XXVI.—*Isolation of Two Predicted Hydrates of Nitric acid.*

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ON plotting out the heat of dissolution of nitric acid in water, as determined by Berthelot (*Méc. Chim.*, **1**, 397), it appears that there is a well-marked break in the curve at a point nearly corresponding to the composition of a trihydrate ($\text{HNO}_3, 3\text{H}_2\text{O} = 53.85$ per cent. HNO_3). Thomsen's results form a similar figure, in which a similar indication occurs. Irregularity is observable also in the case of weaker solutions; this occurs at a point corresponding to about 20 per cent. HNO_3 in the figure derived from Berthelot's results, but cannot well be located in the figure derived from Thomsen's more meagre observations. Berthelot's results are shown in Fig. 1, AB.

In like manner, the specific gravities of solutions of nitric acid, taking Kolb's two sets of values (*Ann. Chim. Phys.* [4], **10**, 140), are expressed by a figure in which breaks occur at points corresponding to 53 and 78 per cent. of acid respectively, both being very well marked. When a somewhat small scale is used, the portions of the figure from 0 to 53 per cent. and from 78 to 100 per cent. are sensibly straight lines, the intermediate portion being considerably curved, and no one who examines the figure with a flexible, or indeed inflexible, lath can avoid the conclusion that, if there are any breaks at all in it, they must be at the points referred to (see Fig. 1, CD). The break at 78 per cent., corresponding to a monohydrate, is not apparent in the heat curves, owing, no doubt, to the small number of values determined for strong solutions, though it may be noticed that Berthelot's results suggest some change in these regions, as the value for the 100 per cent. solution used by him does not lie on the curve drawn in Fig. 1.

On plotting the densities on a sufficiently open scale, or, what is better, the contractions, a fairly well marked but comparatively minor change of curvature appears at a point corresponding to about 18 per cent. of acid, near to the minor change occurring in the curve deduced from Berthelot's results.

FIG. 1.—Heat of Dissolution and Specific Gravities of Solutions of Nitric acid.

In Table I (p. 438) are given the values for the contractions calculated from the specific gravities at 0°, and also the molecular volumes of the acid (63 grams) in its solution; these last values, though they show the breaks, were not found in the present case to offer any special advantages for diagrammatic purposes. The maximum of contraction, 15

may be remarked, appears to coincide exactly with the composition of a definite hydrate, the trihydrate; in the case of sulphuric acid, the maximum did not coincide with any definite hydrate (see *Chem. News*, 65, 14).

TABLE. I.—*Specific Gravities of Nitric Acid Solutions at 0° (Kolb), and Values calculated therefrom.*

Per cent. HNO ₃ .	Sp. gr.	Contraction per c.c. of solution formed.	Mol. vol. of HNO ₃ .
99.84	1.559	0.0002	40.37
99.72	1.558	0.0003	40.37
99.52	1.557	0.0007	40.35
97.89	1.551	0.0059	40.14
95.27	1.542	0.0146	39.76
93.01	1.533	0.0211	39.45
89.56	1.521	0.0320	38.91
87.45	1.513	0.0380	38.57
86.17	1.507	0.0408	38.40
80.96	1.488	0.0555	37.48
74.01	1.462	0.0735	36.10
72.39	1.455	0.0769	35.79
71.24	1.450	0.0792	35.56
69.20	1.441	0.0830	35.14
65.07	1.420	0.0883	34.36
61.21	1.400	0.0924	33.59
59.59	1.391	0.0934	33.28
56.10	1.371	0.0949	32.61
52.33	1.349	0.0956	31.85
50.99	1.341	0.0955	31.58
47.18	1.315	0.0923	31.01
43.53	1.291	0.0893	30.38
37.95	1.253	0.0823	29.48
33.86	1.226	0.0770	28.70
28.00	1.187	0.0677	27.55
25.71	1.171	0.0629	27.22
17.47	1.115	0.0451	25.81
11.41	1.075	0.0310	24.48
7.72	1.050	0.0209	24.14
0	1.000	0	—

The two series of specific gravity results are very concordant as to the positions indicated for two chief breaks; they are

Series at 0° 52.5 p. c. } 52.8 p. c. : HNO₃.3H₂O contains 53.85 p. c.
 „ 15 53.0 „ }
 Series at 0° 78.3 „ } 77.9 p. c. : HNO₃.H₂O contains 78.02 p. c.
 „ 15 77.5 „ }

The prominence with which these breaks were marked led me to consider it probable that one or other of the hydrates indicated by

them might be isolated in the crystalline condition, and to test this view I performed two series of freezing point determinations in the same manner as in my recent investigation of the alkylamines (this vol., p. 145). The results more than justified my anticipations, for I succeeded in isolating *both* the hydrates.

