316. *A Potentiometric Investigation of Electrolytic Dissociation. Parts II and III.*

Part II. Copper and Cadmium Carboxylic Salts.

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THE feeble electrolytic dissociation of certain salts, *e.g.*, mercuric cyanide, thiocyanate, and chloride, copper and nickel malonates, etc., is probably due to two factors, *viz.*, the tendency of the kations and of the anions of these salts to act as electron acceptors and donors respectively—a property demonstrated by the number and stability of the complex ions formed by each type of ion. It is proposed, for brevity, to refer to these two tendencies as the " aniophilic " and the " katiophilic " properties of kations and anions respectively. A salt consisting of a highly aniophilic kation and a highly katiophilic anion will be only feebly dissociated in aqueous solution. The aniophilic property of a kation is in some way connected with its basicity, for the strongly basic alkali-metal ions form salts which are completely dissociated in dilute aqueous solution; only very few co-ordination compounds of these metals are known. The katiophilic property of an anion is in some way connected with the strength of the corresponding acid. The anions of many weak acids, *e.g.*, CN′, CNS′, NO_2', etc., form stable complex ions with many kations. These two connexions are, however, obscure. Little is known of the extent of the electrolytic dissociation of metallic salts other than those of the strongly basic metals. There are instances where the anions of strong acids form feebly dissociated salts and complex salts, *e.g.*, Cl′. To avoid confusion, the word " protophilic " will be used to refer to the affinity of an anion for the hydrion, " katiophilic " being restricted to its affinity for metallic ions.

The present investigation is concerned with three important questions. (i) Are the katiophilic and aniophilic natures of ions invariable characteristic properties, or may the extent of electrolytic dissociation of a salt be determined by something mutually accommodating in the electronic structures of anion and kation? In other words, if we have two salts, XA and YA (X and Y representing two different kations, and A a common anion), and if XA is more highly dissociated in aqueous solution than YA, then will XB, XC, XD, etc. (B, C, and D representing other anions) be more highly dissociated than YB, YC, YD, etc., respectively? (ii) What are the constitutive factors which govern the katiophilic properties of anions? (iii) What is the relationship between (*a*) the katiophilic and the protophilic properties of anions, and between (*b*) the aniophilic natures and the basicities of kations?

The problem of elucidating the electrolytic behaviour of a salt containing both ions of this type is a complex one, for not only does autocomplex formation occur, but highly aniophilic kations are usually multivalent, and this introduces the possibility of dissociation occurring in more than one stage. It has been shown (Part I, J., 1932, 514) that an approximate idea of the electrolytic behaviour of salts of this type can be obtained by a potentiometric method, which has now been extended to some 40 salts of cadmium and copper.

EXPERIMENTAL.

The method employed was essentially the same as that described in Part I (*loc. cit.*). The potentials of the concentration cells were measured at room temperature by means of a

"Cambridge" potentiometer. Oxidation of the electrodes was prevented by using water boiled out in a current of hydrogen, and by carrying out the titrations in an atmosphere of hydrogen (cf. Riley, J., 1930, 1642). Connexion between the half-elements and the buffer solution was made by glass tubes containing a jelly of gelatin and potassium nitrate. The sodium salts employed were either purchased or prepared from the acids. Their purity was checked by analysis. Because of its ready preparation in the pure crystalline condition, lithium lactate was used instead of the sodium salt. Where it was not possible to isolate the pure sodium salt, the standard solution was prepared by adding an equivalent quantity of accurately standardised sodium hydroxide solution to the pure acid. This was necessary with glycine and sarcosine. All the titrations were repeated several times, and the results recorded are means of concordant values. Hydrolysis or sparingly solubility in many instances prevented titrations being carried out with both cadmium and copper electrodes.

The results are given in Tables I—VI. The potentials (in millivolts) are of the cell:

$$\mathrm{E} \mid 0{\cdot}01M\text{-}\mathrm{ESO_4} \mid \text{Satd. } \mathrm{KNO_3} \mid 0{\cdot}01M\text{-}\mathrm{ESO_4} + xM\text{-}\mathrm{NaX} \mid \mathrm{E}$$

where E is either cadmium or copper and xM represents the molarity (shown in millimols./l.) of the particular sodium salt. The experimental results were subjected to the analytical treatment already described in Part I (*loc. cit.*). The concentrations of the free metallic ions in the right-hand half-element of the cell were calculated from the potentials on the assumption that [Cd] in $0{\cdot}01M$-cadmium sulphate = 0·00614 and [Cu] in $0{\cdot}01M$-copper sulphate = 0·00629 (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 475). Values of K_n were calculated from the expression

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

where [E] is the copper- or the cadmium-ion concentration, X the total concentration of added anion, and n a positive integer. It was not possible through lack of data to include an activity correction in the above expression. When the values of K_1 showed a pronounced decrease, values of K_2 were also calculated. These are only given in the tables when they passed through a maximum value. Values of K_3 and K_4 which pass through a maximum are also shown.

