235. *A Potentiometric Investigation of Electrolytic Dissociation. Part IV. The Anion Affinity of Copper, Zinc, Cadmium, Silver, and Hydrogen Ions.*

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The variation of kation concentration caused by the addition of excess of a particular anion to an aqueous solution of a salt provides a means whereby some idea can be gained of the extent and nature of complex-ion formation in the solution (Parts I, II, and III; J., 1932, 514; 1934, 1440, 1448). This method, which is only approximate, has already provided results which leave little doubt as to their qualitative accuracy. It has also been shown, with ten different anions, that the anionophilic nature of the cupric ion is consistently greater than that of the cadmium ion. These studies have now been extended to zinc, silver, and hydrogen ions. The sparing solubility of many silver salts, and the ease with which silver nitrate is reduced by many highly kationophilic anions, restricted the number of experiments which could be performed with silver and it was consequently necessary, for comparison purposes, to extend the series of salts studied in the case of copper and cadmium.

Experimental.

The potentiometric titrations were carried out in the manner already described (*loc. cit.*). The silver electrodes were prepared by plating the metal on to platinum from a 15% silver nitrate solution with a *C.D.* of approx. 0·05 amp./cm.^{2}. Before use, the electrodes were short-circuited over-night in the nitrate bath. The crystalline deposit of silver was washed with oxygen-free water, and the electrodes were used in the half-elements in an atmosphere of hydrogen.

Fig. 1.

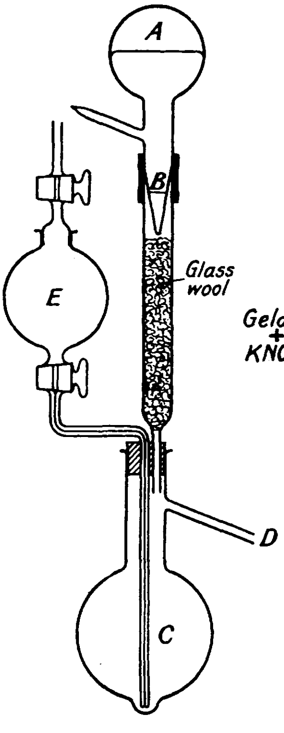
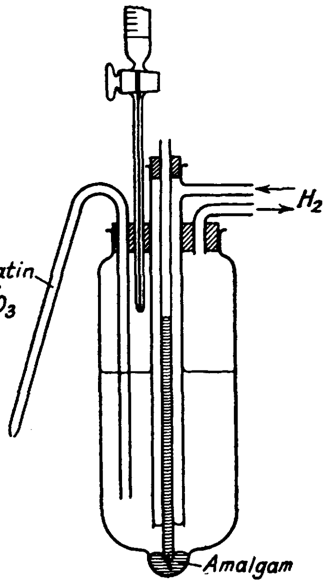


Fig. 2.



For the attainment of steady reproducible potentials with the zinc amalgam (1·5%) electrode employed, rigid exclusion of oxygen and zinc oxide (see below) was essential. In the preparation of the electrode, pure redistilled zinc was introduced into the flask *A* (Fig. 1), and the air swept out by hydrogen. The requisite quantity of pure, freshly distilled mercury was added, the flask evacuated and sealed, and the zinc dissolved in the mercury by gentle warming and shaking. The flask was then connected in an inverted position over the glass-wool filter, and the whole apparatus evacuated. The neck of the flask was broken at the file scratch, *B*, and the amalgam allowed to run down into flask *C*, from whence, by introducing hydrogen through *D*, it was forced up into *E*, where it was stored in an atmosphere of hydrogen. The half-element used in the zinc titrations is shown in Fig. 2. After the 0·01*M*-zinc sulphate solution had been placed in the cell, the latter was swept out by hydrogen, the long bent tube of the storage tap funnel introduced into the half-element, and a little amalgam run into the depression at the bottom of the vessel, whilst hydrogen continued to pass through the cell. Connection with the amalgam was made by a piece of platinum wire sealed through a glass tube.

