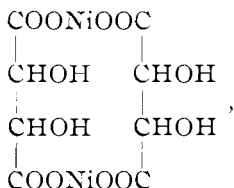


ON THE CONSTITUTION OF CERTAIN ORGANIC SALTS OF NICKEL AND COBALT AS THEY EXIST IN AQUEOUS SOLUTION.¹

BY O. F. TOWER.

Received July 2, 1902.

It has been shown in a former paper that the molecular conductivities of aqueous solutions of nickel and cobalt tartrates are exceptionally small, and furthermore that the apparent molecular weights derived from the freezing-point method considerably exceed the molecular weights calculated from the simple formulas of the salts.² It was suggested that these unusual results could be accounted for on the assumption of polymerization. The formula.



was given as expressing possibly the constitution of a molecule of nickel tartrate. Such a molecule would very likely be much less dissociated in solution than a simple molecule. In order to investigate this problem more fully these same methods have been applied to the tartrates of other metals and to the nickel, cobalt, and magnesium salts of certain other organic acids.

These salts were prepared from pure chemicals of standard make. The solutions were made by treating an excess of the carbonate or oxide of the metal with a sufficiently dilute solution of the acid. In a few instances the hydroxide of the metal was employed. On account of the slight solubility of most of these organic salts, the quantity of salt in solution after the acid had become neutralized was almost never equivalent to the quantity of acid taken, because some of the salt was precipitated while the action was going on. It was therefore necessary to determine the amount of salt actually present in the solution in each case. The temperature of the solution has considerable effect on the solubility

¹ Read at the Pittsburg meeting of the American Chemical Society.

² Tower: This Journal, **22**, 501 (1900).

of these salts. This effect has already been described for nickel and cobalt tartrates,¹ and is similar for the other salts used, although in most cases less pronounced. Heat seemed to decrease the solubility, so that all solutions were made up in the cold or at a temperature not exceeding 50°. The action of the dilute acids was very slow at these low temperatures. To accelerate it the solution was constantly shaken until the reaction was neutral. This required only about fifteen minutes with magnesia and the freshly precipitated hydroxides of nickel and cobalt, while for the carbonates of nickel and cobalt an hour or more was frequently necessary. Solutions of barium tartrate were prepared by neutralizing a solution of barium hydroxide with tartaric acid. Solutions containing more than 1 gram-molecule of barium tartrate in 80 liters were supersaturated. Measurements with these supersaturated solutions revealed no abnormal behavior, which is also the experience of others. Attempts were made to prepare solutions of calcium and zinc tartrates. These salts are, however, so insoluble that the solutions obtained were too weak to render the measurements of any value for the purpose of comparison.

The measurements of the electrical conductivity of the tartrates reported in my former article were made with a small combination Wheatstone-Kohlrausch bridge only 25 cm. long. All the measurements which follow were made with a meter bridge, which had been carefully calibrated. The conductivities of the tartrates of nickel and cobalt were therefore redetermined with the new apparatus. The temperature at which all the determinations were made was $18^{\circ} \pm 0.1^{\circ}$. The conductivity of the water used varied from 2.0 to 3.0×10^{-6} . This has been deducted from the specific conductivity in every case. The results with the salts of tartaric, malic and succinic acids are given in Table I: v is the number of liters in which a gram-molecule of the salt was dissolved; M is the molecular conductivity in reciprocal ohms. In the former article the equivalent conductivity was given, but since some of the salts probably exist in a polymerized condition, the molecular conductivity is given as affording a better basis of comparison.

¹ Tower: *loc. cit.*, pp. 504 and 515.

TABLE I.