When the concentration of metal ion is small and that of the added anion relatively large, the departure from constancy of K_n is largely determined by the denominator of the above expression. When n is made equal to 1, it is tacitly assumed that the only undissociated species in solution is EX, and the rate at which K_1 decreases as the concentration of X increases gives some idea of the rate at which (0·01 — [E]) becomes progressively larger than EX owing to the formation of more complex undissociated units $\mathrm{EX_2}$, $\mathrm{EX_3}$, etc. If the metal kation has a relatively great tendency to form undissociated units, $\mathrm{EX_3}$, $\mathrm{EX_4}$, etc., then K_2 will show a maximum value at relatively low concentrations of the added anion. In the general case, K_n will pass through a maximum value as the concentration of the anion increases if there is any appreciable formation of more complex undissociated units, *e.g.*, EX_{n+1}, EX_{n+2}, etc.

In those titrations where only small potentials were registered, the value of K_1 shows a progressive increase, and in some cases only passes through a maximum at relatively high concentrations of X. This is due in part to the omission of the activity correction and the neglect of the sulphate-ion concentration. When the concentration of metal ions was relatively large, an appreciable amount of undissociated metal sulphate must have been present. Small amounts of complex ions of the type $\mathrm{E_2X}$ might also have been present, but the approximate nature of the analysis does not allow of any definite conclusion on this point. Constant errors are also introduced by the use of metal-ion concentrations calculated from conductivity data on the assumption that $\alpha = \Lambda/\Lambda_0$.

DISCUSSION.

Formate.—The addition of formate caused only a relatively small decrease in the cadmium-ion concentration; K_1 rises and does not pass through a maximum, indicating that the formation of undissociated cadmium formate or formato-complex ions does not occur to any great extent, even in the presence of a relatively large excess of formate ions. The formate ion is only weakly katiophilic.

Acetate.—The results show that the acetate ion is decidedly more katiophilic than the formate, and indicate the formation of an appreciable amount of undissociated cadmium acetate.

Propionate.—The katiophilic property here shows a further increase, and K_1 a similar variation to that for the acetate.

Butyrate, iso*Butyrate, and* iso*Valerate.*—These anions behave in a similar manner to the acetate. It is interesting to compare the potentiometric behaviour of these fatty-acid anions with the conductometric behaviour of their acids. The dissociation constants of the acids are given at the foot of the columns in Tables I and II. A rough parallelism can be traced.

Phenylacetate.—These results are very similar to those of the *iso*butyrate ion, and yet the dissociation constant of phenylacetic acid is approximately three times greater than that of *iso*butyric acid. Although other instances will be cited later, in which there is lack of parallelism between the katiophilic and protophilic properties of anions, this case is interesting because there is no possibility of chelation, apart from that of the carboxyl group itself. This discrepancy is therefore not merely due to the difference in the ionic diameters of hydrogen and cadmium. Possibly, it is caused by the greater polarisability of the phenylacetate ion, the consequences of which will be greater in the presence of the doubly charged cadmium ion than in that of the singly charged hydrogen ion.

TABLE I.

Cadmium Salts.

	Formate.		*Acetate.*		*Propionate.*		*Butyrate.*		iso*Butyrate.*		iso*Valerate.*	
x.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.
11·5	4·2	0·46	2·7	0·63	3·7	0·51	3·2	0·57	1·9	0·76	3·5	0·54
14·3	4·6	0·64	3·3	0·81	4·6	0·64	3·7	0·75	2·4	0·97	4·2	0·68
17·0	5·0	0·78	3·6	0·99	5·3	0·75	4·3	0·88	2·8	1·2	4·8	0·83
19·6	5·4	0·91	4·1	1·1	6·0	0·83	4·8	1·0	3·4	1·3	5·4	0·91
22·2	5·8	1·0	4·5	1·2	6·5	0·92	5·4	1·1	4·0	1·3	5·7	1·0
27·3	6·2	1·3	5·4	1·4	8·0	0·99	6·3	1·2	5·2	1·5	6·8	1·2
32·1	6·4	1·5	6·1	1·6	9·2	1·1	7·1	1·4	6·1	1·6	7·5	1·3
41·4	6·8	2·0	7·5	1·8	11·6	1·1	8·6	1·6	8·0	1·7	9·0	1·5
50·0	7·4	2·3	8·7	1·9	13·6	1·1	9·6	1·7	9·8	1·7	10·0	1·6
58·1	7·8	2·5	10·1	1·9	15·2	1·1	10·6	1·8	11·4	1·7	11·2	1·7
72·7	8·4	3·0	12·0	2·0	18·1	1·1	12·6	1·9	13·1	1·8	13·0	1·8
85·7	8·8	3·5	14·1	1·9	20·6	1·0	14·4	1·9	15·0	1·8	14·8	1·8
100·0	10·2	3·5	15·9	1·9	23·0	1·0	16·3	1·9	16·7	1·8	16·8	1·8
123·5	11·4	3·8	18·0	2·0	26·4	0·93	19·1	1·8	19·5	1·7	19·0	1·8
150·0	12·3	4·3	20·3	2·0	30·2	0·83	22·2	1·7	22·5,	1·6	21·6	1·8
180·0	13·0	4·8	22·9	1·9	33·3	0·78	25·0	1·6	26·3	1·4	24·4	1·7
K_{HX}	21×10^{-5}		$1·81 \times 10^{-5}$		$1·32 \times 10^{-5}$		$1·50 \times 10^{-5}$		$1·55 \times 10^{-5}$		$1·68 \times 10^{-5}$	