In the experiments with hydrogen, the usual platinum-black, hydrogen electrode was used in a half-element fitted with a burette. All the titrations were carried out at room temperature and repeated several times in each instance. The results are in the tables. In each case are recorded, x, the total concentration of the added sodium salt NaX, in millimols. per litre; *P.D.*, the potential of the cell

$$\text{E}|0{\cdot}01M\text{-ESO}_4||0{\cdot}01M\text{-ESO}_4 + xM\text{-NaX}|\text{E}$$

in millivolts (silver nitrate was used in the silver experiments); and the values of K_n derived from the mass-action expression

$$K_n = [\text{E}]\{[x] - n(0{\cdot}01 - [\text{E}])\}^n/(0{\cdot}01 - [\text{E}])$$

by giving n the values 1, 2, 3, etc.; [E], the molarity of the free metal ions in the right-hand half-element, was calculated from the formula $P.D. = RT/nF\,.\ln[\text{E}]''/[\text{E}]'$. (In the $0{\cdot}01M$-solutions, $[\text{Cu}^{\cdot\cdot}]$ was taken as 0·00629; $[\text{Cd}^{\cdot\cdot}]$ as 0·00614; $[\text{Zn}^{\cdot\cdot}]$ as 0·00633; $[\text{Ag}^{\cdot}]$ as 0·00901.)

Cyanide.—Steady reproducible potentials were obtained only with cadmium and silver electrodes. Copper sulphate was, of course, reduced, and the zinc amalgam electrode was rapidly attacked by the cyanide solution (see below). The potentials show that silver is decidedly more anionophilic than cadmium. The K_n values for cadmium indicate that, even in the presence of a large excess of cyanide ions, there is no tendency for the formation of complex ions containing more than four cyanide ions, a result in agreement with the known chemistry of the complex cadmicyanides. Besides salts containing the well-known $[\text{Cd(CN)}_4]''$ ion, Hölzl (*Monatsh.*, 1929, **51**, 397) claimed to have prepared $\text{Ag[Cd(CN)}_3]$. The relative magnitudes of the potentials obtained with cadmium and silver electrodes, however, indicate that in solution this salt would be converted into an argentocyanide.

With silver the K_n values show that complex formation has little tendency to pass the $[\text{Ag(CN)}_3]''$ stage, in agreement with the results of Masaki (*J. Electrochem. Assoc., Japan*, 1933, **1**, 25). A comparison of the above results with those obtained with cadmium and copper and the aminoacetate ion (Part II, *loc. cit.*) is interesting, for here also cadmium showed a decided preference to take up four aminoacetate ions, whereas the cupric ion, in spite of its greater affinity, took up only three.

Thiocyanate.—Owing to the sparing solubility of silver thiocyanate, the initial part of the titration curve for this metal could not be obtained. That the kationophilic nature of the thiocyanate ion is less than that of the cyanide ion is apparent from the potentials, and agrees with the results of Spacu and Grecu (*Bul. Soc. Stiinte Cluj*, 1931, **5**, 422). The constant value of K_3 over a large range of thiocyanate-ion concentration indicates that here also the silver ion has little tendency to co-ordinate with more than three thiocyanate ions even in the presence of a relatively large excess of thiocyanate. Complexes containing three and four thiocyanate radicals attached to a silver ion have been reported (*idem, ibid.*, 1931, **6**, 238), but these results indicate that in aqueous solution these complexes will be highly dissociated.

The relatively small potentials obtained with cadmium and zinc show that these metals have little tendency to co-ordinate with the thiocyanate ion.

Thiosulphate.—The affinity of the thiosulphate ion for the four metal ions studied is in the order, $\text{Ag}^{\cdot} > \text{Cu}^{\cdot\cdot} > \text{Cd}^{\cdot\cdot} > \text{Zn}^{\cdot\cdot}$. In the silver–thiosulphate titrations, the initial presence of excess of thiosulphate was necessary, otherwise a white precipitate formed which darkened in a few seconds, owing to the production of silver sulphide. The K_n values indicate that the silver ion readily co-ordinates with two thiosulphate ions, and at the highest concentrations of thiosulphate, perhaps also with a third. This result is in agreement with evidence from the existence of stable solid complex salts (cf., *inter alia*, Spacu and Murgulescu, *Z. anorg. Chem.*, 1931, **199**, 273; 1932, **207**, 150; **208**, 157; Baines, J., 1929, 2763; Bassett and Lemon, *ibid.*, 1933, 1423; Carrière and Raoulet, *Compt. rend.*, 1931, **192**, 746). Although cadmium again appears to be less anionophilic than silver, the results show that it forms $[\text{Cd(S}_2\text{O}_3)_2]''$ in the presence of a relatively small excess of thiosulphate ions and $[\text{Cd(S}_2\text{O}_3)_3]^{\text{iv}}$ in the presence of a larger excess. There is some indication also of the formation of $[\text{Cd(S}_2\text{O}_3)_4]^{\text{vi}}$ in the most concentrated solution. Complex salts containing these ions have been isolated (see Mellor, " Comprehensive Treatise, etc.," 1930, Vol. 10, p. 547). Although a number of double alkali-metal zinc thiosulphates have been reported, the potentials of the concentration cell show that these must be highly dissociated in aqueous solution.

