# 434. *Reactivity of Anions towards Electron Transfer in the Bismuth $\rightleftharpoons$ Tervalent Bismuth Exchange Reaction.*

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The pseudo-capacity and over-all polarisation resistance during the electroreduction of tervalent bismuth at a dropping-mercury cathode in various media were traced as a series combination; and the general features of the former are described. The combination corresponding to the peak values was then balanced against the equivalent of a simple model of the faradaic admittance, and in this way information was obtained from which the specific rate constant for the above exchange in each medium could be evaluated. In N-perchloric and N-hydrochloric acid, the results agreed excellently with those previously published. In N-nitric and N-sulphuric acid the constants were respectively $3{\cdot}7 \times 10^{-3}$ and $1{\cdot}8 \times 10^{-3}$ cm. sec.$^{-1}$ at 26° ± 0·5°. In mixtures of nitric and perchloric acid of constant ionic strength, the rate increased sensibly with the increase of concentration of the former. The order of reactivity towards electron transfer for the various anions is briefly discussed in the light of possible ionic interactions within the electrical double layer and in the bulk of solution.

Heyrovsky,[1] using oscillographic polarography, showed the reduction of tervalent bismuth to involve three-electron transfer, and to be irreversible in media containing undeformable anions such as $NO_3^-$ and $ClO_4^-$, but highly reversible in complex-forming media of $Cl^-$ or $Br^-$ ions. These conclusions were confirmed by Randles and Somerton,[2] who, investigating the electrodic behaviour in an alternating field, computed, as a measure of the degree of reversibility, the specific rate constant for the exchange $Bi \rightleftharpoons Bi^{3+} + 3e$. In N-perchloric and N-hydrochloric acid the constant was reported as $3 \times 10^{-4}$ and $\geqslant 1$ cm. sec.$^{-1}$, respectively. The reversible behaviour on open circuit of both protected and unprotected bismuth electrodes as metal–metal oxychloride electrodes in hydrochloric acid media is undoubtedly [3] consistent with the above facts. However, the extent to which anions such as $NO_3^-$ and $SO_4^{2-}$ may catalyse the above exchange does not seem to have been studied before. As is well known, these anions, like $ClO_4^-$, do not become specifically adsorbed. In this investigation, using a different experimental technique, we confirmed Randles and Somerton's results, and moreover examined the reactivity of the above anions, alone or in mixtures, towards electron transfer in the above reaction.

## Experimental

The technique used was essentially polarography with superimposed alternating voltage.[4] The capacitative and resistive components of the impedance of a mercury surface were measured

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[1] Heyrovsky, *Discuss. Faraday Soc.*, 1947, **1**, 212.

[2] Randles and Somerton, *Trans. Faraday Soc.*, 1952, **48**, 951.

[3] Sammour and Moussa, *J.*, 1958, 1762.

[4] Delahay, "New Experimental Methods in Electrochemistry," Interscience Publishers Ltd., London, 1954, p. 166.

on an a.c. bridge by the procedure already described.[5] In presence of tervalent bismuth and with no current-maxima suppressor added, the pseudo-capacity and over-all polarisation resistance were traced over an appropriate potential range, and their peak values $C_m$ and $R_m$ determined at 1000, 3000, and (in some experiments) 4000 cycles/sec. The $C_m$–$R_m$ series combination at each frequency was then balanced against a block model representing the faradaic admittance[6] (Fig. 1) through the capacitor $C_r$ and the resistor $R_r$; $C_d$ and $R_s$, the double layer capacity and the solution resistance respectively, were maintained constant at their appropriate values as obtained from measurements in the pure electrolyte alone.

The polarisation cell and the d.c. polarising circuit were essentially the same as described previously. As a dropping-mercury electrode, a thin-walled fine capillary with a drop time of 3·1—3·2 sec. and a rate of flow 1·91 mg. of Hg/sec. was used. As a reliable unpolarisable reference electrode for the present measurements, a saturated calomel electrode was employed, and the necessary precautions to avoid diffusion of chloride ions into the test solution were taken.

Tervalent bismuth solutions in N-perchloric, N-hydrochloric, and N-nitric acid were made from chemically pure bismuth trioxide, and in N-sulphuric acid from the basic carbonate (B.D.H.). Other chemicals were of " AnalaR " grade. Deaeration of the solutions was effected with purified hydrogen, and the measurements in the cell were made at 26° ± 0·5° in an air-bath.