	Phenylacetate.		*Chloroacetate.*		*Cyanoacetate.*		*Glycollate.*		*Lactate.*		*Pyruvate.*		
x.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	100K_1.	*P.D.*, mv.	10^3K_1.	10^5K_2.
11·5	3·3	0·56	0·4	1·1	4·3	0·45	2·6	0·65	3·0	0·59	1·4	8·5	0·76
14·3	3·9	0·75	0·5	1·5	4·7	0·63	3·4	0·79	3·6	0·70	2·5	9·5	1·9
17·0	4·6	0·87	1·2	1·6	5·7	0·70	4·0	0·93	4·2	0·90	3·6	9·9	3·3
19·6	4·9	1·0	1·3	1·9	6·2	0·80	4·6	1·0	4·6	1·0	4·8	10	4·8
22·2	6·1	0·97	1·5	2·1	6·7	0·89	5·0	1·1	5·2	1·1	5·9	10	6·1
27·3	6·6	1·2	1·7	2·6	7·2	1·1	6·1	1·3	6·1	1·3	7·8	10	9·5
32·1	7·4	1·3	2·0	2·9	7·6	1·3	7·2	1·4	7·0	1·4	10·9	8·6	10
41·4	8·8	1·5	2·3	3·8	8·2	1·6	9·1	1·5	8·4	1·6	16·1	6·8	13
50·0	10·8	1·5	2·8	4·3	8·8	1·9	10·7	1·5	9·8	1·7	21·3	5·3	13
58·1	12·0	1·6	3·2	4·8	9·4	2·1	12·1	1·6	10·9	1·8	26·9	3·8	12
72·7	13·3	1·8	4·0	5·4	10·7	2·3	14·9	1·5	13·2	2·0	35·9	2·3	11
85·7	15·8	1·6	4·7	5·9	11·5	2·5	17·0	1·5	15·0	1·8	42·4	1·6	9·5
100·0	18·0	1·5	5·4	6·3	12·1	2·8	19·2	1·4	17·3	1·7	49·8	1·1	7·7
123·5	21·2	1·5	7·1	6·3	12·8	3·3	22·4	1·3	19·6	1·7	58·8	0·66	6·3
150·0	23·8	1·4	8·2	6·7	14·2	3·5	25·6	1·2	22·7	1·6	66·6	0·44	5·3
180·0	26·9	1·3	9·1	7·4	15·0	3·9	28·7	1·1	25·2	1·6	74·2	0·29	4·4
K_{HX}	$5·45 \times 10^{-5}$		$1·52 \times 10^{-3}$		$3·65 \times 10^{-3}$		$1·49 \times 10^{-4}$		$1·36 \times 10^{-4}$			$3·2 \times 10^{-3}$	

Chloro-, Bromo-, and Iodo-acetate.—The introduction of a chlorine atom into the acetate ion brings about a pronounced decrease in the katiophilic nature of the ion, a result in accord with the strong inductive effect (— *I*) of the chlorine atom. The replacement of chlorine by bromine causes a pronounced increase in the katiophilic property, a result in agreement with the weaker inductive effect of bromine. If chelation occurs, then a factor contributing

TABLE II.

Copper Salts.

	Chloroacetate.		*Bromoacetate.*		*Iodoacetate.*		*Glycollate.*			*Lactate.*		
x.	*P.D.*, mv.	$100K_1$.	*P.D.*, mv.	$100K_1$.	*P.D.*, mv.	$100K_1$.	*P.D.*, mv.	10^4K_1.	10^5K_2.	*P.D.*, mv.	10^3K_1.	10^5K_2.
11·5	3·1	0·62	2·7	0·68	3·0	0·64	9·8	18	—	3·8	5·4	0·056
14·3	3·7	0·79	3·0	0·91	3·5	0·82	12·8	19	—	5·7	5·5	0·35
17·0	3·8	1·0	3·2	1·1	4·8	0·85	15·5	20	0·010	8·0	5·2	0·67
19·6	4·1	1·2	3·6	1·3	5·1	1·0	19·3	17	0·084	9·8	5·1	1·2
22·2	4·7	1·3	4·0	1·4	5·5	1·1	20·8	18	0·30	12·5	4·4	1·4
27·3	5·1	1·6	4·8	1·6	5·1	1·6	25·7	16	0·71	16·4	3·9	2·4
32·1	5·2	1·9	5·4	1·8	5·7	1·7	31·0	13	0·99	18·2	4·1	4·0
41·4	6·6	2·1	7·4	1·9	6·6	2·1	38·2	9·9	1·5	24·4	3·2	5·4
50·0	7·4	2·3	9·8	1·7	7·7	2·3	44·4	7·6	1·7	29·6	2·6	6·2
58·1	8·8	2·3	11·6	1·7	8·3	2·5	47·4	7·1	2·2	33·2	2·3	7·2
72·7	9·4	2·8	15·3	1·5	10·2	2·6	56·8	4·4	1·9	39·8	1·7	7·8
85·7	10·4	3·0	19·2	1·2	11·9	2·5	61·9	3·5	2·0	45·6	1·3	7·5
100·0	11·6	3·1	22·3	1·1	13·9	2·4	68·0	2·6	1·8	50·2	1·1	7·6
123·5	12·9	3·4	27·4	0·88	16·2	2·4	75·6	1·8	1·7	56·7	0·80	7·5
150·0	15·4	3·2	33·5	0·65	19·0	2·3	82·3	1·3	1·6	64·3	0·54	6·5
180·0	16·6	3·5	40·0	0·74	22·5	2·0	90·0	0·84	1·3	72·3	0·34	5·2
K_{HX}	$1·52 \times 10^{-3}$		$1·35 \times 10^{-3}$		$0·71 \times 10^{-3}$		$1·49 \times 10^{-4}$			$1·36 \times 10^{-4}$		