In the copper–thiosulphate titrations, with thiosulphate concentrations up to approximately $0{\cdot}02M$, the solution was green and the potentials were unsteady. Above this concentration the solution became colourless and steady reproducible potentials were obtained. It is generally agreed that thiosulphate addition brings about a reduction of the cupric ion to complex cuprous thiosulphates. The magnitudes of the potentials, however, are of interest.

Chlorate.—A further comparison of the anionophilic nature of the silver and the cadmium ion was possible with potassium chlorate. Although the chlorate ion possesses only a small tendency to co-ordinate with these metal ions, the results indicate that here again the silver ion displays the greater affinity for the anion.

Acetate.—The acetate ion apparently shows little tendency to form stable complexes with either the silver or the zinc ions. The potentials obtained with cadmium (Part II, *loc. cit.*) are higher than those obtained with silver. The difference is only small and may be due to the different electrical natures of the kations.

Aminoacetate.—The results obtained in the zinc titration are interesting in that the potentials are distinctly higher than those obtained with cadmium (Part II, *loc. cit.*). Although the other numerous systems studied, with the exception of the acetate, all indicate that the anionophilic nature of a kation is a characteristic invariable property, this result suggests that in certain cases there can be something specifically accommodating in the natures of the kation and the anion concerned, which results in the formation of a stable complex. The steady values of K_3 indicate the formation of $[Zn(NH_2{\cdot}CH_2{\cdot}CO_2)_3]'$ at relatively small aminoacetate-ion concentrations.

Halides.—Titrations were carried out with potassium chloride and potassium bromide, the zinc electrode being used. Activity corrections have been applied in calculating the K_n values (see Part I, *loc. cit.*). Steady potentials could not be obtained by using potassium iodide or concentrated potassium bromide. The results, when compared with those obtained with cadmium (Part I) and copper (Part III), show that the zinc ion has less tendency to form complex halide ions than either copper or cadmium.

The above results, apart from the zinc–aminoacetate and the silver–acetate titrations, show that these kations can be placed in the following order of decreasing anion affinity

$$Ag^{\cdot}>Cu^{\cdot\cdot}>Cd^{\cdot\cdot}>Zn^{\cdot\cdot}.$$

This order is the same as that in the electropotential series. It is unfortunate that only a limited number of silver and zinc salts could be studied. The majority of the anions employed with the copper and cadmium electrodes (Part II) either gave insoluble silver salts or reduced the silver ion to the metal; *e.g.*, sodium aminoacetate, phenylaminoacetate, and pyruvate reduced neutral silver nitrate rapidly, and sodium glycollate and lithium lactate caused a slow reduction. If such reductions are brought about by the transfer of an electron from the anion to the kation, occasioned by the great electron affinity of the kation and the relatively high deformability of the electron orbit in the reducing anion, the following facts indicate that the connection between reduction and complex formation is obscure.

Added anion.	$Cu^{\cdot\cdot}$.	$Ag^{\cdot}$.
Iodide	Reduction	Complex-ion formation
Thiosulphate	"	" "
Cyanide	"	" "
Aminoacetate	Complex-ion formation	Reduction
Lactate	" "	"
Glycollate	" "	"
Pyruvate	" "	"

It is perhaps significant that the possibility of chelate-ring formation exists with the last four anions.