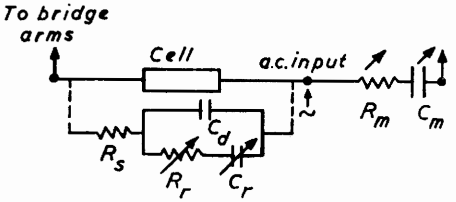


FIG. 1. *Balancing arms of the bridge.*

## RESULTS AND DISCUSSION

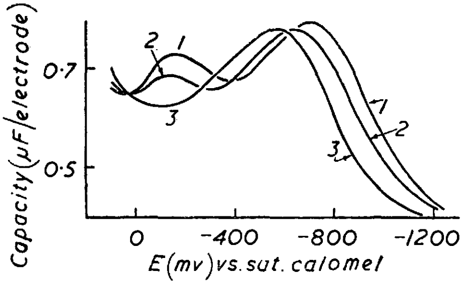
According to Grahame's analysis of the theory of the faradaic admittance,[7] the magnitude of the pseudo-capacity peak, $C_m$, at a certain frequency in one medium may be taken as a qualitative measure of the intrinsic speed of the electrodic reaction leading to it in that particular medium. $C_m$ in this respect is far more sensitive than the corresponding $R_m$, the over-all polarisation resistance, which generally decreases with increase of reaction rate. The traces for the pseudo-capacity at 1000 cycles/sec. as a function of polarisation as obtained during the reduction of tervalent bismuth in the various media used are shown in Figs. 2—5. In N-perchloric acid (Fig. 2*a*) the pseudo-capacities appear as humps preceding that characteristic of the pure electrolyte, and which itself shifts towards more cathodic potentials with increase of [$Bi^{3+}$]. The maxima of the pseudo-capacity humps lie at about —150 mv, far remoted cathodically from the half-wave potentials * (not indicated on the figures) at about —60 and —90 mv for the low and the high values of [$Bi^{3+}$] respectively. This accords with a prediction of Grahame's analysis which does not seem to have been verified before. In the other media, however, the pseudo-capacities were much better defined, and the peaks in almost all cases were in better coincidence with the half-wave potentials. The catalytic effect of chloride ions is well represented by the pseudo-capacity traces obtained for two values of [$Bi^{3+}$] in N-perchloric acid which was made $1 \times 10^{-3}$N with respect to hydrogen chloride (Fig. 2*b*); the composition of the mixtures used with respect to $Bi^{3+}$ and $Cl^-$ ions was such as to avoid apparent hydrolysis (see p. 2156). As is obvious, chloride ions at the above concentration stimulate the appearance of well-defined peaks. In N-hydrochloric acid (Fig. 3) a pronounced capacity

* In our experiments, these could be fairly accurately defined in the absence of a maximum suppressor.

[5] Moussa, Sammour, and Ghaly, *J.*, 1958, 1269.
[6] Randles, *Discuss. Faraday Soc.*, 1947, **1**, 11.
[7] Grahame, *J. Electrochem. Soc.*, 1952, **99**, No. 12, 371c.

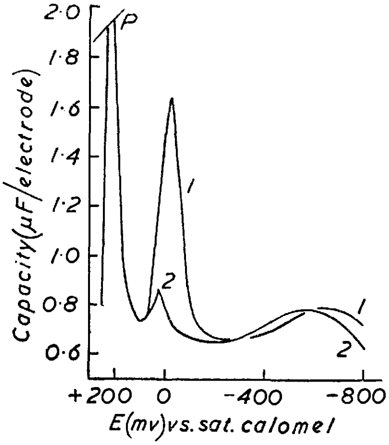
peak could be traced in [$Bi^{3+}$] concentrations as low as $5{\cdot}0 \times 10^{-5}$ g.-ion/l. The catalytic effect of the nitrate ions is well illustrated by the capacity traces (Fig. 4*b*) obtained in three different mixtures of nitric and perchloric acid of constant ionic strength and containing the same amount of $Bi^{3+}$, namely, $2{\cdot}0 \times 10^{-3}$ g.-ion/l. The peak value, as is obvious, becomes greater with the increase of nitric acid in the mixture. In N-sulphuric acid, with [$Bi^{3+}$] = $1{\cdot}9 \times 10^{-3}$ g.-ion/l., limited by the solubility of the basic carbonate, the pseudo-capacity (Fig. 5) was still better defined than that observed in N-perchloric acid, but was far less in magnitude than that traced in N-nitric acid (Fig. 4*a*) for nearly equal values of [$Bi^{3+}$].

FIG. 2*a*. *Pseudo-capacity traces in* N-$HClO_4$.