Nickel tartrate.				Cobalt tartrate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
10.35	9.2	13.46	12.0	25.38	25.4	31.05	32.2
2 × 10.35	13.8	2 × 13.46	16.4	2 × 25.38	34.5	2 × 31.05	43.0
4 × 10.35	20.7	4 × 13.46	22.7	4 × 25.38	47.4	4 × 31.05	57.1
8 × 10.35	30.6	8 × 13.46	29.8	8 × 25.38	63.5	8 × 31.05	74.4
16 × 10.35	44.4	16 × 13.46	45.0	16 × 25.38	83.2	16 × 31.05	96.0
32 × 10.35	62.8	32 × 13.46	61.2	32 × 25.38	105.6	32 × 31.05	120.6
64 × 10.35	81.5	64 × 13.46	81.3	64 × 25.38	133.0	64 × 31.05	150.2
Magnesium tartrate.				Barium tartrate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
19.95	67.4	24.37	71.9	20.03	58.5	21.27	59.3
2 × 19.95	82.0	2 × 24.37	87.7	2 × 20.03	70.4	2 × 21.27	72.8
4 × 19.95	98.1	4 × 24.37	103.0	4 × 20.03	85.2	4 × 21.27	88.6
8 × 19.95	114.6	8 × 24.37	119.2	8 × 20.03	105.1	8 × 21.27	106.4
16 × 19.95	130.5	16 × 24.37	135.1	16 × 20.03	125.6	16 × 21.27	126.5
32 × 19.95	145.8	32 × 24.37	150.0	32 × 20.03	143.0	32 × 21.27	147.3
64 × 19.95	160.7	64 × 24.37	165.9	64 × 20.03	161.4	64 × 21.27	167.1
Manganese tartrate.				Nickel malate. ¹		Cobalt malate.	
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
37.79	66.9	41.71	68.8	14.77	14.5	18.44	23.6
2 × 37.79	81.5	2 × 41.71	83.8	2 × 14.77	17.7	2 × 18.44	28.8
4 × 37.79	98.5	4 × 41.71	99.7	4 × 14.77	22.0	4 × 18.44	36.0
8 × 37.79	114.5	8 × 41.71	117.0	8 × 14.77	28.2	8 × 18.44	45.2
16 × 37.79	132.5	16 × 41.71	133.5	16 × 14.77	37.1	16 × 18.44	58.1
32 × 37.79	148.3	32 × 41.71	148.9	32 × 14.77	51.0	32 × 18.44	74.6
				64 × 14.77	69.9	64 × 18.44	94.3
Magnesium malate.				Nickel succinate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
9.74	43.3	18.42	62.2	19.57	62.7		
2 × 9.74	54.7	2 × 18.42	75.9	2 × 19.57	76.9		
4 × 9.74	67.4	4 × 18.42	91.7	4 × 19.57	92.5		
8 × 9.74	83.0	8 × 18.42	108.8	8 × 19.57	109.5		
16 × 9.74	100.1	16 × 18.42	125.9	16 × 19.57	126.6		
32 × 9.74	118.3	32 × 18.42	143.0	32 × 19.57	145.2		
64 × 9.74	135.0	64 × 18.42	158.4	64 × 19.57	160.3		
128 × 9.74	149.0						
Cobalt succinate.				Magnesium succinate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
17.29	65.0	20.25	68.2	14.31	76.6	15.70	77.6
2 × 17.29	78.3	2 × 20.25	82.2	2 × 14.31	88.7	2 × 15.70	90.0
4 × 17.29	93.0	4 × 20.25	97.1	4 × 14.31	102.8	4 × 15.70	104.2
8 × 17.29	109.7	8 × 20.25	113.6	8 × 14.31	117.4	8 × 15.70	119.8
16 × 17.29	126.6	16 × 20.25	130.2	16 × 14.31	131.9	16 × 15.70	134.6
32 × 17.29	145.0	32 × 20.25	148.0	32 × 14.31	146.2	32 × 15.70	149.0
64 × 17.29	159.0	64 × 20.25	162.3	64 × 14.31	158.8	64 × 15.70	160.8

¹ Only one solution of each salt of malic acid could be prepared with the small quantity of this acid on hand.

From these results interpolations have been made graphically for $v = 16, 32$, etc., by plotting curves with the molecular conductivities as abscissas and the logarithms (base 2) of the dilutions, v , as ordinates. The interpolated values are given in Table II. In cases where the conductivity was determined in two separate solutions only the average is given in the table. The results of Walden¹ for magnesium salts of these acids are given for comparison. They have been reduced to the same units and temperature. The temperature coefficient used for this purpose was 0.027, the average value found by Arrhenius² for sodium salts of organic acids.