That the number of studies with the zinc electrode was limited was due to another cause, *viz.*, the relatively rapid attack of the zinc amalgam electrode by highly kationophilic anions. It has been pointed out (Riley, *Proc. Roy. Soc.*, 1934, *A*, **143**, 399) that the corrosion of a metal involves the transfer of metal ions from the solid metal phase to the solution, and that the tendency of this process to occur must be largely affected by the presence, particularly in neutral solution, of anions which form undissociated complex ions. This view was criticised by Evans and Hoar (*Trans. Faraday Soc.*, 1934, **30**, 430) on the grounds that complex formation which involves the meeting of several particles " appears improbable on kinetic, electrical and steric grounds alike." The reaction of the type suggested is essentially ionic, so this criticism does not appear pertinent. The reaction suggested involves either the absorption of oxygen or the evolution of hydrogen. With an electropositive metal like zinc, which forms complex ions, it is probable that hydrogen discharge will become possible in the presence of highly kationophilic anions, thus making the attainment of equilibrium potentials impossible, even when oxygen is rigidly excluded. With the less electropositive copper, the elimination of traces of oxygen from the electrolyte is usually sufficient to afford steady reproducible potentials, otherwise corrosion of the electrode occurs with the establishment of an irreversible potential.

It was impossible to obtain reversible potentials in the case of zinc in the presence of solutions of potassium cyanide and iodide and sodium citrate and tartrate. The rapid dissolution of metallic zinc in aqueous solutions of the sodium salts of highly kationophilic anions was shown by the following experiments.

To 50 c.c. of a 0·2*N*-solution of the sodium salt was added a piece of pure thin sheet zinc, 2″ × 0·3″ (bent at right angles so that it would stand on its edge on the bottom of the flask), previously polished and washed with alcohol and ether. The flask was kept, with free access of air, at *ca.* 20°, and after a certain period the amount of zinc dissolved was estimated by means of 8-hydroxyquinoline. The experiment was repeated over different periods of time, and the initial rates of solution determined, *i.e.*, the rates before the precipitation of basic salts (cf. Riley, *loc. cit.*) occurred. The following results were obtained :

Sodium salt	Citrate	Oxalate	Tartrate	Malonate	Acetate
Zn dissolved, mg./hr. × 10^3	75	60	100	50	13

With the sodium tartrate solution in an atmosphere of nitrogen the zinc dissolved less rapidly, and the surface of the metal soon became covered with bubbles of hydrogen.

The Corrosion of Platinum and Gold (with S. CHAMBERS).—In the experiments with the hydrogen electrode in concentrated potassium cyanide solution (see below) it was noticed that on standing for a few days the potassium cyanide solution dissolved the platinum black from the electrode, leaving bright platinum. According to Gore (*Proc. Roy. Soc.*, 1880, *A*, **30**, 38), platinum is not attacked by cyanide solution. The dissolution of the platinum under these conditions is, however, consistent with the above views on corrosion, for platinum forms a large number of stable complex ions, and the above potentiometric titrations indicate that the cyanide ion possesses very highly developed kationophilic properties. In order to determine whether the presence of oxygen is necessary or whether the dissolution can occur with the evolution of hydrogen, the following experiments were carried out.

Platinum-black (0·2 g.), prepared by reducing platinic chloride with sodium formate solution and washing and drying the precipitate, was introduced into a small bulb connected directly with a volumeter. The whole apparatus was completely filled with boiled-out 6*N*-potassium cyanide solution. When the bulb was warmed to 85°, small bubbles of gas began to ascend, and in 6 hours almost 0·5 c.c. of gas had collected in the volumeter tube. After cooling, excess of air was admitted, and the mixed gases were exploded. The contraction in volume was consistent with the gas evolved being hydrogen. No gas evolution occurred in blank experiments. Under similar conditions the evolution of hydrogen was relatively rapid in 3*N*-potassium cyanide, slow in *N*, and very slow in 0·5*N*. No action could be detected in 0·1*N*-cyanide solution. Presumably because of its smaller surface area, no action could be detected with bright platinum. Gold precipitated by ferrous sulphate solution also evolved hydrogen slowly under similar conditions in 6*N*- and 3*N*-potassium cyanide, but no appreciable attack occurred in more dilute solutions.

