determine the kinetic parameters of the reduction of IO_3^-. From the slope of the plot of ϕ against $\lg[1-(t/\tau)^{1/2}]$, where τ is the transition time, the authors[182] calculated the change in valency of the I during the slow step (unity), the coefficient $\alpha = 0.5$, and the order $p_C = 0.5$ with respect to iodates. However, according to Vetter[84] $\alpha = 0.6$ and is independent of the concentrations of IO_3^- and I^-, and the rate of the transition is proportional to the square root of the concentration of H^+ ions.

The reduction of iodate ions on platinum is strongly influenced by the state of the platinum surface. The reduction of IO_3^- is found[183] to be more reversible on the oxidised than on a reduced platinum electrode. The positive shift (by ~0.4 V) of the IO_3^- reduction potential caused by oxidising the electrode is explained[183] by postulating a catalytic interaction between the oxide films on the platinum surface and the iodate reduction process. However, the mechanism of the catalytic effect of the oxide films is not stated, though it is pointed out that the reduction of the oxide films begins before the reduction of IO_3^-.[183] The suggestion (from chronopotentiometric data) that oxide films may play a catalytic role is confirmed by voltammetry results: an additional peak at ~0.3 V in the i,ϕ curves for an oxidised platinum electrode, not observed for any other state of the electrode[183].

A mechanism for the electrolytic reduction of IO_3^- which allows for the postulated catalytic effect of oxide films has been proposed[184]. The role of the platinum oxides is interpreted as an increase in the rate constants of the dissociative chemisorption equilibria:

$$IO_2OH\rightleftarrows IO_2^+(\text{chem})+OH^-(\text{chem}) \qquad (44)$$

$$IO_2^+(\text{chem})+H_2O\rightleftarrows IO_2^++H^++OH^-\ . \qquad (45)$$

These catalytic changes produce substances which can be reduced at a lower overvoltage than the starting material.

The cathodic process in an IO_3^- solution in 0.1 M H_2SO_4 is catalysed also by sulphur atoms electrochemically adsorbed on the platinum surface from a solution of H_2S in 0.1 M H_2SO_4 or of 0.1 M Na_2S.[185] By comparing the polarisation curves for electrodes with and without a sulphur coating, and also for electrodes covered with oxygen, we can show that in the first case the half-wave potential ($E_{1/2}$) for IO_3^- is more positive than in the second case, but more negative than in the third. Hence the activating influence of sulphur is less effective than that of oxygen. The activation of the cathodic process by sulphur atoms has been explained[185] by an increased coverage of the electrode surface by IO_3^- ions in the sulphur-covered areas, due to the formation of stable compounds between IO_3^- and the adsorbed sulphur.

Vetter[84] noted a strong increase in the limiting current for the reduction of iodates at high concentrations of I_2. He ascribed the acceleration of the cathodic process by the addition of I_2 or by a decrease in pH to a fast ($E_{eff} = 5$–10 kcal mole^{-1} [186,187]) chemical reaction between IO_3^-, H^+, and I^- (the latter being formed by the direct reduction of IO_3^- or I_2):

$$IO_3^-+6H^++6e\rightarrow I^-+3H_2O\ (\text{slow}) \qquad (46)$$

$$5I^-+IO_3^-+6H^+\rightarrow 3I_2+3H_2O\ (\text{fast}). \qquad (47)$$

Anson[183] rejected Vetter's conclusion[84] and showed that the reduction of IO_3^- is independent of pH in the pH range 1–6, even with allowance for the formation[188] of iodine as an intermediate in the reduction of IO_3^- by a mechanism which includes reactions (46) and (47).

In the polarisation curves measured on a rotating disk electrode the autocatalytic mechanism including reactions (46) and (47) is more important at low rotation speeds ($\omega < 1600$ min^{-1}) than at high speeds[179]. The catalytic reduction is accelerated by increasing the concentration of IO_3^-.[164] The more positive half-wave potential for the reverse plot (i.e. for a potential sweep from the negative towards the positive values) than for the normal plot (Fig. 7) is also explained by the autocatalytic reduction of IO_3^-.[164] The observation that the direct reduction of iodate [reaction (46)] on a smooth platinum electrode in a 1–5 M H_2SO_4 supporting electrolyte requires a high overvoltage has led to the same conclusion[189].

