LXVIII.—*The Magnetic Rotatory Power of Nitrogen Compounds, also of Hydrochloric, Hydrobromic, and Hydriodic Acids, and of some of the Salts of Ammonia and the Compound Ammonias.*

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IN the previous investigations of the magnetic rotatory power of substances, in relation to their chemical composition, which I have had the honour of laying before this Society, my attention has chiefly been directed to compounds containing carbon, hydrogen, oxygen, and the halogens. This inquiry has now been extended, and in this communication an account is given of nitrogenous compounds. The object of this was to accumulate fresh facts, so as to get more material for generalisation, but more especially to study the influence of nitrogen upon the rotation of substances in which it exists in *tri-* and *penta-*valent conditions, because it has been repeatedly shown that compounds containing carbon in an unsaturated state have a considerably greater rotatory power than those in which it is saturated, and it therefore was a matter of interest to see whether other elements exerted a similar influence.

Substances of the following classes were examined in this inquiry: nitrates, nitro-compounds, nitrites, cyanides, ammonia, compound ammonias, and their salts.

With reference to the last-mentioned compounds, it was my original intention to examine the hydrochlorides or chlorides only, but, as these gave peculiar results, it was considered desirable to include ammonium bromide and iodide, and, for further comparison, ammonium nitrate and its sulphates; this made it necessary not only to determine the rotation of the salts themselves, but also of the acids employed in their formation, except sulphuric acid, which had been previously studied.

Before discussing any of the results which have been obtained, it will be most convenient, in the first place, to give an account of the substances employed and their magnetic rotations.

Nitric Acid.

A quantity of nitric acid, sp. gr. 1.52, was distilled with about 10 per cent. of H_2SO_4 (100 per cent.), the first part being rejected. It was then redistilled, while a rapid current of carbonic anhydride was passed through it, according to the directions given by Kolbe (*Ann. Chem. Phys.*, **79**, 136); in this way a fraction was obtained which was very nearly colourless, b. p. $83.7-84.7^\circ$ (corr.). The

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composition of this acid was found to be 98·3 per cent. of HNO_3 , or $\text{HNO}_3 + 0\cdot060$ mol. OH_2 . The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1\cdot5390, & d_{15^{\circ}}^{15^{\circ}} 1\cdot5191, \\ d_{5^{\circ}}^{5^{\circ}} 1\cdot5368, & d_{25^{\circ}}^{25^{\circ}} 1\cdot5043. \end{array}$$

According to Kolbe's table of densities, this acid should have a density of 1·526 at 15°. It is possible, however, that the two acids examined were not quite equally free from lower oxides of nitrogen, and this may account for this small discrepancy.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14°	0·5274	1·235
13	0·5303	1·240
13	0·5289	1·237
12	0·5333	1·246
12	0·5318	1·243
Average 13	0·5303	1·240
Less 0·06 mol. OH_2		0·060
$\text{HNO}_3 =$		1·180

Nitric Acid and Water.

The dilute acid was redistilled before use, nitrate of urea being added to remove lower oxides of nitrogen. Its strength was 56·74 per cent., and its composition $\text{HNO}_3 + 2\cdot67$ mol. OH_2 .

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot3571, \quad d_{25^{\circ}}^{25^{\circ}} 1\cdot3474.$$

Kolbe's table gives 57 per cent. for a density of 1·358 at 15°.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21°	0·7987	3·646
21	0·8006	3·655
21	0·8031	3·667
Average 21	0·8008	3·656
Less OH ₂		2·670
		0·986

Methyl Nitrate.

This was prepared from methyl alcohol, and nitric acid, nitrate of urea being added to the mixture. It boiled constantly at 65° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{5^{\circ}}^{5^{\circ}} 1\cdot2322, & \qquad d_{15^{\circ}}^{15^{\circ}} 1\cdot2167, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot2241, & \qquad d_{20^{\circ}}^{20^{\circ}} 1\cdot2096, \\
 d_{25^{\circ}}^{25^{\circ}} 1\cdot2032.
 \end{aligned}$$

Dumas and Peligot give 1·182 at 20° (A 15, 26).

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·0°	0·5852	2·050
13·5	0·5887	2·066
14·0	0·5863	2·058
14·5	0·5842	2·052
5·0	0·5951	2·065
5·5	0·5930	2·059
5·8	0·5912	2·054
6·0	0·5918	2·057
Average 9·5	0·5894	2·057

Ethyl Nitrate.

The specimen used boiled at 87·5—87·7° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot1305, & \qquad d_{15^{\circ}}^{15^{\circ}} 1\cdot1159, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot1220, & \qquad d_{20^{\circ}}^{20^{\circ}} 1\cdot1099, \\
 d_{25^{\circ}}^{25^{\circ}} 1\cdot1044.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·0°	0·6811	3·073
9·8	0·6847	3·084
9·8	0·6862	3·091
9·5	0·6873	3·095
10·6	0·6831	3·080
10·0	0·6864	3·093
9·5	0·6828	3·075
9·0	0·6846	3·081
Average 9·9	0·6845	3·084

Propyl Nitrate.

This was prepared from propyl alcohol and nitric acid, nitrate of urea being previously dissolved in the acid. After fractioning a few times, it was obtained boiling at 110·2—110·7° (corr.). The boiling point given by Wallach and Schulze (B 14, 421) is 110·5°. The density determinations gave—

$$\begin{aligned}
 d_{5^{\circ}}^{5^{\circ}} 1\cdot0747, & \qquad d_{15^{\circ}}^{15^{\circ}} 1\cdot0631, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot0688, & \qquad d_{20^{\circ}}^{20^{\circ}} 1\cdot0580, \\
 d_{25^{\circ}}^{25^{\circ}} 1\cdot0531.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·0°	0·7483	4·085
10·0	0·7507	4·097
10·0	0·7483	4·083
9·6	0·7489	4·086
5·5	0·7536	4·093
5·5	0·7499	4·072
5·5	0·7539	4·085
5·5	0·7519	4·083
Average 7·7	0·7507	4·085

Isobutyl Nitrate.

This was fractioned a few times, and the portion boiling between

123·5—124·5° selected for examination. Its density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} & 1\cdot0334, & d_{15^{\circ}}^{15^{\circ}} & 1\cdot0215, \\ d_{10^{\circ}}^{10^{\circ}} & 1\cdot0264, & d_{20^{\circ}}^{20^{\circ}} & 1\cdot0168, \\ & & d_{25^{\circ}}^{25^{\circ}} & 1\cdot0124. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	0·8020	5·184
10·5	0·8012	5·163
10·0	0·8035	5·175
9·8	0·8049	5·184
9·6	0·8012	5·158
9·8	0·8070	5·197
9·7	0·8049	5·183
9·6	0·8055	5·186
9·5	0·8056	5·188
6·0	0·8116	5·206
6·0	0·8093	5·190
5·6	0·8057	5·164
5·6	0·8054	5·163
Average 8·9	0·8052	5·180

Ethylene Nitrate. Nitroglycol.

This was prepared in the same way as nitroglycerin, only using glycol instead of glycerin (p. 685). After being well washed with water and then with a solution of sodium carbonate, it was obtained as a pale yellow oil. This was well dried over anhydrous potassium carbonate, allowed to stand until clear, and then decanted for use. This substance was first obtained by Henry (*Ber.*, **3**, 529). As mentioned by him, it detonates when struck on an anvil, but not so easily as nitroglycerin. When heated in a test-tube, it gives off a small quantity of red fumes, boils, and distils up the side of the tube; if strongly heated it explodes with great violence.