	Pyruvate.					N-*Methylaminoacetate.*				N-*Phenylaminoacetate.*			*Salicylate.**	
x.	*P.D.*, mv.	10^7K_1.	10^8K_2.	$10^{10}K_3$.	$10^{11}K_4$.	*P.D.*, mv.	$10^{10}K_1$.	$10^{12}K_2$.	$10^{13}K_3$.	*P.D.*, mv.	10^6K_1.	10^8K_2.	*P.D.*, mv.	10^2K_1.
11·5	20·3	4000	—	—	—	—	—	—	—	5·8	3590	—	−0·4	3·6
14·3	23·4	5700	—	—	—	—	—	—	—	12·7	2530	—	0·6	3·7
17·0	29·9	5300	—	—	—	—	—	—	—	21·0	1100	—	1·4	3·8
19·6	32·0	5300	1·8	—	—	—	—	—	—	36·3	363	0·34	2·0	4·0
22·2	37·1	4300	28	—	—	—	—	—	—	51·0	136	6·5	3·0	3·9
27·3	46·1	2900	96	—	—	160·0	330	102	—	77·4	23	7·2	4·4	3·9
32·1	59·7	1200	82	0·64	—	175·1	127	84	—	92·0	9·4	6·2	5·6	3·9
41·4	82·9	270	40	13	—	195·1	37	54	1·7	107·5	3·9	5·7	6·8	4·4
50·0	100·7	85	19	17	0·21	208·9	16	35	3·2	114·0	3·0	6·6	8·6	4·3
58·1	117·0	28	8·4	13	0·62	218·3	9·0	27	4·1	121·0	2·0	6·1	9·2	4·8
72·7	136·4	7·8	3·5	9·7	1·4	231·6	4·1	18	5·1	129·5	1·4	6·0	12·6	4·1
85·7	149·8	3·3	1·9	7·4	1·9	241·1	2·3	13	5·3	135·1	1·0	6·0	14·5	4·1
100·0	161·9	1·5	1·1	5·6	2·1	250·3	1·3	9·4	5·1	140·6	0·80	5·7	17·3	3·6
123·5	175·5	0·63	0·60	4·6	2·7	261·2	0·70	6·6	5·1	147·8	0·57	5·4	20·4	3·4
150·0	187·7	0·30	0·36	3·7	3·1	270·9	0·40	4·8	5·0	153·4	0·45	5·5	23·8	3·1
180·0	195·9	0·20	0·28	3·7	4·3	278·3	0·27	4·1	5·4	159·9	0·33	4·9	27·4	2·7
K_{HX}	$3·2 \times 10^{-3}$					—				—			$7·7 \times 10^{-4}$	

* In this titration the molarity of the sodium salt solution was twice that employed in the other titrations.

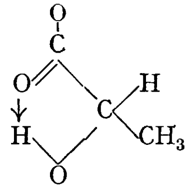
to the above result will be the more highly deformable nature of the bromine atom compared with the chlorine. The replacement of bromine by iodine causes a pronounced decrease in the katiophilic property. This is surprising in view of the stronger protophilic nature of the iodoacetate ion than of the bromo- and the chloro-acetate ion, and of the more highly deformable nature of the iodide ion than of the other halide ions. Accurate results could not be obtained with the cadmium electrode owing to precipitate formation with sodium bromoacetate, and unsteady potentials with sodium iodoacetate. Indications were also obtained, in these titrations, that the iodoacetate was only weakly katiophilic. The cause of this apparently anomalous behaviour of the iodoacetate ion is discussed below.

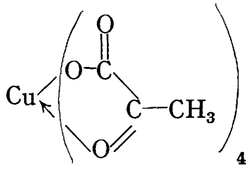
Cyanoacetate.—The results obtained with the copper electrode were somewhat unsteady and are not recorded, but they definitely showed that the cyanoacetate ion is only weakly katiophilic. The cadmium titrations confirm this. In view of the similar result obtained with the iodoacetate ion and of the similarity of the iodide and the cyanide ion, this result is particularly interesting. Both the latter ions are highly deformable, both reduce cupric salts, and both form a large number of stable complex ions. The large decrease of electron-sharing tendencies when these ions are in the combined state in the acetate ion is probably due to the same cause, *viz.*, a predominating electromeric (+ *T*) effect : $\overset{\curvearrowright}{\text{I}}\text{—CH}_2\text{—COO}'$, $\overset{\curvearrowright}{\text{N}}\equiv\text{C—CH}_2\text{—COO}'$.