(1) [$Bi^{3+}$] = $5 \times 10^{-3}$N. (2) [$Bi^{3+}$] = $3 \times 10^{-3}$N. (3) N-$HClO_4$ *alone. For all Figs. E was measured against saturated calomel.*

FIG. 2*b*. *Catalytic effect of chloride ion: pseudo-capacity traces in* N-$HClO_4$ *made* $1 \times 10^{-3}$N *with respect to* HCl.

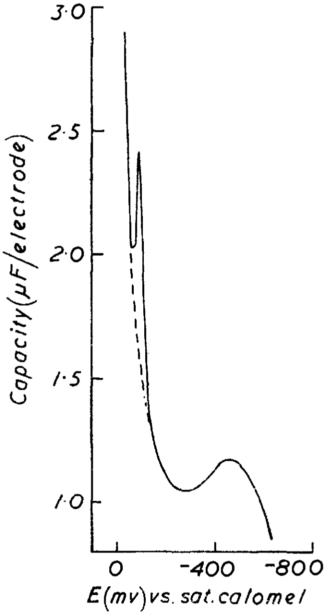


(1) [$Bi^{3+}$] = $3 \times 10^{-3}$N. (2) [$Bi^{3+}$] = $1 \times 10^{-3}$N.

(*P = Pseudo-capacity peak due to dissolution of mercury as mercurous chloride.*[21])

FIG. 3. *Pseudo-capacity trace in* N-HCl: [$Bi^{3+}$] = $5{\cdot}0 \times 10^{-5}$N.

(*Broken line: pure* HCl.)



Calculation of the specific rate constant from the results of the above measurements was mainly founded on Randles's relations,[6] *viz.*,

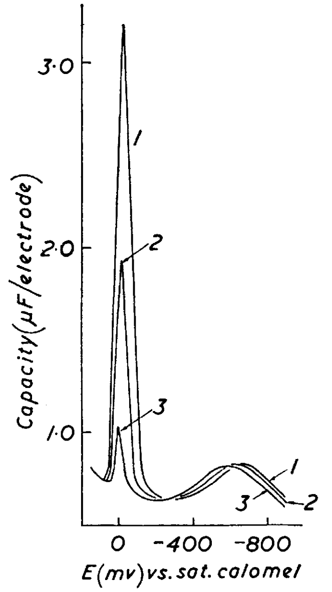
$$R_r = \frac{\boldsymbol{R}T}{n^2\boldsymbol{F}^2AC}\left(\frac{2}{\omega D}\right)^{\frac{1}{2}} + \frac{\boldsymbol{R}T}{n^2\boldsymbol{F}^2AC}\cdot\frac{1}{K} \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{1}{\omega C_r} = \frac{\boldsymbol{R}T}{n^2\boldsymbol{F}^2AC}\left(\frac{2}{\omega D}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

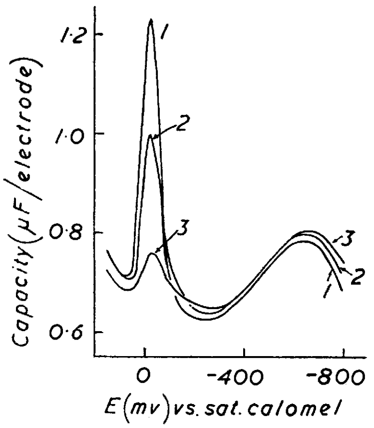
$$R_r - \frac{1}{\omega C_r} = \frac{\boldsymbol{R}T}{n^2\boldsymbol{F}^2AC}\cdot\frac{1}{k} = \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

FIG. 4*a*. *Pseudo-capacity traces in* N-HNO$_3$.



(1) [Bi$^{3+}$] = 3 × 10$^{-3}$N. (2) [Bi$^{3+}$] = 2 × 10$^{-3}$N. (3) [Bi$^{3+}$] = 1 × 10$^{-3}$N.

FIG. 4*b*. *Catalytic effect of the nitrate ion: pseudo-capacity traces in* HClO$_4$–HNO$_3$ *mixtures for* [Bi$^{3+}$] = 2·0 × 10$^{-3}$N.



(1) 0·6N-HNO$_3$ + 0·4N-HClO$_4$. (2) 0·4N-HNO$_3$ + 0·6N-HClO$_4$. (3) 0·2N-HNO$_3$ + 0·8N-HClO$_4$.