Nitroglycol is a somewhat thick, clear, pale yellow oil; the colour is believed to be due to a small amount of impurity, as it disappears after some weeks. It requires several times its volume of alcohol for solution. Aqueous potash has but little action on it in the cold, but decomposes it on boiling, producing a brown liquid. Cold alcoholic potash does not act rapidly upon this substance at first, but the

mixture gradually becomes warm, and afterwards boils violently, becoming brown. The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.5099, & d_{15^{\circ}}^{15^{\circ}} 1.4960, \\ d_{10^{\circ}}^{10^{\circ}} 1.5012, & d_{20^{\circ}}^{20^{\circ}} 1.4908, \\ & d_{25^{\circ}}^{25^{\circ}} 1.4860. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13.5°	0.6657	3.753
13.5	0.6657	3.753
13.5	0.6654	3.752
13.5	0.6664	3.774
13.5	0.6709	3.774
10.6	0.6697	3.767
11.5	0.6700	3.772
11.5	0.6700	3.772
12.4	0.6735	3.795
Average 12.6	0.6686	3.768

Nitroglycerin.

To prepare this, 60 c.c. of nitric acid, density 1.42, freed from any red fumes by nitrate of urea, were mixed with 100 c.c. of sulphuric acid and 20 c.c. of 45 per cent. fuming sulphuric acid; this mixture was cooled with ice, and 20 c.c. of glycerin gradually added. After standing a few hours, the product was poured into a large bulk of water, the nitroglycerin collected and washed with water, and then with a solution of sodium carbonate. A good deal of difficulty was experienced in getting the nitroglycerin sufficiently clear for examination, but it was accomplished eventually by heating it to about 30°, so as to render it more fluid, and placing it in contact with anhydrous potassium carbonate. After keeping it at this temperature, it was allowed to cool, and in about 24 hours it was warmed again and filtered through paper, a vacuum pump being used. Finally a little phosphoric anhydride was shaken with it, and after standing for some time it was decanted for use. Its density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.6144, & d_{15^{\circ}}^{15^{\circ}} 1.6009 \\ d_{10^{\circ}}^{10^{\circ}} 1.6066, & d_{20^{\circ}}^{20^{\circ}} 1.5958, \\ & d_{25^{\circ}}^{25^{\circ}} 1.5910. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14·0°	0·6865	5·404
13·0	0·6860	5·396
12·5	0·6857	5·392
12·0	0·6875	5·404
12·0	0·6877	5·406
12·0	0·6890	5·408
14·8	0·6848	5·393
15·5	0·6897	5·428
16·0	0·6869	5·415
Average 13·5	0·6870	5·405

Isobutyl Nitrite.

This product was purified first by shaking with dry potassium carbonate, and fractionally distilling until the temperature rose to 77°; the distillate was then again treated with potassium carbonate and re-fractionated a few times in a Wurtz flask with a very long neck. The product collected for examination boiled at 67—68°. It was left with potassium carbonate for a short time and then decanted for use. The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0\cdot8878, & \qquad d_{15^{\circ}}^{15^{\circ}} 0\cdot8752, \\
 d_{10^{\circ}}^{10^{\circ}} 0\cdot8806, & \qquad d_{20^{\circ}}^{20^{\circ}} 0\cdot8702, \\
 d_{25^{\circ}}^{25^{\circ}} 0\cdot8652.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
4·5°	0·8545	5·511
4·8	0·8533	5·506
4·8	0·8527	5·502
5·0	0·8521	5·500
13·5	0·8484	5·537
13·0	0·8428	5·497
12·0	0·8475	5·521
Average 8·2	0·8502	5·510

Nitromethane.

This substance was dried with potassium carbonate. When distilled, it nearly all came over at 101° (corr.). The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.1580, & d_{15^{\circ}}^{15^{\circ}} 1.1441, \\ d_{10^{\circ}}^{10^{\circ}} 1.1502, & d_{20^{\circ}}^{20^{\circ}} 1.1382, \\ & d_{25^{\circ}}^{25^{\circ}} 1.1330. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9.8°	0.6289	1.853
9.6	0.6289	1.852
9.6	0.6282	1.853
9.6	0.6304	1.857
10.7	0.6280	1.852
10.3	0.6301	1.857
10.0	0.6363	1.875
9.5	0.6325	1.862
Average 9.9	0.6304	1.858

Nitroethane.

The specimen used was dried with potassium carbonate. It boiled at 114 — 115° (corr.).

The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 1.0685, & d_{15^{\circ}}^{15^{\circ}} 1.0561, \\ d_{10^{\circ}}^{10^{\circ}} 1.0615, & d_{20^{\circ}}^{20^{\circ}} 1.0509, \\ & d_{25^{\circ}}^{25^{\circ}} 1.0461. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·5°	0·7204	2·835
11·5	0·7207	2·833
10·5	0·7244	2·845
9·2	0·7257	2·848
10·5	0·7191	2·824
9·6	0·7284	2·858
9·2	0·7209	2·827
9·0	0·7203	2·824
Average 10·2	0·7224	2·837

Nitropropane.

This substance was prepared in the usual manner with silver nitrite and propyl iodide. These substances when mixed do not react quickly, but after a very few minutes ebullition sets in with vigour, and the silver salt fuses, apparently owing to the formation of a compound of the iodide and nitrite. It was therefore found better to add the nitrite to the iodide in small quantities at a time and to get the reaction over before adding more; in this way no fusible silver compound was formed. On distilling the product, a mixture of nitrite of propyl, nitropropane, and propyl iodide was obtained. The nitrite was roughly fractioned off and the residual oil treated with successive portions of silver nitrite until perfectly free from propyl iodide; it was then distilled and carefully fractioned a number of times. It boiled at 130·5—131·5° (corr.) and was perfectly colourless.

The density determinations gave—

$$\begin{array}{ll}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot0221, & d_{15^{\circ}}^{15^{\circ}} 1\cdot0108, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot0157, & d_{20^{\circ}}^{20^{\circ}} 1\cdot0062, \\
 & d_{25^{\circ}}^{25^{\circ}} 1\cdot0023.
 \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·0°	0·7781	3·824
20·0	0·7763	3·814
18·5	0·7842	3·849
18·5	0·7791	3·823
18·5	0·7763	3·809
18·5	0·7801	3·828
18·5	0·7791	3·823
20·0	0·7762	3·814
19·0	0·7776	3·827
19·0	0·7702	3·782
Average 18·9	0·7777	3·819

Chloropicrin.

This substance was first dried with phosphoric anhydride, and then distilled from anhydrous potassium carbonate. It boiled constantly at 112° (corr.).

The density determinations gave—

$$\begin{array}{ll}
 d_{4^{\circ}}^{4^{\circ}} 1\cdot6855, & d_{15^{\circ}}^{15^{\circ}} 1\cdot6670, \\
 d_{10^{\circ}}^{10^{\circ}} 1\cdot6748, & d_{20^{\circ}}^{20^{\circ}} 1\cdot6594, \\
 d_{25^{\circ}}^{25^{\circ}} 1\cdot6528.
 \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·6°	0·9800	5·376
15·6	0·9804	5·378
15·6	0·9800	5·376
15·6	0·9775	5·363
15·6	0·9810	5·382
9·0	0·9905	5·399
9·0	0·9887	5·389
9·0	0·9905	5·399
9·0	0·9899	5·395
Average 12·7	0·9843	5·384

*Ammonia.**a. Aqueous Solution.*

The product employed contained 31 per cent. of NH_3 , and therefore had the composition $\text{NH}_3 + 2\cdot10 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0.8989, \quad d_{10^{\circ}}^{10^{\circ}} 0.8955,$$

$$d_{15^{\circ}}^{15^{\circ}} 0.8926.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9.5°	1.1523	3.916
9.5	1.1491	3.905
9.5	1.1489	3.904
9.5	1.1516	3.913
9.5	1.1499	3.908
10.0	1.1518	3.916
9.5	1.1527	3.917
9.5	1.1506	3.910
9.5	1.1473	3.899
Average 9.5	1.1505	3.910
Less OH ₃ , 2.10 mol.		2.100
NH ₃		1.810

b. Alcoholic Solution.