In order to explain the *m*-directing power of the cyano-group in aromatic substitution and the acidic character of hydrogen cyanide, Baker, Cooper, and Ingold (J., 1928, 426) suggested that it acts as an electron-attracting group by virtue of the tendency of the sextet of electrons in the triple bond to appropriate 2 or 4 electrons to form a stable octet or decet. Many examples are also known in which the electromeric (+ *T*) effect of iodine has a predominating influence upon the behaviour of an organic compound (see "Substitution in Organic Compounds," J., 1933, 1112). There can be little doubt that the katiophilic behaviour of the iodoacetate and the cyanoacetate ion is intimately connected with these phenomena. The cyanoacetate ion is also less protophilic than the acetate.

Glycollate and Lactate.—The substitution of the hydroxyl group in the acetate ion to form the glycollate brings about a slight increase in the katiophilic, and a considerable reduction in the protophilic, property. The similar change from propionate to lactate causes a slight decrease in the katiophilic property and a large decrease in the protophilic. This difference in the effects of hydroxyl substitution on the katiophilic properties of these ions can be accounted for by the formation of an intra-ionically co-ordinated lactate ion (I). The formation of a similarly co-ordinated anion would not occur to the same extent in an aqueous solution of sodium glycollate owing to the absence of the methyl group and a consequent greater distance between the hydroxyl hydrogen and the carboxyl oxygen.

(I.)





(II.)

The K_n values indicate the formation of appreciable amounts of CdX_2 and CuX_2 and CuX_3' with both the glycollate and the lactate ion.

Pyruvate.—The striking features of these results are (*a*) the relatively great katiophilic nature of this anion in spite of its relatively weak protophilic nature, and (*b*) the pronounced tendency for both copper and cadmium to form complex ions with the pyruvate anion. The K_n values clearly indicate the formation of CdX_3' and CuX_4''. Using a copper electrode, a more extended titration was carried out to determine whether or not there was any evidence of the formation of more complex ions, *e.g.*, CuX_5'''. The value of K_4 remained approximately constant until the pyruvate-ion concentration reached $0{\cdot}5M$; at greater concentrations the value diminished, but it would be unwise to draw conclusions from results in such concentrated solutions. There can, however, be little doubt that complex ions of the type CuX_4'' are formed in solution. If each of the pyruvate ions is chelated as in (II), then the copper atom is displaying a co-ordination number of 8, which is contrary to Sidgwick's covalency rule ("Electronic Theory of Valency," 1927, 152). There is a possibility, however, that some or all of the pyruvate ions are attached to the copper by only one valency linkage. This appears to be probable when the results obtained with the aminoacetate ion are considered.

Aminoacetate.—*Maximum co-ordination numbers of copper and cadmium.* The aminoacetate ion possesses very highly developed katiophilic properties (Riley and Gallafent, J., 1931, 2029) and the above method offered a means of determining whether or not copper and cadmium have any decided preference for the 6- and 8-covalent states respectively, as would be anticipated from Sidgwick's covalency rule (*op. cit.*). The results of extended titrations are shown in Table III. Cadmium gives a rapidly decreasing value for K_1, very sharp maxima for K_2 and K_3, and a value of K_4 which is approximately constant over a considerable range of aminoacetate-ion concentration, *viz.*, $0{\cdot}07$—$2M$. The slight decrease in the value of K_4 towards the end of the titration may possibly be due to an increase in the activity coefficient of the aminoacetate at such concentrations. Although the potentials show that copper has a much greater affinity than cadmium for the aminoacetate ion, the trends of the K_n values show very important differences. With copper, K_1 and K_2 diminish rapidly, whilst K_3 remains approximately constant over a surprisingly long range of aminoacetate-ion concentration, *viz.*, $0{\cdot}08$—$1{\cdot}5M$. A comparison of the cadmium and copper K_n values brings out a striking similarity between the K_4 of the former and the K_3 of the latter. If all the aminoacetate ions in the complexes are chelated, this result indicates that, whereas copper has a decided preference for the 6-covalent state,

TABLE III.