In a hydrochloric acid medium at concentrations up to 3 M the cathodic processes include reaction (46) as the rate-determining step and the following fast reactions:

$$2I^- + IO^-_3 + 3Cl^- + 6H^+ \rightarrow 3ICl + 3H_2O \quad (48)$$

$$ICl + 2e \rightarrow I^- + Cl^-. \quad (49)$$

The electrochemical product I^+ is formed in substantial amounts when the concentration of I_2 is much greater than that of I^-.[164]

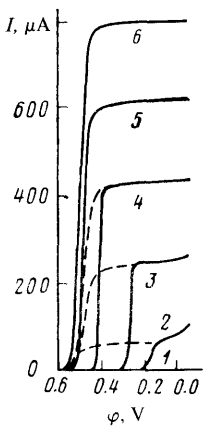


Figure 7. Reduction of IO_3^- in an HCl solution (rotating platinum disk electrode, $A = 0.36$ cm^2, $\omega = 400$ min^{-1}, $\nu = 0.4$ min^{-1}). Full lines denote potential sweep from (+) to (−), broken lines from (−) to (+):[164] *1*) 0.2 M HCl + 0.3 M NaCl, *2*)–*6*) with added KIO [10^4 c_{KIO}, mole litre^{-1}: *2*) 2 *3*) 4, *4*) 6, *5*) 8, *6*) 10].

In an acid 0.1 M phthalate buffer (0.01 M IO_3^- + 0.1 M KCl at pH 3.2) the catalytic effect is observed, and the current density and the kinetic parameters of the process vary with time[188]. Moderately fast stirring lowers the current at a given potential by the partial removal of iodine. In an alkaline 0.05 M borate buffer (0.01 M IO_3^- + 0.1 M KCl at pH 9.2) the current density is effectively independent of time. However, in the presence of camphor changes with time are observed. If KI is added to the borate buffer to a concentration of 0.1 M the current density changes with time both in the absence and in the presence of camphor. According to Vetter[84] a different mechanism should apply in an alkaline solution in which the iodine disproportionates according to reaction (33).

Thus we can infer from the inconsistency of published results on the mechanism and kinetics of the oxidation of I^- that the electrode processes in the I^-/I_2 system are so dominated by diffusion-limited kinetics that $i_0(6)$ and $i_0(9)$ are almost impossible to measure by any of the standard methods. Depending on the state of the I^- in the outer Helmholtz plane, and on the appearance of a ψ^- potential (which is often observed, especially in the presence of a supporting electrolyte, since I^- has "negative hydration"[190]), the rates of transfer of the first and the second electron in the overall reactions (1) and (2) can be very similar. The oxidation of I^- to I^{n+} is also very important; the reduction of IO_3^- to I^- is autocatalytic, but this mechanism has not been observed in the oxidation of I^- to IO_3^- (though it has been observed, at least in part[175], during the formation of ICl in the presence of Cl^-).