This was prepared with absolute alcohol that had been standing over anhydrous copper sulphate for months. It was then decanted and distilled. The solution contained 14.48 per cent. of NH₃, and therefore had the composition NH₃ + 2.18 mol. C₂H₆O. It was saturated as far as would permit of its use with safety, and began to give off gas at about 15°.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0.7829, \quad d_{8^{\circ}}^{8^{\circ}} 0.7794.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
9°	0.9404	7.872
9	0.9385	7.858
9	0.9459	7.920
9	0.9417	7.885
9	0.9429	7.895
Average 9	0.9419	7.886
Less 2.18 mol. C ₂ H ₆ O		6.060
NH ₃ =		1.826

Ethylamine.

This and most of the other compound ammonias examined were obtained from Kahlbaum.

The product used was kept over freshly fused caustic potash some days before distillation. When fractioned, it mostly came over between 17·4 and 18·4°, and the specimen examined had this boiling point. The density determinations gave—

$$d_{\frac{4}{4}}^{\frac{4}{4}} 0.7013, \quad d_{\frac{10}{10}}^{\frac{10}{10}} 0.6946,$$

$$d_{\frac{15}{15}}^{\frac{15}{15}} 0.6892.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
4·5°	1·0068	3·592
4·5	1·0048	3·585
4·5	1·0103	3·605
4·5	1·0106	3·606
5·0	1·0106	3·608
5·0	1·0130	3·617
5·0	1·0180	3·631
4·5	1·0122	3·611
5·0	1·0098	3·605
5·2	1·0125	3·616
5·4	1·0140	3·623
5·4	1·0116	3·614
8·6	1·0054	3·610
8·3	1·0023	3·598
8·6	1·0067	3·615
9·3	1·0057	3·610
Average 5·8	1·0097	3·609

Diethylamine.

This was carefully fractioned several times; the bulk of the product then boiled at 56—57° (corr.), which appears to be about the true boiling point of this base. The density determinations gave—

$$d_{\frac{4}{4}}^{\frac{4}{4}} 0.7226, \quad d_{\frac{15}{15}}^{\frac{15}{15}} 0.7116,$$

$$d_{\frac{10}{10}}^{\frac{10}{10}} 0.7164, \quad d_{\frac{20}{20}}^{\frac{20}{20}} 0.7070,$$

$$d_{\frac{25}{25}}^{\frac{25}{25}} 0.7028.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
5·4°	1·0095	5·682
5·4	1·0054	5·658
5·4	1·0033	5·647
5·4	1·0060	5·662
13·5	0·9952	5·662
14·0	0·9923	5·649
14·5	0·9960	5·674
Average 9·1	1·0011	5·662

Triethylamine.

The specimen employed contained a little diethylamine; it was therefore fractioned several times from sodium, which forms a compound with this base. The portion selected for examination boiled at 89—89·5° (corr.), mostly at 89°. The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 0\cdot7426, \quad d_{15^{\circ}}^{15^{\circ}} 0\cdot7331,$$

$$d_{10^{\circ}}^{10^{\circ}} 0\cdot7372, \quad d_{20^{\circ}}^{20^{\circ}} 0\cdot7294,$$

$$d_{25^{\circ}}^{25^{\circ}} 0\cdot7257.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·4°	1·1151	8·496
10·3	1·1157	8·499
10·3	1·1169	8·508
10·3	1·1189	8·523
10·0	1·1203	8·532
9·8	1·1194	8·522
9·6	1·1192	8·518
9·3	1·1233	8·547
Average 10·0	1·1186	8·518

Propylamine.

The specimen examined boiled at 47·5—48·5° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0.7330, & \quad d_{15^{\circ}}^{15^{\circ}} 0.7222, \\
 d_{10^{\circ}}^{10^{\circ}} 0.7268, & \quad d_{20^{\circ}}^{20^{\circ}} 0.7182, \\
 & \quad d_{25^{\circ}}^{25^{\circ}} 0.7144.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
6.5°	1.0116	4.540
5.5	1.0161	4.554
5.0	1.0190	4.563
5.0	1.0176	4.557
5.0	1.0183	4.560
15.0	1.0134	4.597
14.5	1.0094	4.579
15.0	1.0064	4.568
15.5	1.0050	4.563
Average 9.6	1.0130	4.564

Dipropylamine.

After being distilled two or three times, most of the product was obtained boiling between 109.4° and 110.4°. The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0.7524, & \quad d_{15^{\circ}}^{15^{\circ}} 0.7430, \\
 d_{10^{\circ}}^{10^{\circ}} 0.7471, & \quad d_{20^{\circ}}^{20^{\circ}} 0.7393, \\
 & \quad d_{25^{\circ}}^{25^{\circ}} 0.7357.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
5.8	1.0087	7.539
5.8	1.0051	7.512
5.8	1.0101	7.550
6.5	1.0122	7.571
6.5	1.0101	7.556
15.0	1.0000	7.553
16.2	0.9975	7.558
16.8	0.9960	7.553
17.5	0.9968	7.547
Average 10.7	1.0041	7.549

Tripropylamine.

To obtain this, dipropylamine, alcohol, and propyl iodide in equal volumes were heated in a sealed tube at 100° for two or three hours. On cooling, the product solidified to a crystalline mass. After distilling with water to remove alcohol and propyl iodide, potash was added, and the volatile bases distilled off; these when dried and fractionated gave tripropylamine boiling at 155·5—156·5°. This was again distilled after boiling with sodium for some time, which attacks any dipropylamine present. The boiling point, however, was not changed by this treatment. The iodide of tetrapropylammonium which was left after the removal of the volatile bases was distilled, the mixture of propyl iodide and tripropylamine thus obtained treated with hydrochloric acid, &c. The tripropylamine obtained in this way boiled at 155—157°, but mostly at 156°, which is apparently the boiling point of this base. Römer gives it as 144—146° (*Ber.*, **6**, 1101).

The density determinations gave—

$$\begin{array}{ll} d_{4^{\circ}}^{4^{\circ}} 0\cdot7681, & d_{15^{\circ}}^{15^{\circ}} 0\cdot7600, \\ d_{10^{\circ}}^{10^{\circ}} 0\cdot7634, & d_{20^{\circ}}^{20^{\circ}} 0\cdot7567, \\ & d_{25^{\circ}}^{25^{\circ}} 0\cdot7539. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·9	1·1167	11·631
9·7	1·1238	11·691
9·0	1·1252	11·699
9·2	1·1247	11·696
10·3	1·1205	11·666
10·3	1·1152	11·610
10·3	1·1208	11·669
10·3	1·1194	11·654
Average 10·0	1·1208	11·664

Isobutylamine.

The base employed boiled between about 67° and 74°. On repeatedly fractioning, the chief part was found to come over at 68—69° (corr.). Hughes and Romer (*Ber.*, **7**, 511) give it as 65·5°; this is believed to be too low.