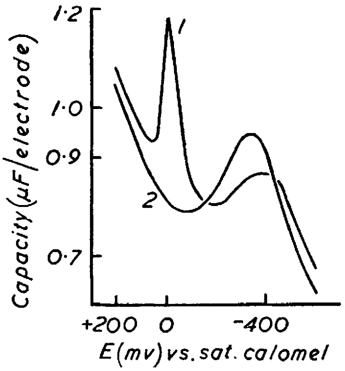


FIG. 5. *Pseudo-capacity trace in* N-H$_2$SO$_4$ *for* [Bi$^{3+}$] = 1·9 × 10$^{-3}$N (*curve* 1) *and pure* N-H$_2$SO$_4$ (*curve* 2).

where $k$ is the specific rate constant in cm. sec.$^{-1}$, $C$ the concentration in g.-ion/cm.$^3$, $A$ the area in cm.$^2$, and $n$ the number of electrons involved in the reduction; $R_r$ and $C_r$ are respectively the resistive and capacitative components of the faradaic admittance, $\omega = 2\,\pi f$ where $f$ is the frequency, and $\boldsymbol{R}$, $T$, and $\boldsymbol{F}$ have their usual significance. As inferred by Randles, and worked out by Grahame[7] and Delahay,[4] with the technique we have been employing, the above relations are strictly applicable for sufficiently fast reactions ($\theta \longrightarrow$ zero), in which case the peak capacity $C_m$ should coincide exactly with the half-wave potential. As an approximation, however, we assumed that equation (3) was applicable under all conditions, and deduced the *k* values on the basis of the experimentally determined $R_r$ and $1/\omega C_r$ values. The results so obtained, together with the various quantities involved in the calculations, are given in the Table. Col. 1 shows the working frequency (cycles/sec.), col. 2 the peak capacity $C_m$ (μF/electrode), col. 3 the over-all polarisation resistance $R_m$ (ohms), col. 4 the resistive component of the faradaic admittance $R_r$ (ohms), col. 5 the calculated impedance of the capacitative component of the faradaic admittance $1/\omega C_r$ (ohms), and col. 6 the calculated *k* values (× $10^3$) (cm. sec.$^{-1}$); $C$ is the concentration (g.-ion/l.), $A$ the electrode area (cm.$^2$), $R_s$ the solution resistance (ohms), and $C_d$ the double layer capacity (μF/electrode).

| (1) | (2) | (3) | (4) | (5) | (6) | (1) | (2) | (3) | (4) | (5) | (6) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (A) N-$HClO_4$: | | | | | | | | | | | |
| $C$ = 5·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 27; $C_d$ = 0·63. | | | | | | $C$ = 3·0 × $10^{-3}$; $A$, $R_s$, and $C_d$ as on left. | | | | | |
| 1000 | 0·727 | 110 | 637 | 48 | 0·37 | 1000 | 0·680 | 83 | 1060 | 101 | 0·38 |
| | | | | | | 3000 | 0·644 | 34 | 1700 | 770 | 0·38 |
| N-$HClO_4$ made $10^{-3}$N with respect to HCl: | | | | | | | | | | | |
| $C$ = 1·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 30; $C_d$ = 0·68. | | | | | | $C$ = 3·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 30; $C_d$ = 0·65. | | | | | |
| 1000 | 0·850 | 117 | 480 | 80 | 2·6 | 1000 | 1·62 | 137 | 187 | 37 | 2·4 |
| 3000 | 0·710 | 54 | 410 | 50 | 3·0 | 3000 | 0·778 | 58 | 224 | 147 | 2·4 |
| (B) N-HCl: | | | | | | | | | | | |
| $C$ = 5·0 × $10^{-5}$; $A$ = 0·0279; $R_s$ = 27; $C_d$ = 1·74. | | | | | | | | | | | |
| 1000 | 2·40 | 47 | 130 | 124 | 3600 | 3000 | 2·09 | 33 | 72 | 53 | 1200 |
| (C) N-$HNO_3$: | | | | | | 0·8N-$HClO_4$ + 0·2N-$HNO_3$: | | | | | |
| $C$ = 1·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 27; $C_d$ = 0·70. | | | | | | $C$ = 2·0 × $10^{-3}$; $A$ = 0·0279; $R_s$ = 28; $C_d$ = 0·65. | | | | | |
| 1000 | 1·03 | 123 | 330 | 16 | 3·5 | 1000 | 0·761 | 100 | 648 | 114 | 1·0 |
| 3000 | 0·735 | 43 | 420 | 32 | 2·8 | 3000 | 0·682 | 39 | 635 | 252 | 1·3 |
| $C$ = 2·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 27; $C_d$ = 0·69. | | | | | | 0·6N-$HClO_4$ + 0·4N-$HNO_3$: | | | | | |
| 1000 | 1·93 | 130 | 167 | 15 | 3·6 | $C$ = 2·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 27; $C_d$ = 0·67. | | | | | |
| 3000 | 0·840 | 56 | 169 | 24 | 3·8 | 1000 | 1·00 | 129 | 346 | 37 | 1·8 |
| 4000 | 0·778 | 45 | 194 | 44 | 3·7 | 3000 | 0·703 | 45 | 390 | 68 | 1·7 |
| $C$ = 3·0 × $10^{-3}$; $A$ = 0·0275; $R_s$ = 27; $C_d$ = 0·68. | | | | | | 0·4N-$HClO_4$ + 0·6N-$HNO_3$: | | | | | |
| 1000 | 3·197 | 110 | 106 | 12 | 3·9 | $C$ = 2·0 × $10^{-3}$; $A$ = 0·0269; $R_s$ = 29; $C_d$ = 0·64. | | | | | |
| 3000 | 1·07 | 62 | 103 | 15 | 4·2 | 1000 | 1·23 | 142 | 250 | neg.* | 2·2 |
| 4000 | 0·91 | 50 | 112 | 25 | 4·2 | 3000 | 0·728 | 53 | 200 | ,, | 2·8 |
| (D) N-$H_2SO_4$: | | | | | | | | | | | |
| $C$ = 1·9 × $10^{-3}$; $A$ = 0·0283; $R_s$ = 30; $C_d$ = 0·83. | | | | | | | | | | | |
| 1000 | 1·18 | 107 | 315 | 15 | 1·8 | 4000 | 0·846 | 37 | 330 | 5 | 1·7 |
| 3000 | 0·866 | 43 | 300 | 7 | 1·9 | | | | | | |

