CXXXIV.—*The Constitution of the Nitroprussides. Part I. Conductivity and Cryoscopic Measurements.*

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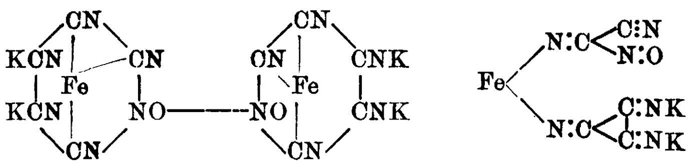
From time to time, the nitroprussides have been made the subject of considerable speculation, but little attempt has been made to verify experimentally the various constitutions assigned to them.

Hofmann, who is responsible for most of the experimental work in this field (*Annalen*, 1900, **312**, 1), assigned to sodium nitroprusside the co-ordination formula $[Fe(CN)_5NO]Na_2$. Friend (T., 1916, **109**, 721), apparently without further experimental work, proposed for potassium nitroprusside the formula (I).



(I.) (II.)

This formula corresponds with the empirical one given in works of reference (for example, Moissan, "Traité de chimie minérale," 1905, 417), which formula, however, seems never to have had any evidence in its favour.

Friend at the same time rejected the formula (II) suggested by Browning (T., 1900, **77**, 1238) for potassium nitroprusside, in view of his theory as to the constitution of the ferrocyanides, which theory has since been shown to be unnecessary (Bennett, T., 1917, **111**, 490).

It was suggested by one of us (T., 1916, **109**, 1130) that a determination of the molecular weights of some nitroprussides would throw light on the problem, and, as a result, a number of nitroprussides have been prepared and investigated cryoscopically and their conductivities measured. From the results so obtained, the number of ions present in a solution of a nitroprusside has been calculated, and conclusions have been drawn as to the molecular weights of the salts in question. In these experiments, the degree of dissociation of the salt at any particular dilution was found in the usual way by dividing the molecular conductivity at that dilution by its value at infinite dilution. From cryoscopic measurements, the molecular depression of the freezing point of water was found for various concentrations of the salt, and by dividing this number by 18·7 (the molecular constant for water), the value for

i (the van't Hoff coefficient) was obtained. The number of ions, k, into which each molecule of the salt dissociates was then obtained by substituting the experimental values of a and i in the equation

$$i=1+(k-1)a.$$

A similar method was used by Petersen (*Zeitsch. physikal. Chem.*, 1902, **39**, 249) in connexion with the cobaltammines. This author was of the opinion that the conclusions drawn by Werner (*Zeitsch. physikal. Chem.*, 1893, **12**, 35, etc.) from measurements of the molecular conductivity at a dilution of 1000 litres (not necessarily at infinite dilution) were in most cases inaccurate.

The figures given by Jones (*Carnegie Institute of Washington, Publication* No. 170) for the molecular conductivities of a large number of salts show that most salts are completely dissociated at dilutions of about 1000 litres. In some cases, however, the molecular conductivity again increases beyond that dilution, owing to causes other than dissociation. From the figures given by Petersen (*loc. cit.*) for the conductivity of the cobaltammines, it would appear that similar difficulties arose in his work.

In the present investigation, the substances considered are salts of a strong acid. (This has been found to be the case from a preliminary examination of the molecular conductivity of nitroprussic acid itself.) The conductivities of the salts were determined for solutions diluted to 2048 litres, and the values were plotted against the concentrations. The value for infinite dilution was found by extrapolation from the curve so obtained. In all cases, the value of μ_∞ differs only slightly from the value actually found for μ_{1024}, a result which was expected from the nature of the salts in question.

In the following tables are given the values of k calculated on the assumption that the nitroprussides are represented by the simple formula $M_2'[Fe(CN)_5NO]$, which will be referred to in future as type I. In addition, the value of k_1 has been calculated in each case for a molecule, $M_4'[Fe_2(CN)_{10}(NO)_2]$ (type II).

In the case of a univalent cation, a molecule of type I will dissociate into three ions, type II giving five ions. The value of k should therefore approximate to 3 if formula I is correct, whilst if II is correct, $k_1=5$. In the same way, a salt of a bivalent cation should give the values $k=2$ or $k_1=3$.

It is considered that the results obtained show conclusively that all the nitroprussides examined conform to the simple formula (type I). They are salts of $H_2[Fe(CN)_5NO]$, and not of

$$H_4[Fe_2(CN)_{10}(NO)_2].$$

The possible effect due to hydration of the ions has not been overlooked (compare Jones, *Carnegie Institute of Washington, Publi-*

cation No. 180), and it is considered that the conclusions drawn from the figures obtained in the present work cannot be regarded as vitiated on this ground. Whereas hydrate formation may account for the differences between the experimental and absolute values of k, the extremely large differences in the case of k_1 cannot be accounted for in this way.