REFERENCES

1. A.N.Frumkin, Uspekhi Khim., 1955, **24**, 933.
2. T.N.Anderson and J.O'M.Bockris, Electrochim. Acta, 1962, **9**, 518.
3. M.Vorsina and A.N.Frumkin, Zhur.Fiz.Khim., 1945, **19**, 171.
4. I.A.Bagotskaya, Zhur.Fiz.Khim., 1952, 26, 659.
5. O.A.Esin and B.F.Markov, Zhur.Fiz.Khim., 1939, **13**, 318.
6. R.Parsons, "Trudy Chetvertogo Soveshchaniya po Elektrokhimii" (Proceedings of the Fourth Electrochemical Congress), Izd.Akad.Nauk SSSR, Moscow, 1959, p.42.
7. Tza Chyuan-sin' and Z.A.Iofa, Dokl.Akad.Nauk SSSR, 1959, **125**, 1065; 1959, **126**, 1303.
8. R.Parson, J.Electroanalyt.Chem., 1969, **21**, 35.
9. A.J.Parker, Uspekhi Khim., 1963, **32**, 1270 [Russ. Chem.Rev., 1963(10)].
10. Ya.Doilido, R.V.Ivanova, and B.B.Damaskin, Elektrokhimiya, 1970, **6**, 3.
11. I.M.Ganzhina, B.B.Damaskin, and R.V.Ivanova, Elektrokhimiya, 1970, **6**, 709, 1540.
12. R.V.Ivanova, L.N.Kuznetsova, and B.B.Damaskin, Elektrokhimiya, 1979, **15**, 1267.
13. T.A.Severeva, R.V.Ivanova, and B.B.Damaskin, Elektrokhimiya, 1976, 12, 1715.
14. V.D.Bezuglyi and L.A.Korshikov, Elektrokhimiya, 1965, **1**, 1422; 1967, **3**, 390.
15. R.Payne, J.Chem.Phys., 1965, **42**, 3371.
16. A.N.Frumkin, L.M.Dubova, and I.A.Bagotskaya, Elektrokhimiya, 1977, **13**, 1084.
17. B.B.Damaskin, N.A.Borovaya, S.L.Dyatkina, and Yu.V.Batrakova, Symposium "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Vol.3, Tartu, 1972, p.100.
18. Z.A.Iofa, E.I.Lyakhovetskaya, and K.Sharifov, Dokl.Akad.Nauk SSSR, 1952, **84**, 543.
19. Z.A.Iofa, Vestnik Moskov.Univ., 1956(2), 139.
20. Z.A.Iofa and G.B.Rozhdestvenskaya, Dokl.Akad. Nauk SSSR, 1953, **91**, 1159.
21. V.V.Losev, Dokl.Akad.Nauk SSSR, 1953, **88**, 499.
22. E.M.Agres, A.I.Altsybaeva, and S.Z.Levin, Elektrokhimiya, 1976, **12**, 29.
23. A.I.Oshe, Zhur.Fiz.Khim., 1958, **32**, 1622.
24. I.I.Keilin and S.A.Balezin, Zhur.Fiz.Khim., 1976, **50**, 1798 [Russ.J.Phys.Chem., 1976(7)].
25. A.B.Sheinin, V.A.Zinov'ev, and V.L.Kheifets, Zhur.Fiz.Khim., 1960, **34**, 98 [Russ.J.Phys.Chem., 1960(1)]; 1961, **35**, 513 [Russ.J.Phys.Chem., 1961(3)].
26. Z.A.Iofa and Vei-Bao-Min, Zhur.Fiz.Khim., 1963, **37**, 2300 [Russ.J.Phys.Chem., 1963(10)].
27. E.I.Mikhailova and Z.A.Iofa, Elektrokhimiya, 1965, 1, 107; 1970, **6**, 231.
28. L.V.Tamm, Yu.K.Tamm, and V.E.Past, Elektrokhimiya, 1973, **9**, 1328; 1975, **11**, 1581.
29. A.T.Sklyarov and Ya.M.Kolotyrkin, Elektrokhimiya, 1967, **3**, 1462.
30. Ya.M.Kolotyrkin, N.Ya.Bune, and L.A.Medvedeva, Zhur.Fiz.Khim., 1951, **25**, 1365; 1955, **29**, 435, 1477; 1957, **31**, 2668.
31. K.V.Rybalka and D.I.Leikis, Elektrokhimiya, 1967, **3**, 1135.
32. K.V.Rybalka, Elektrokhimiya, 1972, **8**, 400.
33. D.C.Grahame, J.Amer.Chem.Soc., 1952, **74**, 4422.
34. Yu.V.Alekseev, Yu.A.Popov, and Ya.M.Kolotyrkin, Elektrokhimiya, 1976, **12**, 907, 915, 997, 1781, 1786.