The Co-ordination Number of Hydrogen.—Numerous examples of the occurrence of bicovalent hydrogen have been cited in recent years, *e.g.*, the anomalous behaviour of hydrofluoric acid has been explained by the existence of the HF_2' ion (Davies and Hudleston, J., 1924, **125**, 260). Associated water molecules are supposed to contain bicovalent hydrogen (Bernal and Fowler, *J. Chem. Physics.*, 1933, **1**, 515; *Trans. Faraday Soc.*, 1933, **29**, 1049). The determination of the variation of hydrogen-ion concentration with the concentration of a particular anion and the analysis of the results by the above method offered a means of determining whether or not such bicovalent complex ions exist in aqueous solution. The cyanide was used up to a total concentration of 3·6*N*. At this concentration the p_H of the solution reached 11·5, so it was necessary to correct the concentration of undissociated hydrocyanic acid by writing $[HCN] = 0{\cdot}01 - [H^{\cdot}] + [OH']$.

Even up to the extreme concentrations of cyanide ion employed, K_1 showed only a slight decrease ($1{\cdot}3 \times 10^{-9}$ at $x = 175$, to $0{\cdot}83 \times 10^{-9}$ at $x = 3600$) and this change is probably not greater than the error introduced by the omission of activity corrections to the cyanide-ion concentrations. The values of K_1 show excellent agreement with the value of the dissociation constant of hydrocyanic acid determined by the conductivity method, *viz.*, $0{\cdot}72 \times 10^{-9}$. This result can leave no doubt that even in the presence of a large excess of the highly kationophilic cyanide ion, hydrogen displays no tendency to form complex ions of the type $[H(CN)_2]'$. This does not, of course, exclude the possibility of a water molecule still being co-ordinated with the hydrogen ion. It is, however, very significant that if hydrogen can display a covalency of two, it should be incapable of taking up two cyanide ions, for the cyanide ion forms, with numerous metal ions, complex ions probably greater in number and stability than those formed by any other anion.

The possibility of chelate-ring formation makes the results obtained with the aminoacetate ion less conclusive, but here also the value of K_1 remained constant. The values obtained ($2{\cdot}2$—$2{\cdot}8 \times 10^{-10}$) are in excellent agreement with the value of

$$[\mathrm{H^{\bullet}}][\mathrm{NH_2{\cdot}CH_2{\cdot}CO_2'}]/[\mathrm{NH_2{\cdot}CH_2{\cdot}CO_2H}] = 1{\cdot}8 \times 10^{-10}$$

obtained by other methods (cf., however, Bjerrum, *Z. physikal. Chem.*, 1923, **104**, 147).

Attempts to carry out similar titrations in acid fluoride solutions were not successful. Relatively small potentials were observed and reproducible readings could not be obtained. The electrodes became abnormally sensitive to traces of oxygen, rapid variations of potential up to one volt being observed. Electrodes, once used in a fluoride solution, gave inconsistent values even in dilute sulphuric acid, and it was evident that permanent poisoning had occurred.

	$\mathrm{Cd^{\cdot\cdot} + CN'}$.					$\mathrm{Ag^{\cdot} + CN'}$.			
x.	*P.D.*	K_1.	K_2.	K_3.	K_4.	*P.D.*	K_1.	K_2.	K_3.
60	327	$1{\cdot}6\times10^{-13}$	$5{\cdot}2\times10^{-15}$	$8{\cdot}8\times10^{-17}$	$5{\cdot}2\times10^{-19}$	1030	$7{\cdot}9\times10^{-19}$	$2{\cdot}5\times10^{-21}$	$4{\cdot}2\times10^{-23}$
80	375	$5{\cdot}0\times10^{-15}$	$2{\cdot}6\times10^{-16}$	$9{\cdot}0\times10^{-18}$	1·8	1053	$4{\cdot}4\times10^{-20}$	2·3	7·9
100	394	1·5	1·1	5·7	2·2	1070	2·9	2·1	$1{\cdot}1\times10^{-22}$
130	414	$4{\cdot}1\times10^{-16}$	$4{\cdot}1\times10^{-17}$	3·4	2·2	1090	1·7	1·8	1·5
160	424	2·3	3·0	3·4	3·2	1105	1·2	1·6	1·8
200	433	1·4	2·3	3·5	4·7	1117	$9{\cdot}4\times10^{-21}$	1·6	2·4
250	443	$8{\cdot}1\times10^{-17}$	1·8	3·6	6·6	1137	5·5	1·2	2·4
300	453	4·3	1·2	3·0	6·7	1149	4·1	1·1	2·8
350	462	2·5	$8{\cdot}0\times10^{-18}$	2·4	6·8	1161	3·0	$9{\cdot}6\times10^{-22}$	2·9
400	469	1·6	6·0	2·1	6·9	1172	2·2	8·1	2·8
500	480	$8{\cdot}5\times10^{-18}$	4·0	1·8	7·7	1191	1·3	6·2	2·8
600	490	3·9	2·2	1·2	6·5	1201	1·0	5·9	3·3
700	502	2·1	1·4	$9{\cdot}0\times10^{-19}$	5·0	1213	$7{\cdot}6\times10^{-22}$	5·1	3·3
850	517	$7{\cdot}7\times10^{-19}$	$6{\cdot}3\times10^{-19}$	5·0	3·9	1230	4·8	3·9	3·2
1000	525	4·8	4·7	4·4	4·1	1243	3·3	3·2	3·1
1200	537	2·3	2·7	3·1	3·5	1262	1·9	2·2	2·6
1500	544	1·7	2·4	3·5	5·1	1286	$9{\cdot}0\times10^{-23}$	1·3	1·9
1750	552	1·0	1·7	2·9	4·9	1293	7·9	1·4	2·3
2000	558	0·73	1·4	2·8	5·4	1306	5·4	1·1	2·1