Its density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} & 0.7464, & d_{15^{\circ}}^{15^{\circ}} & 0.7363, \\ d_{10^{\circ}}^{10^{\circ}} & 0.7408, & d_{20^{\circ}}^{20^{\circ}} & 0.7322, \\ & & d_{25^{\circ}}^{25^{\circ}} & 0.7283. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.8	1.0320	5.699
16.2	1.0355	5.711
15.0	1.0344	5.697
15.0	1.0341	5.696
15.0	1.0350	5.701
15.5	1.0313	5.684
14.5	1.0343	5.694
14.5	1.0284	5.661
14.5	1.0328	5.684
Average 15.3	1.0331	5.692

Isobutylamine and Water.

Isobutylamine, when mixed with water, develops heat. The mixture examined consisted of equal vols. at 15° of each substance; the density of the mixture was for $d_{15^{\circ}}^{15^{\circ}}$ 0.9002; this shows that considerable condensation occurs on making this mixture, the average density of equal vols. of isobutylamine and water being as follows:—

$$\begin{array}{rcl} \text{Isobutylamine } d_{15^{\circ}}^{15^{\circ}} & 0.7362 & \\ \text{Water.....} & 1.0000 & \\ \hline \text{Average density .} & 0.8681 & \end{array}$$

The molecular composition of this mixture is $C_4H_{11}N + 5.51OH_2$.
The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15°	1·0460	11·091
15	1·0484	11·116
15	1·0402	11·080
15	1·0431	11·060
15	1·0460	11·091
Average 15	1·0447	11·077
Less OH ₂		5·510
		5·567

Isobutylamine and Alcohol.

These substances were mixed in equal volumes measured at 15°. The composition of the mixture is represented by C₄H₁₁N + 1·715 mol. C₂H₆O.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 0\cdot791.$$

The average density of equal volumes of isobutylamine and alcohol at 15° is—

Alcohol (spec. used)	0·7948
Isobutylamine	0·7357
Average	0·7652

This shows that considerable contraction takes place on mixing these substances.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15°	0·9556	10·364
15	0·9541	10·348
15	0·9556	10·364
15	0·9548	10·356
15	0·9655	10·418
15	0·9587	10·342
15	0·9620	10·377
15	0·9596	10·351
15	0·9572	10·326
Average 15	0·9581	10·361
Less alcohol		4·768
		5·593

Diisobutylamine.

This product, after several fractional distillations, was obtained with a boiling point of 139—140° (corr.). Merz and Gasiorowski (*Ber.*, **17**, 626) give it as 135—137°. The original substance was very good, very little high and low portions being separated by distillation.

The density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} 0.7577, & \quad d_{15^{\circ}}^{15^{\circ}} 0.7491, \\ d_{10^{\circ}}^{10^{\circ}} 0.7528, & \quad d_{20^{\circ}}^{20^{\circ}} 0.7457, \\ & \quad d_{25^{\circ}}^{25^{\circ}} 0.7425. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.3°	1.0409	9.969
15.3	1.0442	9.992
15.0	1.0412	9.961
15.0	1.0385	9.935
16.0	1.0373	9.933
15.5	1.0334	9.891
15.0	1.0382	9.932
14.5	1.0373	9.918
14.5	1.0378	9.924
14.5	1.0349	9.895
14.5	1.0401	9.945
Average 15.1	1.0385	9.936

Allylamine.

The specimen used came over mostly at 53.2—54°. It was fractioned several times, and the specimen selected boiled at 53.2—53.4 (corr.). The boiling point given by Rinne is 58° (*Annalen*, 168—262). When smelt, it causes sneezing.

The density determinations gave—

$$\begin{aligned} d_{4^{\circ}}^{4^{\circ}} 0.7799, & \quad d_{15^{\circ}}^{15^{\circ}} 0.7688, \\ d_{10^{\circ}}^{10^{\circ}} 0.7739, & \quad d_{20^{\circ}}^{20^{\circ}} 0.7436, \\ & \quad d_{25^{\circ}}^{25^{\circ}} 0.7583. \end{aligned}$$

Rinne gives the density as 0·864 at 15°.

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13·5°	1·3605	5·593
13·0	1·3642	5·609
13·0	1·3615	5·598
13·0	1·3620	5·599
15·5	1·3520	5·572
15·5	1·3508	5·567
15·5	1·3545	5·583
15·5	1·3548	5·584
Average 14·3	1·3575	5·588

Pentamethylenediamine, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$.

The product examined was prepared by my son (W. H. P.). It boiled at 178—179° (corr.). Its density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0\cdot8939, & \qquad d_{15^{\circ}}^{15^{\circ}} 0\cdot8855, \\
 d_{10^{\circ}}^{10^{\circ}} 0\cdot8890, & \qquad d_{20^{\circ}}^{20^{\circ}} 0\cdot8822, \\
 d_{25^{\circ}}^{25^{\circ}} 0\cdot8792.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
13°	1·1719	7·488
13	1·1697	7·473
13	1·1731	7·495
13	1·1709	7·481
13	1·1768	7·519
Average 13	1·1725	7·491

As I had some quantity of this substance at my disposal, and it readily absorbs moisture, it was carefully fractioned. The chief part of the product boiled at 178—180·5° (corr.) (a little of that which came over first, and which probably contained a small quantity of water, being collected separately). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0.8930, & \quad d_{15^{\circ}}^{15^{\circ}} 0.8846, \\
 d_{10^{\circ}}^{10^{\circ}} 0.8881, & \quad d_{20^{\circ}}^{20^{\circ}} 0.8812, \\
 d_{25^{\circ}}^{25^{\circ}} 0.8784.
 \end{aligned}$$

Ladenburgh gives its boiling point as 175—178°, and its density at $d_{4^{\circ}}^{0^{\circ}}$ as 0.9174 (*Ber.*, **18**, 2957).

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14.7°	1.1703	7.496
14.7	1.1673	7.477
14.7	1.1713	7.503
14.7	1.1703	7.496
Average 14.7	1.1698	7.493

This refractioned product, therefore, has given numbers for the molecular rotation practically identical with those obtained with the original product, a small difference being observable in the specific rotation, which is a little lower. The influence of this is neutralised by the slight change in the density. The average molecular rotation is 7.492.

Piperidine.

The specimen of this base used in the investigation boiled at 105.8—106.3 (corr.). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0.8758, & \quad d_{15^{\circ}}^{15^{\circ}} 0.8664, \\
 d_{10^{\circ}}^{10^{\circ}} 0.8704, & \quad d_{20^{\circ}}^{20^{\circ}} 0.8626, \\
 d_{25^{\circ}}^{25^{\circ}} 0.8591.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·0	1·0714	5·826
11·3	1·0676	5·806
11·3	1·0684	5·811
11·0	1·0670	5·803
16·0	1·0641	5·805
14·5	1·0686	5·821
14·5	1·0659	5·803
14·0	1·0665	5·807
Average 13·0	1·0674	5·810

Piperidine and Water.

This base has a great attraction for water. The proportions used were molecular, $C_5H_{11}N + OH_2$. The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}}^{\frac{4}{4}} 0.9227, & \quad d_{\frac{15}{15}}^{\frac{15}{15}} 0.9133, \\
 d_{\frac{10}{10}}^{\frac{10}{10}} 0.9173, & \quad d_{\frac{20}{20}}^{\frac{20}{20}} 0.9097, \\
 & \quad d_{\frac{25}{25}}^{\frac{25}{25}} 0.9063.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0	1·0724	6·724
15·2	1·0709	6·711
15·3	1·0727	6·722
14·5	1·0783	6·753
16·0	1·0696	6·707
16·0	1·0732	6·729
Average 15·5	1·0728	6·724 1·000
		5·724

Pyridine.