Cadmium aminoacetate.						*Copper aminoacetate.*				
x.	*P.D.*, mv.	$10^{12}K_1$.	$10^{11}K_2$.	$10^{11}K_3$.	$10^{11}K_4$.	*x*.	*P.D.*, mv.	$10^{13}K_1$.	$10^{17}K_2$.	$10^{17}K_3$.
11·5	16·5	6·3 × 10^{8}	—	—	—	11·8	24	2·8 × 10^{9}	—	—
14·3	24·2	5·1	—	—	—	17·4	54	6·5 × 10^{8}	—	—
17·0	33·7	3·3	—	—	—	23·0	273	32	220	—
19·6	45·4	1·7	—	—	—	28·6	303	4·2	170	—
22·2	55·6	9·2 × 10^{7}	4100	—	—	34·0	316	1·9	160	0·051
27·3	75·8	2·6	8020	—	—	39·2	321	1·6	200	0·42
32·1	92·6	8·7 × 10^{6}	5900	0·37	—	44·4	332	0·83	130	0·67
41·4	111	2·8	4200	13	0·000035	54·6	344	0·39	100	1·3
50·0	123	1·4	3200	23	0·035	64·2	352	0·25	90	1·8
58·1	130	1·0	3000	46	0·22	82·8	366	0·11	59	2·2
72·7	138	6·7 × 10^{5}	3000	83	1·2	100	375	0·067	47	2·5
85·7	148	3·7	2100	84	2·1	116	382	0·045	39	2·7
100	161	1·6	1100	60	2·3	145	392	0·026	30	2·9
124	186	2·6 × 10^{4}	250	19	1·1	171	399	0·018	25	3·1
150	203	0·89	110	11	0·93	200	401	0·018	30	4·6
180	211	5700	85	11	1·3	227	405	0·015	26	5·2
226	223	2700	53	9·4	1·5	261	412	0·0$_{2}$98	23	4·8
296	239	1000	27	6·6	1·5	296	419	0·0$_{2}$64	17	4·2
364	249	560	19	5·9	1·7	364	429	0·0$_{2}$36	12	3·8
429	257	370	15	5·6	2·0	428	435	0·0$_{2}$26	11	4·0
491	265	220	10	4·6	1·9	552	443	0·0$_{2}$18	9·4	4·7
552	270	160	8·5	4·3	2·1	666	450	0·0$_{2}$13	8·0	4·9
667	279	97	6·2	3·8	2·3	775	458	0·0$_{3}$78	5·8	4·2
774	289	51	3·8	2·7	1·9	969	468	0·0$_{3}$44	4·1	3·8
970	305	19	1·8	1·6	1·5	1143	477	0·0$_{3}$25	2·8	3·1
1143	313	11	1·2	1·4	1·4	1333	484	0·0$_{3}$17	2·2	2·8
1297	320	7·3	0·92	1·2	1·4	1647	496	0·0$_{4}$81	1·3	2·1
1561	329	4·3	0·66	0·99	1·5	2000	506	0·0$_{4}$45	0·88	1·7
1778	338	2·4	0·42	0·73	1·2	2200	511	0·0$_{4}$33	0·72	1·5
2000	344	1·7	0·33	0·65	1·2	2400	517	0·0$_{4}$22	0·53	1·3
2333	355	0·82	0·19	0·43	0·97	2700	524	0·0$_{4}$14	0·39	1·0
2667	364	0·46	0·12	0·32	0·82	3000	531	0·0$_{5}$92	0·27	0·81
3000	373	0·17	0·075	0·22	0·65	3500	544	0·0$_{5}$38	0·13	0·46
3200	377	0·20	0·062	0·20	0·61	4000	552	0·0$_{5}$23	0·092	0·36

under similar conditions cadmium similarly prefers the 8-covalent state, a result which is in accord with the covalency rule. This increase in the covalency maximum with cadmium is not merely a volume effect, for the ionic diameters of copper and cadmium are not greatly different, *viz.*, 1·0 and 1·03 Å. respectively. The greater affinity of copper for the aminoacetate ion, from which one might expect it to co-ordinate with a greater number of aminoacetate ions than cadmium, makes it clear that we must look for an explanation of this difference in the behaviour of copper and cadmium in their electronic structures.

N-*Methyl- and* N-*Phenyl-aminoacetate.*—It has already been shown that α-alkyl substitution makes little or no difference to the katiophilic nature of the aminoacetate ion (Riley and Gallafent, *loc. cit.*), but the results obtained with sarcosine and phenylglycine show that *N*-substitution brings about a pronounced decrease in this property. The K_n values show that there is a pronounced tendency for no more than three *N*-methylaminoacetate ions to co-ordinate with copper, a result similar to that obtained with the aminoacetate ion. The *N*-phenylaminoacetate ion, however, gives a steady value for K_2 over a long range, indicating a preference for the formation of CuX_2. This difference may be due to the larger volume of the latter ion.

Salicylate.—The salicylate K_1 results are remarkably constant over a long range and indicate that the katiophilic properties of this ion are not highly developed, nor is there any great tendency for two salicylate ions to combine with the cupric ion.

Malonate, Succinate, and Adipate.—The results with these ions (see Tables IV and V; also J., 1930, 1642), especially for the malonate, indicate fairly strongly developed katiophilic properties, probably due to the mutual effect of the two carboxyl groups. The K_1 values in each case indicate the formation of appreciable quantities of CdX_2''. The decrease of the tendency in the succinate ion is probably due to the buffering action of the additional methylene group and also to the greater strain in the cadmium succinate chelate ring, whereas the increase in the adipate ion indicates that the cadmium adipate chelate ring is buckled.

Malate, d-*Tartrate, and* meso*Tartrate.*—The introduction of a hydroxyl group into the succinate ion brings about a decided increase in the katiophilic property; that this effect follows that observed in the glycollate, and not that in the lactate, can readily be explained by the valency-deflexion theory. It would be anticipated that a second α′-hydroxy-group would still further increase the katiophilic property; with copper, however, the *d*-tartrate

TABLE IV.

Cadmium Salts.