35. V.Ya.Bartenev, E.S.Sevast'yanov, and D.I.Leikis, Elektrokhimiya, 1968, **4**, 745.
36. K.V.Rybalka and V.A.Panin, Elektrokhimiya, 1972, **8**, 1202.
37. V.A.Bartenev, E.S.Sevast'yanov, and D.I.Leikis, Elektrokhimiya, 1970, **6**, 1869.
38. T.Vitanov, A.Popov, and E.Sevast'yanov, Elektrokhimiya, 1976, **12**, 582.
39. E.B.Brik, R.M.Lazorenko-Manevich, and Ya.M.Kolotyrkin, Elektrokhimiya, 1975, **11**, 1875.
40. Ya.M.Kolotyrkin and L.A.Medvedeva, Dokl.Akad. Nauk SSSR, 1961, **140**, 168; 1962, **143**, 1384.
41. O.P.Metha, Ind.J.Chem., 1974, **12**, 315.
42. V.V.Marinyuk, R.M.Lazorenko-Manevich, and Ya.M.Kolotyrkin, Elektrokhimiya, 1978, **14**, 1747.
43. J.W.Schultze and F.D.Koppitz, Electrochim.Acta, 1976, **21**, 327.
44. M.P.Pyarnaya, U.V.Pal'm, and N.B.Grigor'ev, Elektrokhimiya, 1975, **11**, 575.
45. U.V.Pal'm, V.E.Past, and R.Ya.Pullerits, Elektrokhimiya, 1967, **3**, 376.
46. V.V.Gorodetskii, A.P.Bukin, and E.G.Shapovalova, Symposium "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Vol.48, Tartu, 1975, p.70.
47. D.I.Leikis, K.V.Rybalka, and E.S.Sevast'yanov, Symposium "Adsorbtsiya i Dvoinoi Elektricheskii Sloi v Elektrokhimii" (Adsorption and the Electrical Double Layer in Electrochemistry), Izd.Nauka, Moscow, 1972, p.5.
48. K.A.Kol'k, M.A.Sal've, and U.V.Pal'm, Elektrokhimiya, 1972, **8**, 1533.
49. E.K.Pet'yarv, K.A.Kol'k, and U.V.Pal'm, Elektrokhimiya, 1972, **8**, 100.
50. E.Dutkiewicz and R.Parsons, J.Electroanalyt.Chem., 1966, **11**, 100.
51. A.Ya.Gokhshtein, "Poverkhnostnoe Natyazhenie Tverdykh Tel i Adsorbtsiya" (The Surface Tension of Solids and Adsorption), Izd.Nauka, Moscow, 1976.
52. V.A.Chagelishvili, M.G.Vyaertnyu, U.V.Pal'm, and D.I.Dzhaparidze, Elektrokhimiya, 1978, **14**, 890.
53. U.V.Pal'm and B.B.Damaskin, "Itogi Nauki i Tekhniki. Elektrokhimiya" (Advances in Science and Technology. Electrochemistry), Vol.12, Izd.VINITI, Moscow, 1977, p.99.
54. E.K.Yuriado and U.V.Pal'm, Elektrokhimiya, 1977, **13**, 454.
55. A.N.Frumkin, N.B.Grigor'ev, and I.A.Bagotskaya, Elektrokhimiya, 1966, **2**, 329; Dokl.Akad.Nauk SSSR, 1964, **157**, 957, 1455.
56. I.A.Bagotskaya and T.I.Khalturnina, Symposium "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh" (The Double Layer and Adsorption on Solid Electrodes), Vol.2, Tartu, 1970, p.83.
57. A.M.Morozov, I.A.Bagotskaya, and E.A.Preis, Elektrokhimiya, 1969, **5**, 40.
58. K.Sabo and I.A.Bagotskaya, Dokl.Akad.Nauk SSSR, 1963, **150**, 128.
59. N.A.Balashova and V.E.Kazarinov, Uspekhi Khim., 1965, **34**, 1721 [Russ.Chem.Rev., 1965(10)].
60. A.D.Obrucheva, Zhur.Fiz.Khim., 1958, **32**, 2155.
61. N.A.Balashova, Zhur.Fiz.Khim., 1958, **32**, 2266.
62. V.E.Kazarinov, Elektrokhimiya, 1966, **2**, 1389; 1969, **5**, 616.
63. A.T.Hubbard, R.A.Osteryoung, and F.Anson, Analyt.Chem., 1966, **38**, 692.
64. S.Schuldiner and C.Presbrey, J.Electrochem.Soc., 1964, **111**, 457.