The specimen used was obtained from Schuchardt. When kept with freshly-fused potassium hydrate, it did not show any signs of containing water; after several fractional distillations, the principal part of the product was obtained boiling between 116·2—116·7° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0.9944, & \qquad d_{15^{\circ}}^{15^{\circ}} 0.9855, \\
 d_{10^{\circ}}^{10^{\circ}} 0.9894, & \qquad d_{20^{\circ}}^{20^{\circ}} 0.9816, \\
 & \qquad d_{25^{\circ}}^{25^{\circ}} 0.9778.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.5°	1.9734	8.758
10.8	1.9686	8.738
10.8	1.9731	8.758
10.8	1.9740	8.762
10.8	1.9682	8.736
14.5	1.9741	8.789
14.3	1.9724	8.777
13.0	1.9723	8.770
Average 12.0	1.9720	8.761

Propionitrile.

This was well dried with anhydrous potassium carbonate and then carefully fractioned. The specimen examined boiled at 98—98.5° (corr.). The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 0.7998, & \qquad d_{15^{\circ}}^{10^{\circ}} 0.7896, \\
 d_{10^{\circ}}^{15^{\circ}} 0.7941, & \qquad d_{20^{\circ}}^{20^{\circ}} 0.7853, \\
 & \qquad d_{25^{\circ}}^{25^{\circ}} 0.7815.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10.5	0.8641	3.327
10.5	0.8662	3.335
11.0	0.8668	3.339
11.5	0.8624	3.324
12.0	0.8612	3.322
16.0	0.8624	3.341
16.3	0.8588	3.328
16.7	0.8587	3.329
Average 13.06	0.8626	3.331

Trimethylene Cyanide.

Obtained by digesting trimethylene bromide with cyanide of potassium and alcohol. The portion examined boiled at 285—287·4° (corr.). Henry gives it as 274° (*Bull. Chem. Soc.*, **43**, 618). The density determinations gave—

$$\begin{aligned} d_{\frac{4}{4}}^{\frac{4}{4}} & 1\cdot0031, & d_{\frac{15}{15}}^{\frac{15}{15}} & 0\cdot9952, \\ d_{\frac{10}{10}}^{\frac{10}{10}} & 0\cdot9984, & d_{\frac{20}{20}}^{\frac{20}{20}} & 0\cdot9922, \\ & & d_{\frac{25}{25}}^{\frac{25}{25}} & 0\cdot9894. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
10·0	0·9850	5·152
10·5	0·9841	5·149
11·0	0·9856	5·160
10·5	0·9801	5·128
10·5	0·9786	5·120
10·5	0·9786	5·120
10·5	0·9792	5·123
Average 10·5	0·9816	5·136

Hydrochloric Acid.

The strength of the acids examined was determined by titration, and also by precipitation.

Solution I.—Saturated at about 20°. It contained 41·70 per cent. of HCl; its composition was, therefore, HCl + 2·834 mol. OH₂.

The density determinations gave—

$$\begin{aligned} d_{\frac{4}{4}}^{\frac{4}{4}} & 1\cdot2154, & d_{\frac{10}{10}}^{\frac{10}{10}} & 1\cdot2113, \\ & & d_{\frac{15}{15}}^{\frac{15}{15}} & 1\cdot2082. \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	1·7130	6·882
16·5	1·7115	6·876
16·5	1·7123	6·863
16·5	1·7113	6·875
16·5	1·7112	6·887
19·8	1·7110	6·884
19·7	1·7113	6·885
Average 17·3	1·7117	6·879
Less OH ₂		2·834
		4·045

Solution II.—This contained 36·5 per cent. of HCl. The composition was therefore HCl + 3·51 mol. OH₂.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 1\cdot1939, \quad d_{15^{\circ}}^{15^{\circ}} 1\cdot1866,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot1827.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
11·6°	1·6575	7·724
11·5	1·6590	7·731
11·5	1·6581	7·727
11·5	1·6569	7·721
11·5	1·6557	7·716
10·3	1·6613	7·737
10·3	1·6580	7·722
10·3	1·6599	7·731
10·3	1·6580	7·722
Average 11·0	1·6583	7·725
Less 3·351 mol. OH ₂		3·510
HCl =		4·215

Solution III.—This contained 30·86 per cent. of HCl; its composition was, therefore, HCl + 4·543 mol. OH₂.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot1582, \quad d_{25^{\circ}}^{25^{\circ}} 1\cdot1548.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·5°	1·5554	8·841
21·5	1·5528	8·826
21·5	1·5577	8·854
21·5	1·5580	8·856
21·5	1·5572	8·852
Average 21·5	1·5562	8·846
Less OH ₂		4·543
		4·303

Solution IV.—This contained 25·6 per cent. of HCl; its composition was, therefore, HCl + 5·893 mol. OH₂.

The density determinations gave—

$$d_{15}^{15^{\circ}} 1\cdot1288, \quad d_{25}^{25^{\circ}} 1\cdot1260.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·0	1·4684	10·319
21·0	1·4706	10·334
21·0	1·4643	10·290
21·0	1·4669	10·306
20·0	1·4606	10·261
20·0	1·4643	10·289
20·0	1·4599	10·257
20·0	1·4643	10·288
20·0	1·4721	10·343
Average 20·4	1·4657	10·298
Less OH ₂		5·893
		4·405

Solution V.—This contained 15·63 per cent. of HCl; its composition was, therefore, HCl + 10·856 mol. OH₂.

The density determinations gave—

$$d_{15}^{15^{\circ}} 1\cdot0771, \quad d_{25}^{25^{\circ}} 1\cdot0745.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	1·2748	15·254
16	1·2790	15·303
16	1·2761	15·268
Average 16	1·2766	15·275
Less OH ₂		10·856
		4·419

Hydrochloric Acid in Isoamyl Oxide.

This contained 10·68 per cent. HCl; its composition was HCl + 1·932 mol. C₁₀H₂₂O. The density determinations

$$d_{\frac{4^{\circ}}{4^{\circ}}} 0\cdot8252, \quad d_{\frac{15^{\circ}}{15^{\circ}}} 0\cdot8159,$$

$$d_{\frac{25^{\circ}}{25^{\circ}}} 0\cdot8132.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·0°	1·0223	23·834
19·5	1·0169	23·693
19·5	1·0223	23·834
19·5	1·0178	23·715
19·5	1·0231	23·839
Average 19·6	1·0205	23·783
Less C ₁₀ H ₂₂ O, 11·168 × 1·932..		21·572
		2·211

The above solution was cloudy on account of the absorption of a small quantity of water, and this rendered it difficult to read as the light was obstructed. A second solution was therefore prepared, great care being used to prevent the presence of moisture. It was obtained quite clear, and contained 12·82 per cent. of hydrochloric acid, the composition being HCl + 1·570 mol. C₁₀H₂₂O.

Its density determinations gave—

$$d_{\frac{10^{\circ}}{10^{\circ}}} 0\cdot8265, \quad d_{\frac{15^{\circ}}{15^{\circ}}} 0\cdot8221.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
14	1·0338	19·754
14	1·0382	19·838
14	1·0352	19·782
14	1·0352	19·782
14	1·0382	19·838
Average 14	1·0361	19·799
Less C ₁₉ H ₂₂ O	11·168 × 1·570 ...	17·534
		2·265
Previous No.		2·211
Average.		2·238

Hydrobromic Acid.

This was prepared by acting on amorphous phosphorus with bromine in the presence of water; the gas was freed from bromine vapour by twice washing it with a saturated solution of hydrobromic acid holding amorphous phosphorus in suspension.