	Malonate.		*Succinate.*		*Adipate.*		*Malate.*	
x.	*P.D.*, mv.	10^3K_1.	*P.D.*, mv.	10^3K_1.	*P.D.*, mv.	10^3K_1.	*P.D.*, mv.	10^3K_1.
11·5	10·2	1·6	5·5	3·6	7·2	2·6	8·4	2·1
14·3	12·8	1·9	6·6	4·5	8·2	3·5	10·6	2·5
17·0	15·2	2·0	7·7	5·2	9·1	4·2	13·1	2·5
19·6	17·4	2·0	8·9	5·5	10·3	4·6	15·1	2·6
22·2	18·9	2·2	9·8	5·9	11·5	4·8	16·8	2·7
27·3	22·3	2·1	11·7	6·3	13·7	5·1	19·5	2·8
32·1	24·8	2·2	13·4	7·5	15·5	5·2	22·1	2·8
41·4	29·5	2·0	16·5	6·6	19·7	4·8	26·7	2·6
50·0	32·8	1·9	19·0	6·5	21·5	5·2	31·1	2·2
58·1	36·2	1·7	21·4	6·2	24·1	4·9	33·4	2·2
72·7	39·6	1·7	25·2	5·8	28·0	4·5	37·7	2·0
85·7	42·5	1·6	27·5	5·7	30·7	4·3	41·3	1·8
100·0	45·2	1·6	30·3	5·3	34·0	3·9	44·2	1·7
123·5	49·2	1·4	34·0	4·9	38·4	3·4	48·7	1·5
150·0	52·9	1·3	37·3	4·6	42·5	3·0	53·2	1·3
180·0	56·1	1·2	40·9	4·2	46·5	2·6	56·9	1·2

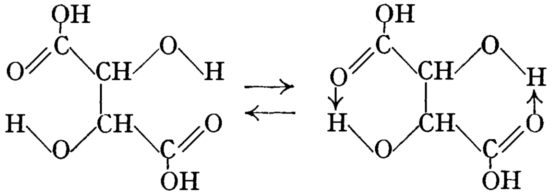
	Maleate.		*Citraconate.*		*Mesaconate.*		*Citrate.*		
x.	*P.D.*, mv.	10^3K_1.	*P.D.*, mv.	10^3K_1.	*P.D.*, mv.	10^3K_1.	*P.D.*, mv.	10^5K_1.	10^7K_2.
11·5	11·6	1·3	17·4	0·56	4·2	4·6	28	15	—
14·3	15·4	1·1	21·0	0·72	4·7	6·3	39	13	—
17·0	18·4	1·4	25·0	0·72	5·2	7·6	48	9·8	—
19·6	21·0	1·4	28·0	0·73	5·7	8·7	53	8·9	—
22·2	22·8	1·5	30·5	0·74	6·2	9·6	59	7·0	0·31
27·3	24·0	1·8	34·2	0·75	7·0	11	66	5·6	1·7
32·1	27·8	1·7	38·5	0·67	7·8	13	73	4·1	2·7
41·4	32·4	1·6	43·3	0·64	9·0	15	79	3·6	5·3
50·0	35·4	1·6	47·9	0·56	10·0	16	83	3·4	7·6
58·1	39·8	1·3	51·0	0·52	10·8	18	91	2·2	6·5
72·7	44·6	1·1	56·0	0·46	12·9	18	102	1·2	5·2
85·7	48·2	1·0	59·6	0·42	14·4	19	107	0·95	5·4
100·0	51·0	0·98	63·4	0·36	17·6	16	112	0·76	5·4
123·5	55·0	0·89	67·7	0·32	20·6	16	117	0·66	5·1
150·0	58·4	0·84	72·4	0·28	24·6	13	128	0·33	4·0
180·0	59·8	0·91	76·5	0·24	29·0	11	138	0·19	2·8

TABLE V.

Copper Salts.