65. R.Osteryoung and F.C.Anson, Analyt.Chem., 1961, **33**, 1123; 1963, **35**, 1100; 1964, **36**, 975.
66. D.C.Johanson, J.Electrochem.Soc., 1972, **119**, 331.
67. T.P.Birintseva and B.N.Kabanov, Zhur.Fiz.Khim., 1959, **33**, 844 [see Russ.J.Phys.Chem.Abs., Vol.33, Nos.1–6].
68. R.Potoya, O.A.Petrii, S.Ya.Vasina, and A.N.Frumkin, Elektrokhimiya, 1972, **8**, 904.
69. N.A.Balashova, N.T.Gorokhova, and M.I.Kulezneva, Elektrokhimiya, 1971, **7**, 448.
70. V.S.Vilinskaya and M.R.Tarasevich, Elektrokhimiya, 1971, **7**, 1515.
71. M.S.Chemeris, A.G.Stromberg, and Yu.B.Vasil'ev, Elektrokhimiya, 1975, **11**, 560.
72. B.D.Kurnikov, A.I.Zhurin, Yu.B.Vasil'ev, and V.S.Bagotskii, Elektrokhimiya, 1972, **8**, 1649.
73. "Spravochnik Khimika" (Chemist's Handbook), Vol.1, Goskhimizdat, Moscow–Leningrad, 1963, p.774.
74. B.N.Nekrasov, "Osnovy Obshchei Khimii" (Fundamentals of General Chemistry), Izd.Khimiya, Moscow, Vol.1, 1965; Vol.2, 1967; Vol.3, 1970.
75. D.Dobosh, "Electrochemical Constants" (Translated into Russian), Izd.Mir, Moscow, 1980, p.222.
76. R.Parson, Trans.Faraday Soc., 1959, **55**, 999.
77. B.N.Kabanov, "Elektrokhimiya Metallov i Adsorbtsiya" (The Electrochemistry of Metals and Adsorption), Izd.Nauka, Moscow, 1966, p.146.
78. M.S.Sytilin, Zhur.Fiz.Khim., 1968, **42**, 1138 [Russ. J.Phys.Chem., 1968(5)].
79. R.Freier and G.Resch, Z.Elektrochem., 1956, **60**, 473.
80. Ya.A.Yaraliev and N.K.Gadiev, Azerb.Khim.Zhur., 1976(3), 125.
81. M.Pourbaiz, "Atlas d'Équilibres Électrochimiques à 25 °C", Paris, 1963, p.614.
82. A.J.Bard (Editor), "Encyclopedia of Electrochemistry of the Elements", Marcel Dekker, New York, 1973, Vol.1, p.91.
83. A.P.Sukhotin (Editor), "Spravochnik po Elektrokhimii" (Handbook of Electrochemistry), Izd.Khimiya, Leningrad, 1981, p.124.
84. K.J.Vetter, "Electrochemical Kinetics" (Translated into Russian), Izd.Khimiya, Moscow, 1967.
85. W.M.Latimer, "Oxidation States of the Elements and Their Potentials in Aqueous Solutions", (Translated into Russian), Inostr.Lit., Moscow, 1954, p.65.
86. V.M.Bigelis, M.Kh.Makhkamova, and O.A.Abrarov, Elektrokhimiya, 1978, **14**, 748, 1424.
87. K.I.Tikhonov, L.Yu.Lamanskii, and D.Vol'ter, Elektrokhimiya, 1977, **13**, 1207.
88. L.G.Lavrenova, T.V.Zegzhda, and V.M.Shul'man, Elektrokhimiya, 1971, **7**, 83.
89. R.Guidelli and G.Pezzatini, Coll.Czech.Chem.Comm., 1971, **36**, 855.
90. V.Nelsonivory and R.Iwamoto, J.Electroanalyt. Chem., 1964, **7**, 218.
91. R.Spitz and H.Liefbafsky, J.Electrochem.Soc., 1975, **122**, 363.
92. K.J.Vetter, Z.phys.Chem., 1952, **199**, 22, 285.
93. A.B.Thomas and R.J.Brodd, J.Phys.Chem., 1964, **68**, 3363.
94. J.Llopis, J.Biarge, and M.Fernandez, Electrochim. Acta, 1959, **1**, 130.
95. L.M.Dane, L.J.J.Janssen, and J.G.Hoogland, Electrochim.Acta, 1968, **13**, 507.
96. V.A.Tyagai, Symposium "Adsorbtsiya i Dvoinoi Elektricheskii Sloi v Elektrokhimii" (Adsorption and the Electrical Double Layer in Electrochemistry), Izd.Nauka, Moscow, 1972, p.234.