Solution I, fully saturated at about 20°, contained 65·59 per cent. of HBr; its composition was, therefore, HBr + 2·361 mol. OH₂. The density determinations gave—

$$d_{\frac{4}{4}}^{\frac{4}{4}} 1·7978, \quad d_{\frac{10}{10}}^{\frac{10}{10}} 1·7919,$$

$$d_{\frac{15}{15}}^{\frac{15}{15}} 1·7874.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·5°	2·6154	10·047
16·5	2·6134	10·039
16·5	2·6123	10·036
16·5	2·6119	10·033
16·5	2·6093	10·023
19·5	2·6017	10·006
19·5	2·6058	10·022
Average 17·4	2·6100	10·030
Less OH ₂		2·361
		7·669

Solution II.—This contained 56 per cent. HBr; its composition

was, therefore, $\text{HBr} + 3.533 \text{ mol. OH}_2$. The density determinations gave—

$$d_{15}^{15^\circ} 1.6117, \quad d_{25}^{25^\circ} 1.6064.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22°	2.3213	11.597
22	2.3206	11.594
22	2.3202	11.591
22	2.3199	11.590
22	2.3213	11.597
Average 22	2.3207	11.594
Less OH_2		3.533
		8.061

Solution III.—This contained 39.71 per cent. HBr ; its composition was, therefore, $\text{HBr} + 6.831 \text{ mol. OH}_2$. The density determinations gave—

$$d_{4}^{4^\circ} 1.3850, \quad d_{15}^{15^\circ} 1.3786, \\ d_{25}^{25^\circ} 1.3748.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22.3°	1.8482	15.224
22.3	1.8436	15.186
21.0	1.8498	15.247
21.0	1.8462	15.224
21.0	1.8523	15.273
21.0	1.8534	15.276
20.0	1.8510	15.242
20.0	1.8539	15.266
20.0	1.8549	15.275
Average 21.0	1.8503	15.246
Less OH_2		6.831
		8.415

Solution IV.—This contained 24.6 per cent. of HBr ; its composition was, therefore, $\text{HBr} + 13.789 \text{ mol. OH}_2$. The density determinations gave—

$$d_{15^\circ}^{15^\circ} 1.2049,$$

$$d_{25^\circ}^{25^\circ} 1.2028.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18°	1.4684	22.261
18	1.4728	22.367
18	1.4721	22.356
18	1.4716	22.349
18	1.4718	22.351
Average 18	1.4713	22.336
Less OH ₂		13.789
		8.547

Solution V.—This contained 15.47 per cent. of HBr; its composition was, therefore, HBr + 24.580 mol. OH₂. The density determinations gave—

$$d_{15^\circ}^{15^\circ} 1.1172,$$

$$d_{25^\circ}^{25^\circ} 1.1149.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16.5	1.2687	33.036
16.5	1.2716	33.112
16.5	1.2731	33.151
Average 16.5	1.2711	33.099
Less OH ₂		24.580
		8.519

Hydriodic Acid.

Solution I.—This contained 67.02 per cent. HI; its composition was, therefore, HI + 3.498 mol. OH₂. This acid was freshly prepared, colourless, and pure.

The density determinations gave—

$$d_{4^\circ}^{4^\circ} 1.9600,$$

$$d_{15^\circ}^{15^\circ} 1.9489,$$

$$d_{10^\circ}^{10^\circ} 1.9537,$$

$$d_{20^\circ}^{20^\circ} 1.9448,$$

$$d_{25^\circ}^{25^\circ} 1.9414.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·5°	3·9033	21·242
22·0	3·8974	21·236
20·0	3·8949	21·248
20·0	3·9027	21·291
Average 21·1	3·8996	21·267
Less OH ₂		3·498
		17·769

Solution II.—This contained 65·1 per cent. HI; its composition was, therefore, HI + 3·827 mol. OH₂.

The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 1.9182, & \qquad d_{15^{\circ}}^{15^{\circ}} 1.9073, \\
 d_{10^{\circ}}^{10^{\circ}} 1.9118, & \qquad d_{20^{\circ}}^{20^{\circ}} 1.9035, \\
 & \qquad d_{25^{\circ}}^{25^{\circ}} 1.9003.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0°	3·7713	21·640
16·0	3·7833	21·709
17·0	3·7802	21·712
17·0	3·7791	21·705
16·5	3·7827	21·710
Average 16·5	3·7793	21·695
Less OH ₂		3·827
		17·868

Solution III.—This contained 61·97 per cent. HI; its composition was, therefore, HI + 4·364 mol. OH₂.

The density determinations gave—

$$\begin{aligned}
 d_{4^{\circ}}^{4^{\circ}} 1.8349, & \qquad d_{15^{\circ}}^{15^{\circ}} 1.8244, \\
 d_{10^{\circ}}^{10^{\circ}} 1.8280, & \qquad d_{20^{\circ}}^{20^{\circ}} 1.8220.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·0°	3·5713	22·483
17·5	3·5768	22·514
17·5	3·5713	22·479
17·5	3·5681	22·459
17·5	3·5705	22·474
Average 17·6	3·5716	22·481
Less OH ₂		4·364
		18·117

Solution IV.—Freshly distilled, colourless, and pure; it contained 56·78 per cent. HI; its composition was, therefore, HI + 5·413 mol. OH₂.

The density determinations gave—

$$\begin{aligned}
 d_{\frac{4}{4}}^{\frac{4}{4}} & 1\cdot7115, & d_{\frac{15}{15}}^{\frac{15}{15}} & 1\cdot7021, \\
 d_{\frac{10}{10}}^{\frac{10}{10}} & 1\cdot7059, & d_{\frac{20}{20}}^{\frac{20}{20}} & 1\cdot6988, \\
 d_{\frac{25}{25}}^{\frac{25}{25}} & 1\cdot6962.
 \end{aligned}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	3·2108	23·688
21·0	3·2166	23·723
21·0	3·2169	23·725
22·0	3·2220	23·764
21·0	3·2134	23·700
21·5	3·2171	23·731
22·0	3·2137	23·710
22·0	3·2203	23·759
22·0	3·2220	23·764
21·0	3·2166	23·723
21·5	3·2171	23·731
Average 21·5	3·2170	23·721
Less OH ₂		5·413
		18·308

Solution V.—This contained 42·7 per cent.; its composition was, therefore, HI + 9·542 mol. OH₂.

The density determinations gave—

$$\begin{array}{ll} d_{10}^{10^{\circ}} 1.4536, & d_{20}^{20^{\circ}} 1.4484, \\ d_{15}^{15^{\circ}} 1.4507, & d_{25}^{25^{\circ}} 1.4467. \end{array}$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15.0°	2.4354	27.958
14.5	2.4367	27.989
14.5	2.4350	27.947
14.0	2.4340	27.930
17.0	2.4326	27.945
16.0	2.4385	28.003
15.5	2.4327	27.930
Average 15.2	2.4350	27.945
Less OH ₂		9.542
		18.403

Solution VI.—This contained 31.77 per cent.; its composition was, therefore, HI + 15.272 mol. OH₂.

The density determinations gave—

$$d_{15}^{15^{\circ}} 1.2977, \quad d_{20}^{20^{\circ}} 1.2962.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	1.9544	33.763
15.5	1.9515	33.702
15.5	1.9500	33.676
15.5	1.9544	33.752
Average 15.9	1.9526	33.723
Less OH ₂		15.272
		18.451

Solution VII.—This contained 20.77 per cent.; its composition was, therefore, HI + 27.128 mol. OH₂.

The density determinations gave—

$$d_{15}^{15^{\circ}} 1.1770, \quad d_{25}^{25^{\circ}} 1.1754.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
23·0°	1·5636	45·539
21·0	1·5673	45·631
20·5	1·5644	45·544
20·0	1·5644	45·540
20·0	1·5649	45·554
20·0	1·5649	45·554
19·5	1·5653	45·562
19·5	1·5642	45·523
Average 20·4	1·5650	45·556
Less OH ₂		27·128
		18·428

Ammonium Chloride.