Two series of determinations with different samples of acid are given in Table II (p. 440), and the first of these is illustrated in Fig 2.

FIG. 2.—Freezing Points of Solutions of Nitric acid.

Starting with the weakest solutions, water, of course, crystallises, the temperature falling at an increasing rate down to -40° ,* when the strength of the solution reaches 32.5 per cent. This "water" curve indicates a not very well-marked break at 18 per cent., which agrees well with the minor break indicated by the density and heat

* The molecular depression increases with the strength from about 2.2° to 2.9° .

results. An 18 per cent. solution corresponds to a composition of $\text{HNO}_3, 16\text{H}_2\text{O}$.

At 32.5 per cent., the well-known opaque, flocculent, water crystal-

TABLE II.—*Freezing Points of Aqueous Solutions of Nitric Acid.*
 $\text{HNO}_3 = 63$; $\text{H}_2\text{O} = 18$.

Per cent. HNO_3 .	Mols. HNO_3 to $100\text{H}_2\text{O}$.	Freezing point.	Per cent. HNO_3 .	Mols. HNO_3 to $100\text{H}_2\text{O}$.	Freezing point.
<i>First Series.</i>			<i>Second Series.</i>		
The monohydrate crystallises.			The trihydrate crystallises.		
86.19	178.38	None at -77°	68.54	62.26	-38.5°
83.86	133.10	-42.95°	65.93	55.29	-30.45
82.24	132.27	-40.15	63.51	49.72	-25.6
80.05	114.65	-37.85	61.01	44.71	-22.0
77.90	100.74	-36.8	58.01	39.47	-18.95
75.26	86.90	-37.45	55.20	35.20	-18.0
72.72	76.16	-39.3	52.27	31.29	-18.2
			43.30	27.78	-19.15
			46.15	24.49	-21.15
			43.83	22.30	-24.2
			39.48	18.64	-29.5
			36.08	16.13	-35.95
The trihydrate crystallises.			Water crystallises.		
69.46	64.99	-39.9	32.95	14.04	-40.2
66.04	55.57	-29.95	30.29	12.41	-35.9
62.48	47.58	-23.5	27.62	10.90	-30.6
60.63	44.01	-21.4	25.09	9.57	-26.5
58.85	40.87	-19.7	22.53	8.31	-22.6
56.51	37.13	-18.5	20.08	7.18	-19.4
54.11	33.68	-18.45	17.72	6.15	-16.1
52.09	31.07	-18.50	15.54	5.25	-13.6
49.93	28.49	-18.95	13.62	4.51	-11.25
47.84	26.20	-20.0	11.70	3.79	-9.15
45.60	23.95	-21.75	9.46	2.95	-7.1
43.27	21.79	-23.9	7.24	2.23	-5.5
40.64	19.56	-27.55	5.34	1.61	-3.9
37.65	17.26	-32.6	3.82	1.13	-2.6
34.77	15.23	-35.5	2.64	0.77	-1.7
			1.82	0.53	-1.2
Water crystallises.					
31.77	13.30	-38.95			
28.27	11.26	-30.55			
26.79	9.42	-24.3			
21.40	7.78	-19.25			
18.10	6.31	-15.4			
14.63	4.90	-10.75			
11.07	3.56	-7.55			
8.05	2.50	-4.6			
5.68	1.72	-2.9			
3.12	0.92	-0.95			

The position of maximum, which, as is well known, must correspond exactly with the composition of the crystallising substance, was found, by drawing a bent lath curve through the points, to be at

1st Series 53.7 per cent. } 53.8 per cent.,
2nd " 53.9 " }

After 70 per cent., the crystallisation of the trihydrate gives place to the formation of smaller, more opaque, and gritty crystals, the freezing points rising from -45° to -36.8° , after which they fall again, and were followed as far as -43° with an 84 per cent. solution. The maximum of this second crystallising hydrate is reached at 77.9 per cent., and corresponds almost exactly with the monohydrate, which contains 78.02 per cent. of acid.

Although the evidence as to the composition of a crystallising hydrate which is afforded by the position at which the maximum temperature of crystallisation is attained is much more satisfactory than any analysis, I did, in the case of the trihydrate, analyse the crystals. A solution containing over 50 per cent. of nitric acid was taken and recrystallised, the mother liquor being simply run off; the crystals were then found to contain 54.42 per cent. of acid, and after a second crystallisation, 54.05 per cent.; a third crystallisation would evidently have rendered them practically pure, the trihydrate containing 53.85 per cent.