97. Yu.M.Povarov, A.M.Trukhan, and P.D.Lukovtsev, Elektrokhimiya, 1970, **6**, 602, 1734.
98. V.A.Zakharov and O.A.Songina, Zhur.Fiz.Khim., 1962, **36**, 1226 [Russ.J.Phys.Chem., 1962(6)].
99. N.A.Zakhodyakina, M.A.Novitskii, L.A.Sokolov, and P.D.Lukovtsev, Elektrokhimiya, 1965, 1, 138.
100. A.Ya.Gokhshtein, Elektrokhimiya, 1965, 1, 906.
101. A.Ya.Gokhshtein, Elektrokhimiya, 1965, 1, 285, 1052; 1967, **3**, 600, 1262.
102. A.Ya.Gokhshtein, Elektrokhimiya, 1967, 3, 32.
103. E.C.Toren and C.P.Driscoll, Analyt.Chem., 1966, **38**, 872.
104. M.Kolthoff and J.Jordan, J.Amer.Chem.Soc., 1953, **75**, 1571.
105. J.Badoz-Lambling, Analyt.Chim.Acta, 1957, **16**, 285.
106. J.J.Lingane and F.C.Anson, Analyt.Chim.Acta, 1957, **16**, 165.
107. G.Durand and B.Tremillon, Analyt.Chim.Acta, 1970, **49**, 135.
108. M.Mastragostine, G.Casabore, and S.Valcher, J.Electroanalyt.Chem., 1973, **44**, 37.
109. R.Guidelli and G.Piccardi, Anal.Letters, 1968, 1(12), 779.
110. R.T.Iwamoto, Analyt.Chem., 1959, **31**, 955.
111. V.A.Macagno, M.C.Giordano, and A.J.Arvia, Electrochim.Acta, 1969, **14**, 335.
112. G.Dryhurst and P.J.Elving, Analyt.Chem., 1967, **39**, 606.
113. A.I.Popov and D.H.Geske, J.Amer.Chem.Soc., 1958, **80**, 1340.
114. I.M.Kolthoff and J.F.Coetzee, J.Amer.Chem.Soc., 1957, **79**, 1852.
115. I.V.Nelson and R.T.Iwamoto, J.Electroanalyt.Chem., 1964, **7**, 218.
116. A.V.Chizhov, Yu.M.Povarov, P.D.Lukovtsev, and S.D.Pirozhkov, Elektrokhimiya, 1972, **8**, 1089.
117. I.E.Barbasheva, Yu.M.Povarov, and P.D.Lukovtsev, Elektrokhimiya, 1967, **3**, 1149.
118. I.E.Barbasheva, Yu.M.Povarov, and P.D.Lukovtsev, Elektrokhimiya, 1972, **8**, 1275.
119. L.N.Ivanovskaya and S.V.Gorbachev, Trudy Moskov.Khim.-Tekh.Inst. imeni Mendeleeva, 1963, **44**, 50.
120. M.C.Giordano, J.C.Bazan, A.J.Arvia, and J.J.Podesta, Elektrochim.Acta, 1966, **11**, 741, 1553; 1967, **12**, 723; 1969, **14**, 389.
121. G.Adhami and M.Herlem, J.Electroanalyt.Chem., 1970, **26**, 363.
122. B.Lopez, T.Iwasita, and M.C.Giordano, J.Electroanalyt.Chem., 1973, **47**, 409.
123. R.A.Zingaro, C.A.Vander Werf, and J.Kleinberg, J.Amer.Chem.Soc., 1951, **73**, 88.
124. J.Nigretto and M.Jozefowicz, Electrochim.Acta, 1974, **19**, 809.
125. J.Verhoef and E.Barendrecht, Electrochim.Acta, 1978, **23**, 433.
126. L.N.Ivanovskaya and S.V.Gorbachev, Zhur.Fiz. Khim., 1976, **37**, 2305 [Russ.J.Phys.Chem., 1976(9)].
127. J.-Y.Cabon, M.L'Her, and M.Le Demezet, Compt. rend., 1975, No.C280, p.357.
128. E.Sutzkover, Y.Nemirovsky, and M.Ariel, J.Electroanalyt.Chem., 1972, **38**, 107.
129. R.Benoit, M-Guay, and J.Desbarres, Canad.J.Chem., 1968, **46**, 1261.
130. L.I.Krishtalik, Zhur.Fiz.Khim., 1957, **31**, 2403.
131. Abdul Aziz Ramadan, P.K.Agasyan, and S.I.Petrov, Zhur.Obshch.Khim., 1974, **44**, 983, 2299.
132. R.Guidelli and G.Piccardi, Electrochim.Acta, 1967, **12**, 1085.