TABLE II.
Molecular conductivity of tartrates.

v .	Nickel.	Cobalt.	Magnesium.	Magnesium.	Barium.	Manganese.
			(Walden.)	(Walden.)		
16	12.3	63.0
32	18.1	30.5	77.5	66.8	63.2
64	25.8	41.1	93.0	92.3	81.2	78.0
128	37.1	55.5	109.8	107.8	98.5	94.2
256	52.0	72.4	125.5	124.5	117.3	110.7
512	70.4	94.2	140.8	138.9	136.2	127.1
1024	93.0	118.0	156.0	151.5	155.0	143.9

Molecular conductivity of malates.

v .	Nickel.	Cobalt.	Magnesium.	Magnesium.
			(Walden.)	(Walden.)
16	14.8	22.8	51.1
32	18.1	27.8	63.6
64	22.6	34.2	78.2	80.9
128	29.3	43.0	95.0	96.9
256	38.5	55.2	113.4	113.9
512	53.0	70.7	129.2	130.5
1024	72.3	90.3	146.0	145.1

Molecular conductivity of succinates.

v .	Nickel.	Cobalt.	Magnesium.	Magnesium.
			(Walden.)	(Walden.)
16	59.5	63.7	78.2
32	73.0	76.8	90.7
64	88.0	91.2	104.8	106.8
128	105.2	107.9	120.2	121.6
256	122.3	124.6	134.7	135.6
512	139.7	142.4	148.9	147.8
1024	155.6	157.5	160.8	158.6

¹ *Ztschr. phys. Chem.*, **11**, 537 (1887).

² *Ibid.*, **4**, 99 (1889).

The molecular conductivities of the tartrates of magnesium, barium and manganese do not vary from one another more than may be expected for different salts of the same acid. The conductivities of the tartrates of nickel and cobalt are, however, so small as to be of an entirely different order. The same is true of the conductivities of the malates of nickel and cobalt. The conductivity of magnesium malate is somewhat less than that of the tartrate, as was also observed by Walden. The conductivities of the succinates of nickel and cobalt present no abnormal behavior when compared with the conductivity of magnesium succinate.

Determinations of the lowering of the freezing-point were made with the apparatus described in my former article. Determinations of the freezing-point of the same solution never varied more than 0.001° , but the freezing-points of two solutions made up as nearly alike as possible gave larger differences. Since the solutions used were rather dilute, a difference of two or three thousandths of a degree would frequently make a difference of ten or twenty units in the molecular weights calculated from them. So much reliance cannot therefore be placed on the absolute or on the relative value of the results obtained by this method, as on those obtained by measuring the electrical conductivity. The depressions of the freezing-point together with the apparent molecular weights calculated from them are given in Table III.

TABLE III.

Nickel tartrate.			Cobalt tartrate.		
Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.	Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
1.8795	0.139°	260	0.6739	0.062°	207
1.7205	0.121	273	0.6505	0.059	207
1.6450	0.117	268	0.3370	0.037	173
0.8602	0.081	202	0.3252	0.036	170
0.8225	0.076	206	0.1685	0.021	153
0.4301	0.042	193	0.1626	0.021	146
Magnesium tartrate.			Barium tartrate.		
0.8642	0.139°	118	0.7136	0.063°	216
0.8428	0.137	117	0.3568	0.036	189
0.4321	0.079	104	0.3568	0.039	174
0.4214	0.076	106	0.1784	0.020	170
0.2160	0.045	91	0.1784	0.021	162
Manganese tartrate.			Nickel malate.		
0.6130	0.083°	141	1.2912	0.147°	167

Manganese tartrate.			Nickel malate.		
Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.	Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
0.5805	0.078°	142	0.6456	0.086°	143
0.3075	0.046	127	0.3228	0.050	123
0.2902	0.041	135			
Cobalt malate.			Magnesium malate.		
1.0360	0.114°	173	1.6060	0.244°	125
0.5180	0.068	144	0.8030	0.130	118
0.2590	0.040	123	0.4015	0.079	97
Nickel succinate.			Cobalt succinate.		
0.9488	0.169°	107	1.0125	0.176°	110
0.8931	0.160	106	0.8646	0.156	106
0.4744	0.095	95	0.5062	0.094	103
0.4466	0.082	104	0.4323	0.084	98
0.2233	0.049	87	0.2531	0.057	85
Magnesium succinate.					
0.9808	0.207°	90			
0.8942	0.185	81			
0.4904	0.115	81			
0.4471	0.098	76			
0.2452	0.065	72			

In order to render these results more readily comparable, by means of graphical interpolation the molecular weights have been calculated for dilutions of 16 and 32 liters. These figures together with the molecular weights calculated from the simple formulas of the respective salts are given in Table IV.

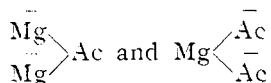
TABLE IV.