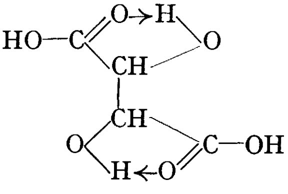
	Malate.		d-*Tartrate.*		meso-*Tartrate.*			*Phthalate.*			*Citrate.*		
x.	*P.D.*, mv.	10^5K_1.	*P.D.*, mv.	10^5K_1.	*P.D.*, mv.	10^5K_1.	10^7K_2.	*P.D.*, mv.	10^3K_1.	10^4K_2.	*P.D.*, mv.	10^9K_1.	$10^{11}K_2$.
11·5	29·3	14	39·8	4·9	26·1	20	—	0·6	11	0·18	73·4	2800	—
14·3	40·8	12	52·1	4·5	38·5	14	—	3·8	7·8	0·11	115·4	280	—
17·0	50·4	8·3	59·5	4·0	51·6	7·5	—	5·3	7·8	0·20	147·8	35	—
19·6	58·4	5·9	63·5	3·9	60·9	4·8	—	7·9	6·6	0·20	166·5	11	—
22·2	63·8	4·9	66·1	4·0	65·5	4·3	0·18	8·7	7·1	0·33	179·9	4·8	0·19
27·3	75·3	2·8	70·8	4·0	76·4	2·5	0·78	11·7	6·5	0·50	196·3	1·9	0·57
32·1	82·3	2·0	74·4	3·8	84·0	1·8	1·1	13·5	6·7	0·74	205·4	1·2	0·76
41·4	91·1	1·4	79·8	3·5	94·8	1·1	1·6	19·6	5·0	0·89	216·4	0·68	0·99
50·0	99·0	0·97	83·6	3·2	102·0	0·76	1·7	26·1	3·5	0·86	222·9	0·52	1·2
58·1	104·2	0·77	85·1	3·5	106·0	0·67	2·0	31·7	2·6	0·82	228·0	0·42	1·3
72·7	111·8	0·55	90·1	3·1	112·5	0·52	2·3	36·2	2·3	1·05	234·0	0·34	1·5
85·7	116·2	0·47	93·5	2·8	118·0	0·41	2·3	41·8	1·8	1·01	237·4	0·31	1·8
100·0	120·4	0·40	95·9	2·8	122·4	0·34	2·4	47·1	1·4	0·98	240·2	0·30	2·1
123·5	126·1	0·32	99·9	2·6	128·4	0·27	2·5	52·4	1·1	1·07	243·4	0·29	2·7
150·0	131·1	0·27	104·3	2·2	134·5	0·20	2·4	59·6	0·78	0·94	246·1	0·29	3·5
180·0	133·7	0·26	105·8	2·4	140·3	0·16	2·3	65·1	0·61	0·92	249·4	0·27	4·0

ion is decidedly less katiophilic than that of the malate (see Table V). The *meso*tartrate is decidedly more katiophilic than the *d*-tartrate and slightly more than the malate. The behaviour of the *d*-tartrate and the *meso*tartrate ions suggests the existence of the following equilibrium in solution :



(III.)

or

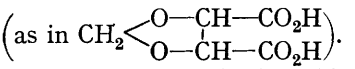


(IV.)

Although it is possible that both (III) and (IV) are present, the stronger katiophilic nature of the *meso*tartrate ion indicates that (III) is present in predominating amount; were this not so, there is no apparent reason why the *meso*tartrate should be more katiophilic than the *d*-tartrate ion. The existence of (III) explains this behaviour, for in the position of minimum potential energy, the α-carboxyl and hydroxyl groups are much nearer to the α′-hydroxyl and carboxyl groups respectively in the *d*-tartrate ion than in the *meso*tartrate.

The above view is supported by the work of Wolf (*Trans. Faraday Soc.*, 1930, **26**, 315, 351; " The Structure of Molecules," Blackie, 1932), who has shown that ethyl *meso*tartrate has a greater dipole moment ($3{\cdot}66 \times 10^{-18}$ e.s.u.) than ethyl *d*-tartrate ($3{\cdot}10 \times 10^{-18}$), which he explains by the restriction of free rotation, due to intramolecular forces.

It is of interest that Lowry and Austin (*Nature*, 1924, **114**, 430) suggested the existence of (III) or (IV) in order to explain the anomalous rotatory dispersion of tartaric acid and the fact that this is not removed on esterification but is on etherification



$\left(\text{as in } CH_2\!<\!\begin{matrix}O—CH—CO_2H\\ |\\ O—CH—CO_2H\end{matrix}\right)$. This view, however, was recently modified (Jones, J., 1933, 788) on the grounds that this type of co-ordination is impossible in such derivatives as diacetyltartaric esters, which also display anomalous rotatory dispersion. Whatever be the ultimate explanation of these phenomena, it appears probable that all three, anomalous rotatory dispersion, dipole moment, and katiophilic properties, are intimately connected.

Maleate.—The introduction of a double bond into the succinate ion brings about a very decided increase in the katiophilic property, in spite of the carboxyl groups being further apart, indicating a very pronounced polar effect. Unfortunately, the sparing solubility of cadmium fumarate prevented a very interesting comparison. This, however, proved possible with the higher homologues.

Citraconate and Mesaconate.—That the citraconate ion is more katiophilic than the maleate can be explained by valency deflexion. The very pronounced difference in the katiophilic properties of the citraconate and the mesaconate ion is interesting; in fact, provided suitably soluble compounds were available, this method could be adapted for the determination of the configuration of *cis*- and *trans*-isomerides. The katiophilic property of the mesaconate ion is only slightly greater than that of the acetate ion. This is noteworthy, in view of the presence of an additional carboxyl group and a double bond in the mesaconate ion.

Phthalate.—The copper phthalate titration shows that the phthalate ion has a strong katiophilic nature, and provides evidence of the formation of complex ions of the type CuX_2''.

Citrate.—The citrate ion co-ordinates with copper much more readily than with cadmium, but the latter shows a very pronounced maximum value of K_2 at a citrate-ion concentration of $0{\cdot}05M$, whereas no such maximum value of K_2 is shown with copper over the whole range of citrate-ion concentration, *i.e.*, up to $0{\cdot}18M$. This indicates that, although copper has a much greater affinity than cadmium for the citrate ion, yet it shows little tendency to co-ordinate with more than two citrate ions, whereas the cadmium ion gives evidence of combining with three citrate ions. These observations are interesting in view of the covalency rule, and should be compared with the aminoacetate results (*vide supra*).