* *I.e.*, negligible.

Consideration of the results in the following table shows that the agreement between the *k* values obtained in one particular medium for one or more concentrations and at different frequencies are highly satisfactory. With only few exceptions, the deviation from the average value in any set of measurements scarcely exceeds 5—6%. Use of equation (3) seems, therefore, justifiable. The experimentally determined values of $1/\omega C_r$ (col. 5), however, differed in most cases in both magnitude and direction of change with frequency from those computed theoretically on the basis of equation (2) with a diffusion coefficient value $D = 5 \times 10^{-6}$ cm.$^2$ sec.$^{-1}$. Difficulties in choosing the appropriate values of $D$ may, at least in part, be responsible for the discrepancies. It is also possible that with the technique used, the a.c. behaviour of the capacitative component $C_r$ and that part of the resistive component which is also independent of $k$ (first term of the right-hand side of equation 1), is rather more complicated than denoted by the model chosen.[8,9]

The values of $k$ obtained in N-perchloric and N-hydrochloric acid (sections A and B) agree excellently with those reported by Randles and Somerton[2] from measurements with amalgam electrodes at equilibrium potentials, namely, $3 \times 10^{-4}$ and $\geqslant 1$ cm. sec.$^{-1}$, respectively. In N-nitric and N-sulphuric acid (sections C and D) the average constants, for which no values had been published, were respectively $3{\cdot}7 \times 10^{-3}$ and $1{\cdot}8 \times 10^{-3}$ cm. sec.$^{-1}$. The order of reactivity for the various anions towards electron transfer in the reaction studied may then be given as: $Cl^- > NO_3^- > SO_4^{2-} > ClO_4^-$. Obviously, for the last three anions, which do not become specifically adsorbed, the reactivites vary widely too. Apparently, this order cannot be simply explained on the basis of Frumkin's correction[10] of the theory of retarded discharge, in which account was taken of the effect of anionic adsorption, general and specific, on the $\psi_1$ potential, *i.e.*, potential at the point of surface where the centre of the reacting particle is located. In solutions of the same anionic strength, at approximately equal $\phi$ potentials,[11] *viz.*, potentials with respect to the zero charge of mercury, $E_{\text{max.}}$, specific adsorption of chloride ions, leading to highly negative $\psi_1$ potentials would account for the high reactivity of these anions. For the nitrate and perchlorate ions, however, which are adsorbed almost to the same extent as judged by the quantity $\Gamma_{\text{max.}}$ at $E_{\text{max.}}$,[12,13] the difference in reactivity would only be expected if it is assumed that the former anions approach the surface more closely. The gradual increase in reactivity with the increase of nitric acid concentration in the mixtures investigated (Fig. 4*b*, section C) could similarly be explained. It is still difficult, however, to reconcile the order of reactivity for the two structurally identical $SO_4^{2-}$ and $ClO_4^-$ anions with the theory, since, as inferred from the results of electrocapillary measurements,[12] $\Gamma_{\text{max.}}$ for the former anion is almost negligible; further, this ion does not seem to be completely desolvated at the surface. A supplementary but not necessarily completely independent alternative is Heyrovsky's theory of ion-pair formation.