	Tartrates.					Malates.			Succinates.		
	Nickel.	Cobalt.	Magnesium.	Barium.	Manganese.	Nickel.	Cobalt.	Magnesium.	Nickel.	Cobalt.	Magnesium.
Mol. wt. from formula	207	207	172	286	203	191	191	156	175	175	140
Values interpolated from Table III	$\left\{ \begin{array}{l} v = 16 \dots 230 \quad 244 \quad 122 \quad \dots \quad \dots \quad 164 \quad 179 \quad 120 \quad 108 \quad 111 \quad 82 \\ v = 32 \dots 196 \quad 207 \quad 109 \quad 234 \quad 143 \quad 140 \quad 150 \quad 100 \quad 100 \quad 103 \quad 77 \end{array} \right.$										

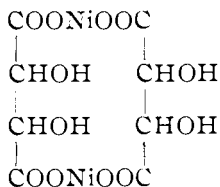
From this table it is seen that all the salts yield in the more concentrated solutions apparent molecular weights considerably less than the molecular weights calculated from the formula, except the tartrates and possibly the malates of nickel and cobalt. According to the dissociation theory we should expect all of the salts in solutions of this concentration to give apparent molecular

weights much less than the true ones. The nickel and cobalt salts just mentioned, which give such high molecular weights, are the ones calling for special explanation. These exceptional results yielded by the freezing-point method are, however, in line with the conductivity determinations with the same salts.

An adequate explanation of this peculiar behavior of the tartrates and malates of nickel and cobalt is difficult to find. It was Walden¹ who first pointed out, working with magnesium salts, that the dissociation of the salts of dibasic acids with bivalent metals as measured by the conductivity was of a very different nature from the dissociation of the neutral sodium salts of the same acids. Bredig² has attempted to explain this difference on the assumption that the molecules of a salt, $MgAc$ (Ac being the radical of a dibasic acid), split up into complex ions of the nature



as well as the simpler ones \overline{Mg} and \overline{Ac} . As the dilution increases the complex ions gradually tend to decompose into the simpler ones. The behavior of nickel and cobalt tartrates and malates has been shown to be very different from that of the magnesium salts of the same metals. The suggestion was made in the article to which reference has already been made, that the abnormal behavior of the tartrates of nickel and cobalt might be ascribed to polymerization of the molecules. The same would also apply to the malates. The molecule of nickel tartrate, for example, in solution would have the formula



and would be dissociated in concentrated solutions into complex ions and as dilution proceeds into simpler ones in a manner similar to that indicated above for magnesium salts, the dissociation, how-

¹ *Loc. cit.*, p. 529, *et seq.*

² *Ztschr. phys. Chem.*, **13**, 202 (1894).

ever, being much less. This explanation differs from that of Bredig for magnesium salts in assuming the existence of *double molecules* in solution as well as of complex ions, and seems to have support in the apparent molecular weights derived from the freezing-point method.

The application of Ostwald's formula for basicity, as developed by Walden¹ for dibasic salts of bivalent metals, throws but little light on this question. The formula is $\Delta = Cn_1n_2$, where Δ is the difference between the *equivalent* conductivities at $v = 32$ and $v = 1024$, n_1 is the basicity of the acid radical, n_2 is the valence of the metal, and C is a constant, equal usually to 10 or a little less. Only molecular conductivities are given in Table II so that the difference between the values at $v = 32$ and $v = 1024$ must be divided by two to make it comparable with the difference obtained with equivalent conductivities. When this is carried out for the nickel and cobalt salts the basicity is found to be two, just the same as when applied to the magnesium salts. Since, however, the formula is wholly empirical, the results obtained by using it cannot be accepted without other support in the face of the values derived by the freezing-point method. If the Ostwald rule shows anything in this instance, it is rather to be interpreted as indicating that the complex ions decompose but little below the dilution, 1024.²

If then the tartrates and malates of nickel and cobalt are polymerized in aqueous solution, the molecules of the succinates are surely not, for their conductivities are normal and the apparent molecular weights found by the freezing-point method also preclude any such condition. This seems to show that the presence of the hydroxyl groups in the tartaric and malic acids may have some influence in inducing polymerization of the nickel and cobalt salts. There appears to be ground for this in the fact that the results obtained with the tartrates reveal a greater degree of polymerization than those with the malates; that is, the polymerizing influence is apparently greater where two hydroxyl groups are present than where only one is present.

¹ *Loc. cit.*

² From the electromotive force of a cell containing a $\frac{1}{50}$ molecular solution of nickel tartrate only about one-tenth of the nickel was found to exist in the ionic state. Tower: *Loc. cit.*, p. 511.