The specimen of this salt used was recrystallised several times and then dried over sulphuric acid in a vacuum.

The solution used contained 27·08 per cent. of salt, and therefore had the composition NH₄Cl + 8OH₂ as nearly as possible. This solution was a supersaturated one, and although its tendency to crystallise was very inconvenient, especially in determining the density, it was thought better to put up with that than work with a weaker solution.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot0787, \quad d_{20^{\circ}}^{20^{\circ}} 1\cdot0783,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot0777.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
25·0°	1·3851	14·108
22·0	1·3861	14·108
22·0	1·3846	14·090
21·0	1·3842	14·089
20·0	1·3832	14·076
20·0	1·3865	14·109
20·0	1·3850	14·095
20·0	1·3850	14·095
Average 21·2	1·3850	14·096
Less 8 mol. OH ₂		8·000
NH ₄ Cl =		6·096

Attempts were made to determine the molecular weight of this substance by Raoult's process with acetic acid, but it was found to be insufficiently soluble in acetic acid.

Ethylamine Hydrochloride.

A nearly saturated solution of this salt was made and its strength found by determining the chlorine several times. It contained 60.58 per cent. of $\text{EtH}_2\text{N}, \text{HCl}$, and therefore had the composition $\text{EtH}_2\text{N}, \text{HCl} + 2.946 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{10^\circ}^{10^\circ} 1.0535, \quad d_{20^\circ}^{20^\circ} 1.0505.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17.0°	1.5439	10.966
17.0	1.5401	10.939
16.0	1.5393	10.929
16.0	1.5401	10.934
15.8	1.5350	10.989
15.8	1.5381	10.920
15.7	1.5401	10.934
15.7	1.5401	10.934
Average 16.1	1.5396	10.943
Less 2.946 mol. OH_2		2.946
		7.997

A determination of the molecular weight of this substance by Raoult's process in glacial acetic acid gave 115.1. Theory requires 81.5. This is high; the solution, however, was rather strong, 1.307 of salt in 100 of acid: this may have had a little to do with this result, but probably dissociation was the chief cause.

Diethylamine Hydrochloride.

A very nearly saturated solution of this salt was prepared. Chlorine determinations showed that it contained 61.58 per cent. The solution therefore had the composition $\text{Et}_2\text{HN}, \text{HCl} + 3.79 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{10^\circ}^{10^\circ} 1.0198, \quad d_{20^\circ}^{20^\circ} 1.0164.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15°	1·4113	13·694
15	1·4125	13·705
15	1·4125	13·705
15	1·4116	13·697
15	1·4100	13·682
15	1·4063	13·646
15	1·4085	13·667
15	1·4071	13·694
Average 15	1·4100	13·686
Less 3·97 mol. OH ₂		3·790
		9·896

A determination of the molecular weight of this salt by Raoult's process with acetic acid gave 139·9. Theory requires 109·5. This as in the case of the ethylamine salt is high. The proportions used were 1·072 of salt to 100 of acid.

Solution of Diethylamine Hydrochloride in Absolute Alcohol.

The salt used, which was dried by fusion and heated until it boiled, was dissolved while hot in alcohol of $d_{15}^{15^{\circ}}$ 0·7947. The solution was very nearly saturated at the ordinary temperature. The strength was known from the amount of salt used, and afterwards checked by chlorine estimations. The solution contained 22·63 per cent. of salt, and had the composition (C₂H₅)₂HN·HCl + 8·138 mol. C₂H₆O.

The density determinations gave—

$$d_{15}^{15^{\circ}} 0·8417, \quad d_{25}^{25^{\circ}} 0·8361.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·0°	1·0117	32·356
17·0	1·0161	32·497
18·0	1·0132	32·424
18·0	1·0118	32·376
18·0	1·0103	32·339
Average 17·6	1·0126	32·298
Less alcohol 2·780 × 8·138....		22·624
		9·674

Triethylamine Hydrochloride.

A nearly saturated solution of this compound was found to contain 57.26 per cent. of the pure salt. Its composition calculated from this is represented as $\text{Et}_3\text{N}, \text{HCl} + 5.75 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{15}^{15^\circ} 1.0202, \quad d_{20}^{20^\circ} 1.0184,$$

$$d_{25}^{25^\circ} 1.0167.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16°	1.3285	17.441
16	1.3317	17.485
16	1.3328	17.498
16	1.3351	17.528
16	1.3319	17.487
16	1.3326	17.496
16	1.3331	17.502
16	1.3318	17.473
Average 16	1.3322	17.489
		5.750
		11.739

Tetretethylammonium Chloride.

The solution employed was somewhat supersaturated and deposited very large transparent crystals in cold weather. Chlorine determinations showed that it contained 55.62 per cent. of the salt; it would therefore have the composition $\text{Et}_4\text{N}, \text{Cl} + 7.333 \text{ mol. OH}_2$.

The density determinations gave—

$$d_8^{8^\circ} 1.0358, \quad d_{15}^{15^\circ} 1.0323,$$

$$d_{25}^{25^\circ} 1.0285.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
15·3	1·3069	20·926
15·3	1·3084	20·951
15·2	1·3094	21·016
15·2	1·3120	21·008
18·0	1·3068	20·950
18·0	1·3039	20·902
18·0	1·3068	20·950
18·0	1·3072	20·955
Average 16·6	1·3076	20·957
Less 7·333 mol OH ₂		7·333
Et ₄ Cl =		13·624

Piperidine Hydrochloride.

The strongest solution which could be conveniently used contained 52·7 per cent. of this hydrochloride, and had the composition C₆H₁₁N, HCl + 6·055 mol. OH₂.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 1\cdot0716, \quad d_{15^{\circ}}^{15^{\circ}} 1\cdot0677,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot0647.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·5	1·3436	16·097
12·5	1·3430	16·090
13·0	1·3430	16·097
13·5	1·3413	16·080
14·0	1·3412	16·080
Average 13·1	1·3424	16·089
Less OH ₂		6·055
C ₆ H ₁₁ N, HCl =		10·034

Ammonium Bromide.

Two solutions containing different quantities of this salt were examined. The strength of the solutions was found by bromine determinations.

Solution I.—This contained 40·423 per cent. of salt; its composition was, therefore, $\text{NH}_4\text{Br} + 8\cdot024 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{4^{\circ}}^{4^{\circ}} 1\cdot2867, \quad d_{15^{\circ}}^{15^{\circ}} 1\cdot2816,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot2794.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·0°	1·7291	18·193
20·0	1·7332	18·233
20·0	1·7258	18·156
20·0	1·7252	18·149
Average 20·0	1·7283	18·183
Less OH_2		8·024
$\text{NH}_4\text{Br} =$		10·159

Solution II.—This contained 25 per cent. of salt; its composition was, therefore, $\text{NH}_4\text{Br} + 16\cdot339 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot1586, \quad d_{25^{\circ}}^{25^{\circ}} 1\cdot1574.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
22·0°	1·4135	26·594
22·0	1·4162	26·657
22·0	1·4147	26·629
16·5	1·4045	26·406
16·5	1·4075	26·462
16·5	1·4071	26·454
Average 19·2	1·4106	26·535
Less OH_2		16·339
		10·196

Ammonium Iodide.

This salt was purified by recrystallisation from alcohol, and in this way was obtained quite white. It was dried in a vacuum. The strength of the solution used was found from iodine determinations, made by precipitation with silver nitrate. In the first preparation, the solution was filtered through paper, but it was found that this caused it to turn brown very rapidly, and made the readings of the magnetic rotations very difficult. It is much better, therefore, not to filter the solution, but to decant it if necessary.

