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Abstract

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ON THE QUESTION OF THE OXIDATION POTENTIALS OF PURE OXIDIZED FORMS AND THE LIMITS OF APPLICABILITY OF THE PLATINUM INDICATOR ELECTRODE

(Presented by Academician A. A. Grinberg, 15 I 1962)

A. A. Grinberg, B. V. Ptitsyn, and V. N. Lavrent' ev noted that in oxidation-reduction systems of halide acid complexes of palladium, platinum, and iridium, equilibria of the following type are probably established:

$$[\mathrm{MeX_6}]^{2-} \rightleftarrows [\mathrm{MeX_4}]^{2-} + \mathrm{X_2}, \tag{1}$$

where $\mathrm{Me} = \mathrm{Pd, Pt, Ir};\ \mathrm{X} = \mathrm{Cl, Br, I, SCN}$ (^{1,3}).

The free halogen formed in solution in this process was considered by the above-mentioned investigators to be responsible for establishing the potential on a smooth platinum electrode. On the basis of comparison of the values of the normal potentials of the systems $[\mathrm{MeX_6}]^{2-}+2e \rightleftarrows [\mathrm{MeX_4}]^{2-}+2\mathrm{X}^-$ and $\mathrm{X_2}+2e \rightleftarrows 2\mathrm{X}^-$, the equilibrium concentrations of free halogens were estimated.

The considerations cited assume the simultaneous presence in solution of complex ions corresponding to two oxidation states of the central atom. Let us try to apply this concept to the explanation of the mechanism of potential formation for the case in which only one oxidized form of the complex (a "pure" form) is present in solution, for example, one corresponding to the higher valence of the metal.

Suppose that, by one method or another, a compound $\mathrm{M_2[MeX_6]}$ has been obtained that is completely free from impurities, including from the reduced form ($\mathrm{M_2[MeX_4]}$). Upon dissolution of this substance in water, one might expect that the potential of an indicator electrode immersed in such a solution would be equal to $+\infty$. However, as Michaelis rightly noted (^{2}), in real solutions the electrode potential always assumes a finite value. In our view, the reasons for this phenomenon lie not only in the fundamental impossibility of obtaining a pure oxidized form, as Michaelis postulated, but in the transformations undergone by the substance after its dissolution.

Indeed, in the general case, in a solution of an initially pure oxidized form, at least two coupled equilibria will be established:

$$[\mathrm{MeX}_n]^p \rightleftarrows [\mathrm{MeX}_{n-2}]^q + \mathrm{X}_2 \tag{1 bis}$$

and

$$[\mathrm{MeX}_n]^p + \mathrm{H_2O} \rightleftarrows [\mathrm{MeX}_{n-1}\mathrm{H_2O}]^{1-p} + \mathrm{X}^-. \tag{2}$$

Consequently, even in the absence of X^- ions and $[\mathrm{MeX}_{n-2}]^q$ specially introduced into the solution, as a result of self-reduction (1 bis) and dissociation (2), two additional coupled redox systems will arise. Hence the potential of the indicator electrode in the solution under consideration will be determined by the equation:

$$E = E_0' + \frac{RT}{2F} \ln \frac{[\mathrm{MeX}_n^{p-}]}{[\mathrm{MeX}_{n-2}^{q-}][\mathrm{X}^-]^2} = E_0'' + \frac{RT}{2F} \ln \frac{[\mathrm{X}_2]}{[\mathrm{X}^-]^2}. \tag{3}$$

Equation (3) is a special case of the equation applied by A. A. Grinberg (^{3}) to describe oxidation-reduction equilibria in solutions of complex compounds.

Thus, we are entitled to expect that any solution of a pure oxidized form will be characterized by a definite and—given favorable kinetics of potential establishment—reproducible value of the latter. The specific value of this potential is determined by two constants:

a) The instability constant:

$$K_{\text{inst}} = \frac{\left[\mathrm{MeX}_{n-1}\mathrm{H_2O}^{1-p}\right][\mathrm{X}^-]}{[\mathrm{MeX}_n^{p-}]}. \tag{4}$$

b) The "self-reduction" constant:

$$K_{\text{sr}} = \frac{[\mathrm{MeX}_{n-2}^{q-}] \cdot [\mathrm{X}_2]}{[\mathrm{MeX}_n^{p-}]} = e^{(E_0' - E_0'')\frac{2F}{RT}}. \tag{5}$$

The considerations presented can obviously also be extended to the case of a solution of a pure complex form corresponding to a lower oxidation state of the central atom. In this case the self-reduction constant will be replaced by the disproportionation constant.