That the presence of an hydroxyl group is the determining influence in causing polymerization of the nickel and cobalt salts receives, however, no support from the results obtained by applying methods similar to the above to the malonates and tartronates of nickel and cobalt. Conductivity and freezing-point determinations were carried out with these salts and also with the magnesium salts of the same acids. The malonic acid was a preparation of Merck. The tartronic acid was made from dinitrotartaric acid according to Demole.¹ The yield was small, which accounts for only one set of determinations having been made. Molecular conductivities are given in Table V, and depressions of the freezing-point in Table VI.

TABLE V.

Nickel malonate.				Cobalt malonate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
15.61	23.7	20.55	23.3	12.82	28.5	19.17	30.6
2 × 15.61	27.3	2 × 20.55	26.9	2 × 12.82	33.2	2 × 19.17	35.7
4 × 15.61	32.1	4 × 20.55	31.8	4 × 12.82	39.6	4 × 19.17	42.4
8 × 15.61	39.9	8 × 20.55	39.0	8 × 12.82	48.6	8 × 19.17	52.3
16 × 15.61	49.4	16 × 20.55	49.5	16 × 12.82	61.1	16 × 19.17	64.9
32 × 15.61	64.0	32 × 20.55	64.0	32 × 12.82	78.4	32 × 19.17	81.5
64 × 15.61	80.2			64 × 12.82	96.0		
Magnesium malonate.				Nickel tartronate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
8.02	34.6	11.00	38.2	30.50	29.7		
2 × 8.02	42.7	2 × 11.00	47.1	2 × 30.50	34.7		
4 × 8.02	51.7	4 × 11.00	59.2	4 × 30.50	40.3		
8 × 8.02	64.7	8 × 11.00	73.2	8 × 30.50	46.9		
16 × 8.02	77.5	16 × 11.00	88.7	16 × 30.50	54.5		
32 × 8.02	93.8	32 × 11.00	106.9	32 × 30.50	63.8		
64 × 8.02	110.9	64 × 11.00	126.8				
Cobalt tartronate.				Magnesium tartronate.			
<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>	<i>v.</i>	<i>M.</i>
28.10	36.5	15.77	42.0				
2 × 28.10	43.3	2 × 15.77	51.3				
4 × 28.10	50.6	4 × 15.77	61.9				
8 × 28.10	58.7	8 × 15.77	74.8				
16 × 28.10	68.5	16 × 15.77	89.2				
32 × 28.10	79.4	32 × 15.77	105.7				
		64 × 15.77	122.5				

¹ *Ber. d. chem. Ges.*, 10, 1789 (1877).

TABLE VI.

Nickel malonate.			Cobalt malonate.		
Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.	Substance in 100 cc. Grams.	Depression.	Apparent mol. wt.
1.0300	0.150°	131	1.1995	0.201°	114
0.7824	0.141	106	0.8402	0.169	95
0.5150	0.090	109	0.5998	0.115	99
0.2575	0.054	91	0.2999	0.066	86
Magnesium malonate.			Nickel tartronate.		
1.5750	0.298	101	0.5798	0.102	108
1.1477	0.233	94	0.2899	0.065	85
0.5738	0.134	82	0.1450	0.039	71
0.2869	0.075	73			
Cobalt tartronate.			Magnesium tartronate.		
0.6302	0.119	101	0.9944	0.200	95
0.3151	0.071	85	0.4972	0.121	78
0.1576	0.043	70	0.2486	0.072	66

To bring the results of these two tables to a uniform basis, interpolations have been made graphically, exactly as in the preceding cases. These interpolated values will be found in Tables VII and VIII.

TABLE VII.

<i>v</i> .	Molecular conductivity.						
	Malonates.			Tartronates.			
	Nickel.	Cobalt.	Magne- sium.	Magnesium. (Walden.)	Nickel.	Cobalt.	Magne- sium.
16.....	23.0	30.0	43.0	25.5	32.0	42.3
32.....	26.5	34.7	52.6	29.9	37.8	51.5
64.....	31.2	41.2	65.7	62.9	35.1	44.7	62.4
128.....	38.2	51.2	79.5	77.5	40.8	52.2	75.3
256.....	47.8	64.0	95.9	95.4	47.3	60.3	89.9
512.....	61.4	80.4	113.9	114.7	59.2	70.4	106.3
1024.....	77.2	99.3	135.0	134.9	64.3	81.2	123.0

TABLE VIII.