133. B.Mylene and S.Christiane, Compt.rend., 1965, **260**, 5016.
134. Ya.A.Yaraliev, Elektrokhimiya, 1974, **10**, 148.
135. Ya.A.Yaraliev and N.K.Gadiev, Elektrokhimiya, 1979, **15**, 980.
136. Ya.A.Yaraliev, Zhur.Fiz.Khim., 1977, **51**, 98 [Russ. J.Phys.Chem., 1977(1)].
137. S.P.Tevosov and Ya.A.Yaraliev, Elektrokhimiya, 1971, **7**, 824.
138. S.P.Tevosov and Ya.A.Yaraliev, Uch.Zap.Azerb. Univ., Ser.Khim.Nauk, 1974(4), 64.
139. S.V.Gorbachev and V.A.Belyaeva, Zhur.Fiz.Khim., 1961, **35**, 2153 [Russ.J.Phys.Chem., 1961(9)].
140. L.N.Ivanovskaya and S.V.Gorbachev, Trudy Moskov.Khim.-Tekh.Inst. imeni Mendeleeva, 1963, **44**, 59.
141. A.M.Averbuch, M.A.Novitskii, L.A.Sokolov, and P.D.Lukovtsev, Elektrokhimiya, 1965, 1, 251.
142. I.E.Barbasheva, Yu.M.Povarov, and P.D.Lukovtsev, Elektrokhimiya, 1970, **6**, 92, 306; 1971, **7**, 79.
143. A.N.Frumkin and G.A.Tedoradze, Dokl.Akad.Nauk SSSR, 1958, **118**, 530.
144. J.Newson and A.Riddiford, J.Electrochem.Soc., 1961, **108**, 699.
145. D.P.Gregory and A.C.Riddiford, J.Chem.Soc., 1956, **78**, 3756.
146. A.N.Frumkin, V.S.Bagotskii, Z.A.Iofa, and B.N.Kabanov, "Kinetika Elektrodnykh Protsessov" (Kinetics of Electrode Processes), Izd.Moskov. Univ., 1952.
147. J.Jordan and R.A.Javick, Electrochim.Acta, 1962, **6**, 23.
148. L.T.Shanina, Dokl.Akad.Nauk SSSR, 1960, **134**, 141.
149. S.Schuldiner and T.B.Warner, Analyt.Chem., 1964, **36**, 2510.
150. A.M.Trukhan, Yu.M.Povarov, and P.D.Lukovtsev, Elektrokhimiya, 1970, **6**, 425, 744, 826.
151. I.E.Barbasheva, Yu.M.Povarov, and P.D.Lukovtsev, Elektrokhimiya, 1970, **6**, 175, 1450; 1968, **4**, 464.
152. S.F.Belevskii and L.A.Leonova, Elektrokhimiya, 1970, **7**, 440.
153. S.F.Belevskii, E.S.Men', and S.V.Gorbachev, Elektrokhimiya, 1975, 11, 466.
154. J.D.Voorhies and E.J.Schurdak, Analyt.Chem., 1962, **34**, 939.
155. J.Kleinberg, E.Cotton, J.Sattizahn, and C.A.Vander Werf, J.Amer.Chem.Soc., 1953, **75**, 442.
156. H.S.Wroblowa and A.Saunders, Electroanalyt. Chem., 1973, **42**, 329.
157. V.A.Tyagai and G.Ya.Kolbasov, Elektrokhimiya, 1970, **6**, 473; 1971, **7**, 1722.
158. Yu.M.Povarov, A.M.Trukhan, and P.D.Lukovtsev, Elektrokhimiya, 1971, **7**, 147.
159. Yu.M.Povarov, I.E.Barbashova, and P.D.Lukovtsev, Elektrokhimiya, 1967, **3**, 1202.
160. A.I.Fedorova, G.L.Vidovich, Dokl.Akad.Nauk SSSR, 1956, **109**, 135.
161. R.Landsberg and R.Thiele, Electrochim.Acta, 1966, 11, 1243.
162. G.N.Mansurov and V.E.Kazarinov, Elektrokhimiya, 1966, **2**, 1438.
163. C.A.Emery and H.E.Hintermann, Electrochim.Acta, 1968, **13**, 127.
164. P.Beran and S.Bruckenstein, Analyt.Chem., 1968, **40**, 1044.
165. I.E.Barbashova and Yu.M.Povarov, Elektrokhimiya, 1971, **7**, 782.
166. S.V.Gorbachev and L.M.Khitrova, Zhur.Fiz.Khim., 1973, **47**, 1624, 2682 [Russ.J.Phys.Chem., 1973(6,7)].