It is hoped in a future communication to describe the alkyl nitroprussides, some of which have been prepared, although in an impure state only.

Experimental.

The conductivity measurements were all made at 25·0°. The degree of dissociation of salts at 0° differs only slightly from that at 25°, and the latter temperature allows of greater accuracy in determining the conductivity. In the following tables, v is the number of litres containing one gram-molecule of the salt (calculated for the simple formula I), μ is the molecular conductivity, a is the degree of dissociation and is equal to μ_v/μ_∞, Δ_t is the observed depression of the freezing point of water, $M\Delta_t$ is the molecular depression and is equal to $v \times \Delta_t \times 10$, i is the van't Hoff coefficient and is equal to $M\Delta_t/18{\cdot}7$, and k is the number of ions into which a molecule dissociates, and is obtained from the equation $i = 1 + (k-1)a$; k_1 is the corresponding value of k calculated for a molecule of type II by doubling i and then substituting in the equation $i = 1 + (k_1 - 1)a$.

The values of a in the cryoscopic tables are taken from the curves obtained from conductivity data.

Sodium Nitroprusside, $Na_2[Fe(CN)_5NO],2H_2O$.

The salt used was a pure specimen.

Conductivity Measurements.

v.	μ.	a.
4	155·2	0·63
8	169·4	0·69
16	181·8	0·74
32	194·3	0·79
64	204·9	0·84
128	214·2	0·87
256	222·0	0·91
512	229·2	0·94
1024	236·2	0·96
2048	244·6	—
∞	245·0	—

Cryoscopic Measurements.

v	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
47·1	0·115	54·1	2·90	0·81	3·35	6·9
24·4	0·218	53·2	2·84	0·77	3·40	7·1
14·55	0·345	50·2	2·68	0·73	3·30	7·0
10·81	0·456	49·3	2·64	0·71	3·30	7·0
8·76	0·560	49·1	2·62	0·70	3·31	7·0
7·12	0·678	48·3	2·58	0·68	3·32	7·1

Type I requires $k=3$. Type II requires $k_1=5$.

Potassium Nitroprusside, $K_2[Fe(CN)_5NO]$.

This salt was prepared by decomposing the barium salt with the calculated weight of pure potassium sulphate, filtering off the barium sulphate, and evaporating the filtrate at a low temperature under diminished pressure. The residue so obtained was crystallised from aqueous alcohol containing about 95 per cent. of alcohol. It crystallises in pale pink crystals without water of crystallisation:

0·4010 gave 0·1076 Fe_2O_3. Fe = 18·8.

$C_5ON_6FeK_2$ requires Fe = 19·0 per cent.

Conductivity Measurements.

v.	μ.	a.
8	199·2	0·745
16	205·2	0·795
32	215·7	0·836
64	227·2	0·881
128	236·6	0·917
256	244·0	0·946
512	249·3	0·966
1024	257·0	0·996
2048	258·1	—
∞	258·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
34·4	0·150	51·6	2·76	0·85	3·07	6·32
24·1	0·213	51·3	2·74	0·82	3·12	6·46
14·66	0·316	46·3	2·48	0·79	2·87	6·01
11·65	0·405	47·2	2·52	0·77	3·00	6·25
7·02	0·641	45·0	2·41	0·74	2·91	6·16
4·78	0·909	43·4	2·32	0·71	2·86	6·11

Type I requires $k=3$. Type II requires $k_1=5$.

Barium Nitroprusside, $Ba[Fe(CN)_5NO],3H_2O$.

This salt was prepared by precipitating a solution of the sodium salt with zinc sulphate and boiling the zinc salt so obtained with a suspension of precipitated barium carbonate. The filtered solution of the barium salt was evaporated under diminished pressure at a low temperature, and the salt crystallised from aqueous alcohol:

0·8344 gave 0·4734 $BaSO_4$. Ba = 33·4.

$C_5ON_6BaFe,3H_2O$ requires Ba = 33·7 per cent.

The anhydrous salt was found to be extremely hygroscopic.

Conductivity Measurements.

v.	μ.	a.
8	152·9	0·63
16	165·9	0·68
32	177·1	0·73
64	190·7	0·79
128	203·0	0·84
256	216·2	0·89
512	223·6	0·92
1024	236·9	0·98
2048	240·5	—
∞	243·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a = \mu_v/\mu_\infty$.	k.	k_1.
37·7	0·093	35·1	1·88	0·74	2·19	4·73
16·5	0·180	29·7	1·59	0·68	1·87	4·21
9·87	0·285	28·1	1·50	0·64	1·78	4·13
6·67	0·413	27·6	1·47	0·61	1·77	4·18
4·73	0·575	27·2	1·45	0·59	1·76	4·22

Type I requires $k = 2$. Type II requires $k_1 = 3$.