	Malonates.			Tartronates.				
	Nickel.	Cobalt.	Magne- sium.	Nickel.	Cobalt.	Magne- sium.		
Molecular weight from formula....	161	161	126	177	177	142		
Values interpolated	{	<i>v</i> = 16.....	121	104	87	94
from Table V.		<i>v</i> = 32.....	101	91	77	106	98	77

It is seen in these cases as heretofore, that the nickel and cobalt salts possess lower molecular conductivities and higher apparent molecular weights than the corresponding magnesium salts. Al-

though the conductivities of all these salts are less than for the corresponding succinates, still the relative differences between the conductivities of the nickel, cobalt, and magnesium salts are about the same as in the case of the succinates. No such differences exist, as were found between the conductivities of the tartrates and malates of magnesium and those of the corresponding nickel and cobalt salts. The conductivities of the magnesium salts of malonic and tartronic acids are considerably less than the conductivities of any of the other magnesium salts investigated. This was noticed by Walden in the case of the malonate. Bredig's explanation of such behavior has already been referred to. The important point to notice in connection with these last results is, however, that the conductivities of the nickel and cobalt tartronates are not appreciably less than the conductivities of the same malonates, although tartronic acid possesses an hydroxyl group. Any explanation of the conduct of these salts based on the presence of an hydroxyl group in the molecule, therefore, appears to be untenable.

Before letting the question rest here, however, a few considerations bearing upon the point under discussion will be mentioned. The strength of the acids of the succinic acid series (*i. e.*, succinic, malic, and tartaric acids), as is well known, increases with the number of hydroxyl groups present, Ostwald's affinity constants being for succinic acid 0.0066, for malic acid 0.0395, for tartaric acid 0.097.¹ The hydroxyl groups have therefore a distinct effect on the strength of the acids. In the case of malonic and tartronic acids a very different effect is observed. The Ostwald constant for malonic acid is 0.158 and for tartronic acid 0.107; that is, the introduction of an hydroxyl group has here decreased the strength of the acid. Such being the facts with regard to the acids, it seems probable that salts of the succinic acid series might show very different gradations in properties from the same salts of the malonic acid series. Then before asserting that the presence of the hydroxyl groups in malic and tartaric acids has no effect on the behavior of their nickel and cobalt salts, it is necessary to extend investigations similar to these to the salts of the glutaric acid series or some higher one. Such work is contemplated in the future.

¹ The values given are for $K = 1000$. See *Zschr. phys. Chem.*, **3**, 418 (1889).

In conclusion, however, it may be stated that aqueous solutions of nickel and cobalt salts of dibasic organic acids offer greater resistance to the passage of the electric current than solutions of similar salts of the other metals investigated, notably magnesium, and that this resistance is exceptionally great in the case of the tartrates and malates of nickel and cobalt. This abnormal behavior of the last-named salts is also confirmed by the results obtained with the freezing-point method for determining molecular weights.

WESTERN RESERVE UNIVERSITY,
CLEVELAND, O., June, 1902.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 69.]

ON THE MANGANESE FERROCYANIDES.

BY ALBERT ERNEST DICKIE.

Received August 7, 1902.

THIS work was undertaken to throw further light on the composition of the manganese ferrocyanides as seemed warranted by the discrepancies in the results obtained previously by Wyruboff,¹ Stone and Van Ingen,² and Miller and Mathews.³

Wyruboff, by precipitating a manganous salt with potassium ferrocyanide, obtained a compound to which he ascribes the formula $5\text{Mn}_2\text{Fe}(\text{CN})_6 \cdot 4\text{K}_4\text{Fe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$, and by using hydroferrocyanic acid he obtained the normal manganese ferrocyanide $\text{Mn}_2\text{Fe}(\text{CN})_6 \cdot 7\text{H}_2\text{O}$. In either case he found it to be immaterial which reagent was used in excess.

Stone and Van Ingen obtained results expressed in atomic ratios as follows:

	Mn.	Fe.
In neutral solution, excess ferrocyanide.....	93	: 100
“ “ “ “ manganese	95	: 100
“ “ “ “ “ hot	92	: 100
“ faintly acid solution, excess manganese.....	101	: 100
“ more “ “ “ “	133	: 100
“ “ “ “ “ hot.....	107	: 100

¹ *Ann. chim. phys.*, [5], 8, 474.

² This Journal, 19, 542.

³ *Ibid.*, p. 547.