	$\mathrm{Zn^{\cdot\cdot} + CNS'}$.		$\mathrm{Cd^{\cdot\cdot} + CNS'}$.	
x.	*P.D.*	10^2K_1.	*P.D.*	10^3K_1.
11·5	2·8	0·67	4·5	4·4
14·3	3·0	0·92	5·5	5·4
17·0	3·5	1·1	6·6	6·1
19·6	3·8	1·3	7·3	6·8
22·2	4·1	1·4	8·0	7·5
27·3	5·4	1·5	9·6	8·1
32·1	5·9	1·7	11·0	8·5
41·4	6·9	2·0	13·3	9·1
50·0	8·0	2·2	15·2	9·4
58·1	9·2	2·2	16·8	9·6
72·7	10·8	2·4	19·6	9·5
85·7	12·0	2·5	22·0	9·2
100·0	13·2	2·6	24·2	9·0
123·5	15·3	2·7	27·7	8·3
150·0	17·6	2·6	31·0	7·8
180·0	19·4	2·7	35·2	6·6

	$\mathrm{Ag^{\cdot} + CNS'}$.			
x.	*P.D.*	$10^{11}K_1$.	$10^{11}K_2$.	$10^{11}K_3$.
600	580	5·4	3·1	1·7
612	580	5·4	3·2	1·8
634	581	5·4	3·3	1·9
655	583	5·2	3·2	1·9
674	585	4·9	3·2	2·0
700	591	4·1	2·7	1·8
739	596	3·5	2·5	1·7
771	600	3·1	2·3	1·6
800	602	2·9	2·6	1·7
825	605	2·7	2·2	1·7
847	608	2·5	2·0	1·6
867	610	2·3	2·0	1·6
884	612	2·2	1·9	1·6
900	614	2·1	1·9	1·6

	$\mathrm{Zn^{\cdot\cdot} + S_2O_3''}$.		$\mathrm{Cu^{\cdot\cdot} + S_2O_3''}$.
x.	*P.D.*	10^3K_1.	*P.D.*
11·5	6·5	3·2	—
14·3	7·4	4·2	—
17·0	8·2	5·1	37
19·6	10·1	4·9	85
22·2	11·0	5·3	241
27·3	12·6	6·0	356
32·1	14·6	6·0	383
41·4	17·0	6·5	409
50·0	19·2	6·6	426
58·1	21·0	6·7	439
72·7	23·8	6·7	458
85·7	26·0	6·7	473
100·0	28·1	6·6	487
123·5	31·5	6·2	507
150·0	35·2	5·7	526
180·0	39·2	4·9	545