To confirm the concept set forth, the redox potentials were measured in solutions of the bromide complex of gold(III), obtained from $\mathrm{HAuCl_4}$ by the action of a large excess of KBr and acidified with hydrochloric acid to pH 2. In this process, as special experiments showed, the coordinatively bound chlorine is practically completely replaced by bromine, while hydrolysis is suppressed (^{4}).

Let us assume, in accordance with equation (1 bis), that in the self-reduction of $[\mathrm{AuBr_4}]^-$ an equimolecular amount of $\mathrm{Br_2}$ is formed. Then, starting from the separately determined value ${}_0E'_{\mathrm{AuBr_4^-/AuBr_2^-}} = 0.813 \pm 0.003$ V, the known $[\mathrm{Br^-}] = C_{\mathrm{Br}} - 4C_{\mathrm{Au}}$, and the measured potential of the solution E, one can calculate the normal potential of the system $\mathrm{Br_2} \rightleftarrows 2\mathrm{Br^-}$ (E''_0).

The data obtained are compared in Table 1.

Table 1

Results of the calculation of the normal potential of the bromine–bromide system
(temperature 25°; concentration of hydrochloric acid $0.8 \cdot 10^{-2}$ mol/l; chloride-ion concentration $= 4C_{\mathrm{Au}}$)

No.	Measured potential	Equilibrium conc. of bromide ion, mol/l	Gold conc., mol/l C_{Au}	Normal potential ${}_0E''_{\mathrm{Br_2/Br^-}}$, in volts
1	0.903	0.973	$5.17 \cdot 10^{-3}$	1.085
2	0.933	0.320	$2.88 \cdot 10^{-3}$	1.086
3	0.952	0.154	$1.24 \cdot 10^{-3}$	1.076
4	0.981	0.035	$9.00 \cdot 10^{-4}$	1.079
			Average	1.082

The values of the normal potential of the system $\mathrm{Br_2} \rightleftarrows 2\mathrm{Br^-}$ were calculated from the equation

$$ {}_0E''_{\mathrm{Br_2/Br^-}} = 2E_{\mathrm{meas}} - {}_0E'_{\mathrm{AuBr_4^-/AuBr_2^-}} + 0.0295\{4\lg[\mathrm{Br^-}] + $$

$$ + \lg(1 + 17[\mathrm{Br^-}]) + 2\lg\gamma_{\pm} - \lg C_{\mathrm{Au}}\}, \qquad (6) $$

in which the formation of $\mathrm{Br_3^-}$ and the activity coefficient of potassium bromide $(^5)$ are taken into account. The satisfactory constancy and good agreement of the E''_0 found with the value of the normal potential of the bromine–bromide system, $E_0 = 1.087$ V, included in all reference books, testify to the validity of the authors' initial assumptions, in particular that the emergence of the potential is determined precisely by the self-reduction of the initially pure form $[AuBr_4^-]$. Otherwise E''_0 would depend to a considerable degree on dilution.

A phenomenon similar to that described—stability and reproducibility of the potential of the pure form—was observed by Bézier $(^6)$ in the example of solutions of $[FeCN_6]^{3-}$. The authors believe that in this case as well the considerations developed above are fully applicable. They may also be used to estimate the limits of applicability of the indicator platinum electrode. Indeed, if in the system $Ox + ne \rightleftharpoons Red$ the ratio Ox/Red is gradually increased while keeping $[Ox]$ constant, then, beginning from some $[Red]$, the measured potential acquires a constant value (^{6}).

The reason for this phenomenon lies in the reduced form reaching a value equal to or smaller than its concentration that was already present in solution as a result of self-reduction of the pure oxidized form. This characteristic quantity (threshold concentration), at which the potential of the system ceases formally to obey the Nernst equation, can easily be calculated for each particular case from equation (5).

Let us note in passing that measurement of the redox potential in a solution of the pure oxidized form makes it possible to estimate the value of the stepwise instability constant of the complex ion, if the self-reduction constant is known (see equations 2-5). Such a method appears especially valuable as applied to stable compounds.

Here, as before, it is assumed that the system under study is reversible thermodynamically and kinetically. Otherwise the magnitude and stability of the potential will depend on the competition of exchange currents at the electrode surface for the principal (studied) and parasitic processes.

In this connection one may expect that in some cases the introduction into a solution of the pure oxidized form of a complex of X_2 molecules (which are, in essence, the oxidized form of the addend) will lead to an increase in the stability of the potential.

Thus, the method proposed by one of us (^{7}) for determining instability constants, based on potentiometry of addend—oxidized form of addend—systems, is generalized.

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