[14] The order of reactivity as given is in fact comparable with that reported by Rabinowitch and Stockmayer[15] from spectrophotometric measurements for the tendency of anions to associate into complexes with multivalent cations ($Fe^{3+}$). In hydrochloric acid solutions co-ordination of tervalent bismuth with chloride ions is well known.[16] In non-complex-forming media containing relatively low [$Cl^-$], co-ordination seems also to be possible, a fact which limited the number of our experiments in testing the catalytic effect of chloride ions. As pointed out before, the mixtures used for this purpose did not show obvious hydrolysis. In mixtures of N-perchloric acid made $10^{-2}$N with respect to $Cl^-$ and $1 \times 10^{-2}$, $8 \times 10^{-3}$, $5 \times 10^{-3}$, or $3 \times 10^{-3}$N with respect to $Bi^{3+}$, immediate hydrolysis leading to separation of crystalline bismuth oxychloride occurred in each case. With [$Bi^{3+}$] = $1 \times 10^{-3}$N, the rate of hydrolysis was slow and the precipitate became visible only after about 6 hr. With [$Bi^{3+}$] = $1 \times 10^{-3}$N and [$Cl^-$] = $10^{-3}$N, no visible precipitate could be detected after 72 hr. Possible ionic interactions which may account for these observations are

$$Bi^{3+} + xCl^- \longrightarrow BiCl_x^{(3-x)+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

followed by

$$BiCl_x^{(3-x)+} + H_2O \longrightarrow BiO^+ + (x-2)Cl^- + 2HCl. \quad . \quad . \quad . \quad (ii)$$

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[8] Ref. 4, p. 173.
[9] Grahame, *Ann. Rev. Phys. Chem.*, 1955, **6**, 346.
[10] Frumkin, *Z. phys. Chem.*, 1933, *A*, **164**, 121.
[11] Antropov, *J. Indian Chem. Soc.*, 1958, **35**, No. 5, 309.
[12] Grahame, *Chem. Rev.*, 1947, **41**, 441.
[13] Ammar and Hassanein, *J. Phys. Chem.*, 1958, **62**, 805.
[14] Heyrovsky, " Polarographie," Springer, Vienna, 1941, p. 74.
[15] Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.
[16] Noyes, Hall, and Beattie, *J. Amer. Chem. Soc.*, 1917, **39**, 2526.

This hydrolysis scheme is not identical with that of Sillén,[17] yet it does indicate that the appearance of bismuth oxychloride will be determined largely by the rate of reaction (2) for which the existence of the species denoted by (1) is a prerequisite. Association of the $SO_4^{2-}$ and $NO_3^-$ anions with metal cations into complexes and ion pairs has been indicated from different sources.[18,19] The $NO_3^-$ ion, however, is known to be less addicted to acting as ligand than $SO_4^{2-}$, yet the rate constant in nitric was found to be higher than in sulphuric acid. This may be accounted for by the fact that in 1N-sulphuric acid the principal anion is $HSO_4^-$ rather than $SO_4^{2-}$.

In the light of the above discussion it is concluded that if anionic and cationic bridges are considered necessary during the elementary act of electron transfer in cation and anion reduction, respectively,[9,20] their formation within the double layer could be a manifestation of ionic association in the bulk of solution.

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[17] Sillén, *Quart. Rev.*, 1959, **13**, 146.

[18] Smithson and Williams, *J.*, 1958, 457; Hurst, "The Kinetics and Mechanism of Inorganic Reactions in Solution," Chem. Soc. Special Publication No. 1, 1954, p. 55; Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, 5th edn., 1949, p. 711.

[19] Sutton, *Nature*, 1952, **169**, 71; Whiteker and Davidson, *J. Amer. Chem. Soc.*, 1953, **75**, 3081.

[20] Frumkin, *Trans. Faraday Soc.*, 1959, **55**, 156.

[21] Moussa, Sammour, and Ghaly, *J. Phys. Chem.*, 1958, **62**, 1017.