This salt is of especial interest, owing to the rough equality in weights of the anion and cation.

Ammonium Nitroprusside, $(NH_4)_2[Fe(CN)_5NO]$.

This salt was obtained by decomposing the barium salt with an equivalent weight of ammonium sulphate, filtering, evaporating under diminished pressure, and crystallising from aqueous alcohol, when reddish plates, very readily soluble in water, were obtained:

0·2390 gave 0·0768 Fe_2O_3. Fe = 22·5.

$C_5ON_6Fe(NH_4)_2$ requires Fe = 22·2 per cent.

Conductivity Measurements.

v.	μ.	a.
16	206·7	0·77
32	218·0	0·82
64	228·5	0·85
128	236·7	0·89
256	245·6	0·92
512	251·2	0·94
1024	261·3	0·98
2048	266·2	—
∞	268·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
26·3	0·214	56·4	3·01	0·80	3·51	7·27
10·73	0·450	48·3	2·58	0·74	3·14	6·62
6·68	0·704	47·0	2·51	0·69	3·19	6·83

Type I requires $k=3$. Type II requires $k_1=5$.

Methylammonium Nitroprusside, $(MeNH_3)_2[Fe(CN)_5NO]$.

This salt and the nitroprussides of di- and tri-methylamine were obtained by treating a solution of the free acid (obtained from the barium salt and the calculated sulphuric acid) with a slight excess of an alcoholic solution of the amine. The solution so obtained was evaporated under diminished pressure, and the solid residue crystallised from alcohol. The alkylammonium nitroprussides crystallise in reddish plates, which are very readily soluble in water. In appearance they resemble the barium or ammonium salts:

0·1117 gave 0·0306 Fe_2O_3. Fe=19·2.
$C_5ON_6Fe(MeNH_3)_2$ requires Fe=20·0 per cent.

Conductivity Measurements.

v.	μ.	a.
32	185·2	0·77
64	197·7	0·82
128	208·0	0·87
256	218·5	0·91
512	225·8	0·94
1024	233·4	0·97
∞	240·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
36·6	0·148	54·2	2·90	0·78	3·45	7·2
19·05	0·262	49·9	2·67	0·71	3·35	7·1
14·15	0·339	48·0	2·57	0·68	3·31	7·1
10·13	0·466	47·2	2·52	0·62	3·45	7·5
8·35	0·541	45·2	2·42	0·59	3·41	7·5

Type I requires $k=3$. Type II requires $k_1=5$.

Dimethylammonium Nitroprusside, $(Me_2NH_2)_2[Fe(CN)_5NO]$.

0·1028 gave 0·0272 Fe_2O_3. Fe=18·5.
$C_5ON_6Fe(Me_2NH_2)_2$ requires Fe=18·1 per cent.

Conductivity Measurements.

v.	μ.	a.
16	156·5	0·68
32	172·1	0·75
64	185·2	0·81
128	196·3	0·85
256	205·8	0·90
512	212·5	0·92
1024	220·2	0·96
2048	227·3	—
	230·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
35·2	0·149	52·4	2·80	0·76	3·37	7·05
16·4	0·294	48·1	2·57	0·68	3·31	7·09
8·84	0·500	44·2	2·36	0·61	3·23	7·10
5·92	0·714	42·3	2·26	0·57	3·21	7·20

Type I requires $k=3$. Type II requires $k_1=5$.

Trimethylammonium Nitroprusside, $(Me_3NH)_2[Fe(CN)_5NO]$.

0·2234 gave 0·0512 Fe_2O_3. Fe = 16·0.

$C_5ON_6Fe(Me_3NH)_2$ requires Fe = 16·7 per cent.

Conductivity Measurements.

v.	μ.	a.
16	137·1	0·65
32	154·0	0·73
64	167·3	0·80
128	183·0	0·86
256	191·7	0·90
512	201·1	0·95
1024	208·0	0·98
2048	210·5	—
∞	212·0	—

Cryoscopic Measurements.

v.	Δ_t.	$M\Delta_t$.	i.	$a=\mu_v/\mu_\infty$.	k.	k_1.
39·0	0·134	52·2	2·79	0·75	3·39	7·11
14·47	0·290	42·0	2·24	0·63	2·97	6·52
6·56	0·588	38·6	2·06	0·50	3·12	7·24

Type I requires $k=3$. Type II requires $k_1=5$.

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