The two hydrates isolated here are the second and third instances of hydrates isolated owing to their existence having previously been recognised in solutions by means of breaks in various properties examined. The first instance was that of the tetrahydrate of sulphuric acid (Trans., 1890, 57, 339), and it is somewhat remarkable that those who have criticised my conclusions as to the existence of breaks should have entirely ignored the very strong evidence afforded in favour of them by the isolation of a hydrate the existence of which was predicted by a break, especially as the break at the tetrahydrate was one of those (in one case the only one) against which their criticisms were directed. It may be that they considered

that the fact that the composition of the isolated hydrate corresponded with the break was merely a coincidence, although, as I showed, the odds were at least 11 : 2 against such a chance ; but the multiplication of coincidences of this sort must put any such explanation entirely out of court, especially as in the present instance it is not that one hydrate was isolated out of a large number indicated, but that only two breaks representing hydrates of a sufficiently low order to render their existence in the solid condition probable were recognised, and both these, and these only, have been isolated. It is difficult to imagine how more conclusive evidence could be obtained as to the reality of breaks, and the existence of hydrates in solution, than by the isolation of the very hydrates indicated by the breaks.

The hydrates must evidently exist in solution throughout a considerable range of temperature, for the indication of the monohydrate was obtained at a temperature 52° above its freezing point, and that of the trihydrate at a temperature 36° above its freezing point.

The existence and position of the breaks, both in the specific gravity and in the heat results, must, as I have said, be apparent to any one who takes the trouble to examine the results even superficially, and it may, therefore, appear curious that Berthelot, who was on the look out for evidence of hydrates in solutions, should not only have missed the indication of the trihydrate, but should have thought that his results showed some indications of hydrates with 2 and $5\text{H}_2\text{O}$, respectively (*Méc. Chim.*, 2, 157). The explanation, no doubt, is, not that Berthelot did not make use of that most valuable instrument the flexible lath, but that he plotted out his results against molecular composition, and thereby got a hyperbolic figure, which of all figures is the least amenable for graphic analysis (see *Trans.*, 1890, 57, 97). In Thomsen's case the matter was different: he obtained numerous series of results, and examined them by deducing empirical equations from them, and comparing the calculated with the observed values. His conclusions, expressed in the most unhesitating language, were that in no case was there any indication of the existence of hydrates. Thomsen's great reputation as a worker may explain how it has happened that these conclusions have been so generally accepted by others, but it is difficult to explain how he could have persuaded himself of their validity. In most cases his determinations were far too meagre for an examination by fitting on equations, and in four cases only did he attempt to do so: in the case of hydrochloric acid (*loc. cit.*, p. 12) and copper chloride (p. 25; there are only five experimental points in this case), the differences between the observed and calculated values arrange themselves without exception, into groups with the same signs, and in magnitude they are often in considerable excess over the 5—10 cal. at which the experimental error is esti-

mated; whilst in the other two cases—sulphuric acid (p. 9) and nitric acid (p. 10)—he displays those only of his experimental values which agree with the calculated values, and omits those which do not. With sulphuric acid, the agreement extends over only 1 per cent. of the whole curve which he examined, and in the remaining 99 per cent., the differences reached nearly 700 cal. (see Trans., 1890, 57, 96, where a fuller discussion of these results will be found), whereas in the case of nitric acid, matters were even worse, for, though the agreement may be said to extend through the first 1·6 per cent. of his whole curve, in the remaining 98·4 per cent. the differences attain more than 1420 cal. I give below a full table of the observed and calculated results, Thomsen's table containing only those marked by an asterisk.

TABLE III.— $\text{HNO}_3, x\text{H}_2\text{O}$ (Thomsen).

x .	Observed.	Calculated $= \frac{x \times 8974}{x + 1 \cdot 737}$.	Difference.
0·175	833 cal.	821 cal.	+ 12 cal.
0·5	2005 "	2008 "	— 3 " *
1·0	3285 "	3285 "	0 " *
2·0	4160 "	4160 "	0 " *
2·5	5276 "	5301 "	— 25 " *
3·0	5710 "	5690 "	+ 20 " *
5·0	6665 "	6668 "	— 3 " *
10·0	7318 "	7650 "	— 332 "
20·0	7458 "	8257 "	— 799 "
40·0	7436 "	8601 "	— 1165 "
80·0	7421 "	8783 "	— 1362 "
160·0	7450 "	8878 "	— 1428 "
320·0	7495 "	8926 "	— 1431 "