167. W.Geissler, R.Nitzsche, and R.Landsberg, Electrochim.Acta, 1966, **11**, 389, 495.
168. F.Miller and H.Zittel, J.Electroanalyt.Chem., 1966, 11, 85.
169. D.I.Semchenko, V.A.Smirnov, V.M.Lyubushkin, V.V.Karapysh, and Sh.Sh.Khidirov, Elektrokhimiya, 1971, **7**, 971.
170. F.C.Anson and J.J.Lingane, J.Amer.Chem.Soc., 1957, **79**, 1015.
171. A.Hickling and W.J.Wilson, Electrochem.Soc., 1951, **98**, 425.
172. I.M.Kolthoff and M.Tanaka, Analyt.Chem., 1954, **26**, 632.
173. I.M.Kolthoff and J.Jordan, Analyt.Chem., 1953, **25**, 1833.
174. S.B.Gorbachev and Yu.A.Korostelin, Zhur.Fiz. Khim., 1965, **39**, 1469, 1773 [Russ.J.Phys.Chem., 1965(6, 7)]; 1966, **40**, 2324 [Russ.J.Phys.Chem., 1966(9)].
175. Ya.A.Yaraliev and N.K.Gadiev, Azerb.Khim.Zhur., 1979(3), 115.
176. G.Raspi, F.Pergola, and D.Cozzy, J.Electroanalyt. Chem., 1966, **12**, 36; 1967, **15**, 35.
177. G.Piccardi and R.Guidelli, J.Phys.Chem., 1968, **72**, 2782.
178. R.Guidelli and F.Pergola, J.Inorg.Nuclear Chem., 1969, **31**, 1373.
179. P.Beran and S.Bruckenstein, J.Phys.Chem., 1968, **72**, 3630.
180. D.I.Dzhaparidze, V.V.Shavgulidze, V.A.Chegelishvili, T.R.Chelidze, and Sh.S.Dzhaparidze, Elektrokhimiya, 1974, **10**, 1414.
181. A.M.Shams El Din, T.M.H.Saber, and H.A.El Shyeb, J.Electroanalyt.Chem., 1974, **57**, 241.
182. P.Delahay and G.Mamontov, Analyt.Chem., 1955, **27**, 478.
183. F.Anson, J.Amer.Chem.Soc., 1959, **81**, 1554.
184. L.Müller, J.Electroanalyt.Chem., 1968, **16**, 531.
185. R.Wetzel, L.Müller, and B.Krüger, Electrochim. Acta, 1973, **18**, 247.
186. Yu.V.Efremov, Zhur.Neorg.Khim., 1968, **13**, 58 [Russ.J.Inorg.Chem., 1968(1)].
187. A.F.M.Barton and G.A.Wright, J.Chem.Soc., 1968, **A**, 2096.
188. H.A.Laitinen and W.J.Subcasky, J.Amer.Chem.Soc., 1958, **80**, 2623.
189. P.G.Desideri, J.Electroanalyt.Chem., 1965, **9**, 218, 229; 1968, **17**, 229.
190. J.Denoyer and C.Jolicoeur, Symposium "Modern Problems in Electrochemistry" (Translated into Russian), Izd.Mir, Moscow, 1971, p.55.

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