	$\mathrm{Cd^{\cdot\cdot} + S_2O_3''}$.				$\mathrm{Ag^{\cdot} + S_2O_3''}$.		
x.	*P.D.*	10^6K_1.	10^6K_2.	10^7K_3.	*P.D.*	$10^{13}K_1$.	$10^{14}K_2$.
41·4	66	100	1·5	0·048	—	—	—
50·0	74	72	1·6	0·14	585	30	6·7
58·1	80	53	1·6	0·25	603	17	5·3
72·7	89	33	1·5	0·41	621	11	5·0
85·7	96	23	1·5	0·52	632	8·7	4·9
100·0	104	14	1·0	0·55	642	7·1	5·0
123·5	115	7·9	0·74	0·57	654	5·4	5·1
150	122	5·5	0·67	0·68	666	4·1	5·0
180	126	4·6	0·69	0·91	677	3·3	5·0
225	129	4·6	0·90	1·6	690	2·5	4·8
286	137	3·2	0·82	2·0	708	2·1	4·0
390	151	1·5	0·53	1·8	733	0·79	2·8
500	161	0·85	0·40	1·8	748	0·57	2·7
667	176	0·34	0·22	1·4	765	0·38	2·4
750	185	0·19	0·14	0·96	775	0·29	2·1

	$Cd^{\cdot\cdot} + ClO_3'$.		$Ag^{\cdot} + ClO_3'$.		$Ag^{\cdot} + AcO'$.		$Zn^{\cdot\cdot} + AcO'$.		$Zn^{\cdot\cdot} + NH_2{\cdot}CH_2{\cdot}CO_2'$.			
x.	*P.D.*	10^2K_1.	*P.D.*	10^2K_1.	*P.D.*	10^2K_1.	*P.D.*	10^2K_1.	*P.D.*	10^9K_1.	$10^{11}K_2$.	$10^{13}K_3$.
11·5	1·2	0·89	4·7	3·0	6·5	1·9	2·4	0·74	18	520,000	—	—
14·3	1·3	1·2	5·4	3·1	7·1	2·4	3·2	0·89	29	320,000	—	—
17·0	1·4	1·5	6·2	3·3	7·7	2·7	4·0	0·99	42	170,000	—	—
19·6	1·5	1·8	7·0	3·5	7·9	3·1	4·3	1·2	65	37,000	—	—
22·2	1·6	2·1	7·7	3·7	8·4	3·4	4·5	1·3	94	4,400	170	—
27·3	1·7	2·6	8·8	4·1	9·1	4·0	5·1	1·9	132	300	93	—
32·1	1·8	3·1	9·5	4·6	9·8	4·4	6·1	1·7	153	77	51	0·32
41·4	2·1	4·0	11·0	5·2	10·2	5·7	7·5	1·9	179	13	19	6·3
50·0	2·3	4·8	12·3	5·6	10·7	6·6	8·5	2·1	197	4·0	8·9	7·9
58·1	2·5	5·4	13·3	6·1	11·1	7·4	9·6	2·1	209	1·8	5·5	8·5
72·7	2·8	6·5	14·8	6·8	12·0	8·7	11·4	2·3	225	0·67	3·0	8·3
85·7	3·1	7·4	16·1	7·3	12·8	9·6	12·4	2·4	236	0·34	2·0	7·8
100·0	3·3	8·5	17·2	7·9	13·7	10	14·0	2·4	246	0·19	1·3	7·2
123·5	3·7	10	19·0	8·7	15·0	12	15·9	2·5	258	0·094	0·89	6·8
150·0	4·2	11	20·5	9·6	—	—	18·1	2·5	267	0·055	0·66	6·8
180·0	4·5	13	21·9	11	—	—	20·4	2·5	276	0·033	0·50	6·6

	$Zn^{\cdot\cdot} + Cl'$.	
x.	*P.D.*	10^2K_1.
10	1·6	0·60
20	2·8	1·3
40	4·0	2·4
60	5·2	3·1
80	5·9	3·8
100	6·5	4·3
130	7·2	5·7
160	7·7	5·8
200	8·3	6·6
250	9·0	7·5
300	9·7	8·3

	$Zn^{\cdot\cdot} + Cl'$.	
x.	*P.D.*	10^2K_1.
350	10·3	8·9
400	10·9	9·5
500	11·7	11
600	12·4	12
700	13·1	12
850	14·1	14
1000	15·0	14
1200	16·3	15
1500	18·4	15
1800	20·6	14

	$Zn^{\cdot\cdot} + Br'$.	
x.	*P.D.*	10^2K_1.
10	1·7	0·59
20	3·0	1·3
40	4·5	2·3
60	5·6	2·9
80	6·4	3·5
100	7·0	4·0
130	7·8	4·7
160	8·3	5·4

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ARMSTRONG COLLEGE (UNIVERSITY OF DURHAM),
NEWCASTLE UPON TYNE.

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