Part III. Copper Halides.

By H. L. Riley and H. C. Smith.

Before drawing any conclusions as to the relative magnitude of the aniophilic properties of copper and cadmium ions, it appeared desirable to extend these studies to other types of anion; those employed in Part II were all carboxylic, and the halides of cadmium were described in Part I, so it was decided to carry out similar copper halide measurements.

Attempts to carry out titrations in the above manner gave extremely discordant results owing to the rapid formation of cuprous chloride and bromide during the titrations. This difficulty was overcome as follows. The condition of the electrodes was checked before the titration by using 0·01*M*-copper sulphate in each half-element. The halide–copper sulphate was then run into the right-hand half-element of the concentration cell, the electrolyte being stirred by bubbling hydrogen through it, and the *P. D.* of the two electrodes then measured. Only two potentials were measured at each titration, and the concentration range was covered by carrying out several titrations. The values obtained were checked by preparing a copper halide solution of a particular concentration and measuring the potential of a freshly plated copper electrode when dipped into this solution. Curves were drawn from approximately 70 readings in each case. The results recorded in Table VI are the smoothed values obtained from these curves. Values of K_n were also determined in the manner already described, the activity correction being included in the calculation. An attempt was made, by a method similar to that described in Part I, to evaluate the dissociation constants of the various undissociated species in solution. The nature of the experimental results permitted only a very approximate computation. The results are given below :

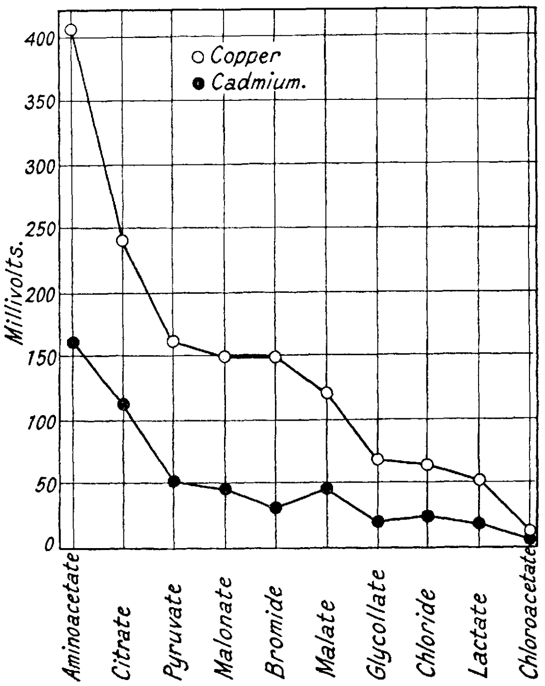
Table VI.

	Copper Chloride.					*Copper Bromide.*				
x.	*P.D.*, mv.	10^5K_1.	10^6K_2.	10^7K_3.	10^7K_4.	*P.D.*, mv.	10^7K_1.	10^9K_2.	10^9K_3.	10^9K_4.
12	4·4	500	0·62	—	—	44·0	420	—	—	—
15	7·5	430	2·0	—	—	69·0	130	—	—	—
18	12·0	330	2·6	—	—	82·2	71	—	—	—
22	18·2	220	4·1	—	—	94·7	38	1·3	—	—
28	26·8	140	6·6	—	—	107·7	20	7·3	—	—
34	33·6	98	8·4	0·065	—	117·2	12	9·2	0·0034	—
40	39·4	74	9·4	0·30	$0{\cdot}0_6 38$	123·9	8·8	11	0·028	—
52	47·7	52	12	1·1	0·0026	133·2	5·8	12	0·12	0·00024
70	55·7	38	14	3·2	0·037	141·7	4·1	15	0·33	0·0038
100	63·1	30	17	8·0	0·26	149·0	3·3	19	0·87	0·028
160	72·6	23	23	20	1·6	160·6	2·1	22	1·9	0·15
250	85·0	13	22	33	4·5	171·8	1·3	22	3·4	0·47
400	101·7	5·4	14	36	8·4	185·3	0·70	19	4·7	1·1
600	120·8	1·7	6·7	25	9·1	200·6	0·31	12	4·4	1·6
900	143·3	0·42	2·4	14	7·5	223·1	0·074	4·3	2·4	1·3
1200	161·4	0·13	1·0	7·5	5·5	244·7	0·018	1·4	1·0	0·74
1500	174·2	0·059	0·56	5·2	4·7	264·4	0·0046	0·43	0·40	0·37
1800	183·0	0·036	0·41	4·7	5·2	281·0	0·0015	0·17	0·20	0·22
2000	188·0	0·027	0·35	4·4	5·4	—	—	—	—	—

	$CuCl$.	$CuCl_2$.	$CuCl_3'$.	$CuCl_4''$.
$K =$	$1{\cdot}6 \times 10^{-3}$	$4{\cdot}0 \times 10^{-5}$	$1{\cdot}3 \times 10^{-5}$	$2{\cdot}4 \times 10^{-6}$
	$CuBr^{\cdot}$.	$CuBr_2$.	$CuBr_3'$.	$CuBr_4''$.
$K =$	$2{\cdot}1 \times 10^{-6}$	$5{\cdot}7 \times 10^{-8}$	$1{\cdot}2 \times 10^{-8}$	$5{\cdot}1 \times 10^{-9}$

Conclusion.

It is now possible to compare the affinities of ten anions for the cupric ion with their affinities for the cadmium ion. The Fig. shows the anions arranged in descending order of their affinityf or the cupric ion plotted against the potential of the cell shown on p. 1441 (E = Cu; $x = 0{\cdot}1$). The corresponding potentials observed when cadmium is used instead of copper are plotted in the same order. The copper concentration cells give consistently higher potentials than the cadmium. Apart from small discrepancies in the position of the chloride and bromide results, which is not surprising in view of the difficulties encountered in carrying out the copper halide measurements, both sets of potentials show very similar trends. Although it is not possible to generalise, this result does indicate that the cupric and the cadmium ion possess characteristic, invariable (or only slightly variable) aniophilic properties. There is a widely held belief, based presumably on the behaviour of cadmium iodide solution in the transport-number apparatus, that cadmium possesses an exceptionally high tendency to form complex ions in aqueous solution (cf. Sidgwick, *op. cit.*, p. 264: cadmium salts form complexes in water with "unparalleled ease"). We can, however, safely conclude from the above results that the aniophilic property of the cupric ion is considerably greater than that of the cadmium ion. What is the reason for this pronounced difference in the properties of these two ions? Their diameters are not greatly different, so this behaviour is not merely a volume effect. It has been suggested that certain metallic ions possess localised charges at their surfaces, due to the imperfect screening of the excess positive charge on the nucleus (Riley and Fisher, J., 1929, 2006). (Is it possible that the localisation is a manifestation of a non-uniform field of force due to a discrete structure of the nucleus?) It is in some such direction that we must look for an explanation of these differences in the behaviour of copper and cadmium ions.



The above results also show that there are very pronounced and fundamental differences between the protophilic and the katiophilic natures of anions.

Armstrong College, University of Durham.
Newcastle-upon-Tyne.

[*Received, July* 28*th*, 1934.]