Solution I.—This contained 60·44 per cent. salt = NH_4I + 5·273 mol. OH_2 .

The density determinations gave—

$$d_{40}^{40} 1\cdot6021, \quad d_{15}^{15} 1\cdot5961,$$

$$d_{25}^{25} 1\cdot9525.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
20·5°	3·0124	25·193
21·5	3·0115	25·191
21·5	3·0145	25·217
21·5	3·0175	25·235
Average 21·2	3·0140	25·209
Less OH_2		5·273
NH_4I =		19·936

Solution II.—This contained 58·46 per cent. of ammonium iodide; its composition was, therefore, NH_4I + 5·722 mol. OH_2 .

The density determinations gave—

$$d_{10}^{10} 1\cdot5727, \quad d_{15}^{15} 1\cdot5701,$$

$$d_{25}^{25} 1\cdot5665.$$

The magnetic rotations gave—

t .	Sp. rotation.	Mol. rotation.
14.5°	2.9277	25.688
14.5	2.9340	25.743
15.0	2.9415	25.812
15.0	2.9475	25.804
20.0	2.9331	25.747
18.0	2.9301	25.733
Average 16.1	2.9356	25.754
Less OH ₂		5.722
NH ₄ I =		20.032

Solution III.—This contained 54.64 of salt; its composition was, therefore, NH₄I + 6.685 mol. OH₂.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.5122, \quad d_{25^{\circ}}^{25^{\circ}} 1.5090.$$

The magnetic rotations gave—

t .	Sp. rotation.	Mol. rotation.
20.0°	2.7332	26.672
20.0	2.7317	26.657
20.0	2.7332	26.671
20.0	2.7333	26.686
20.0	2.7264	26.621
20.0	2.7334	26.674
20.0	2.7274	26.615
Average 20.0	2.7312	26.656
Less OH ₂		6.685
NH ₄ I =		19.971

Solution IV.—This contained 30.5 per cent. of salt; its composition was, therefore, NH₄I + 18.333 mol. OH₂.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1.2351, \quad d_{25^{\circ}}^{25^{\circ}} 1.2334.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
21·0	1·7949	38·405
21·0	1·7977	38·465
22·0	1·7896	38·323
21·5	1·7909	38·394
22·0	1·7905	38·323
Average 21·5	1·7927	38·382
Less OH ₂		18·333
		20·049

Results of the Four Solutions.

Solution I.	60·44 per cent.....	19·936
„ II.	58·46 „	20·032
„ III.	54·64 „	19·971
„ IV.	30·5 „	20·049
	Average.....	19·997

Solution of Ammonium Iodide in Absolute Alcohol.

The iodide of ammonium was well dried at 100°, and then boiled and kept with absolute alcohol some days; this was poured off and the salt twice more boiled with fresh quantities of absolute alcohol, the third solution being kept for use. The alcohol used had a density of $d_{15}^{15^{\circ}}$ 0·7947°. The strength of the solution was found by iodine determinations; it contained 21·10 per cent. of salt, and had the composition NH₄I + 11·782 mol. C₂H₅O.

The density determinations gave—

$$d_{10}^{10^{\circ}} 0\cdot9460, \quad d_{15}^{15^{\circ}} 0\cdot9421.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
17·0°	1·2790	51·561
16·0	1·2848	51·762
16·0	1·2834	51·702
15·0	1·2848	51·730
15·0	1·2863	51·788
Average 15·8	1·2836	51·709
Less alcohol, 2·780 × 11·782 =		32·754
		18·955

Ammonium Nitrate.

The aqueous solution used contained 59·7 per cent. of this salt; its composition was, therefore, $\text{NH}_4\text{NO}_3 + 5\text{OH}_2$.

The density determinations gave—

$$d_{6^{\circ}}^{6^{\circ}} 1\cdot2864, \quad d_{15^{\circ}}^{15^{\circ}} 1\cdot2814,$$

$$d_{25^{\circ}}^{25^{\circ}} 1\cdot27764.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0	0·9147	5·315
16·0	0·9191	5·341
16·0	0·9172	5·329
16·0	0·9176	5·332
15·0	0·9127	5·302
15·0	0·9130	5·304
Average 15·6	0·9157	5·320
Less 3OH_2		3·000
		2·320

Acid Sulphate of Ammonium.

The solution of this salt used was slightly supersaturated; it contained 66·67 per cent. of salt, and had the composition $\text{NH}_4\text{HSO}_4 + 3\cdot193 \text{ mol. OH}_2$.

The density determinations gave—

$$d_{15^{\circ}}^{15^{\circ}} 1\cdot4429, \quad d_{25^{\circ}}^{25^{\circ}} 1\cdot4387.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
18·0	1·0000	6·647
17·0	1·0061	6·656
17·0	0·9956	6·615
15·0	1·0061	6·664
15·0	1·0000	6·658
Average 16·4	1·0016	6·648
Less OH_2		3·193
$\text{NH}_4\text{HSO}_4 =$		3·455

Ammonium Sulphate.

An aqueous solution containing 40·00 per cent. of this salt was used; its composition was, therefore, $(\text{NH}_4)_2\text{SO}_4 + 11\text{OH}_2$.

The density determinations gave—

$$d_{10^\circ}^{10^\circ} 1.2308, \quad d_{15^\circ}^{15^\circ} 1.2296, \\ d_{20^\circ}^{20^\circ} 1.2285.$$

The magnetic rotations gave—

<i>t.</i>	Sp. rotation.	Mol. rotation.
16·0	1·0740	16·016
14·5	1·0721	15·984
11·5	1·0754	16·023
10·5	1·0743	16·005
23·0	1·0690	15·952
23·0	1·0690	15·952
23·0	1·0695	15·958
23·0	1·0685	15·945
18·0	1·0721	15·988
Average 18·05	1·0715	15·980
Less 11OH ₂		11·000
		4·980

Observations on the Nitrates, Nitro-compounds, and Nitrites.

On placing the boiling points of the nitrates, nitro-compounds, and nitrites side by side, the differences between them are seen to be very remarkable, thus the nitrates, which are the more highly oxygenated compounds, do not boil at so high a temperature as the nitro-compounds, whilst the nitrites, which are isomeric with the latter, are extremely volatile: thus—

	B. p.	B. p.
Nitro-compounds....	$\text{CH}_3\cdot\text{NO}_2$... 101°	$\text{C}_2\text{H}_5\cdot\text{NO}_2$... 114·5°
Nitrates	$\text{CH}_3\cdot\text{O}\cdot\text{NO}_2$.. 65°	$\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NO}_2$.. 87·5°
	Difference..... 36°	 27°
	B. p.	B. p.
Nitro-compounds.	$\text{C}_3\text{H}_7\cdot\text{NO}_2$... 131°	$(\text{CH}_3)_2\text{C}_2\text{H}_3\cdot\text{NO}_2$.. 140°
Nitrates	$\text{C}_3\text{H}_7\cdot\text{O}\cdot\text{NO}_2$.. 110·5°	$(\text{CH}_3)_2\text{C}_2\text{H}_3\cdot\text{O}\cdot\text{NO}_2$.. 124°
	Difference ... 20·5°	 16°

OF NITROGEN COMPOUNDS.

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	B. p.		B. p.
Nitro-compounds...	$\text{CH}_3\cdot\text{NO}_2\ldots 101^\circ$	$\text{C}_2\text{H}_5\cdot\text{NO}_2\ldots 114\cdot5^\circ$	
Nitrites	$\text{CH}_3\cdot\text{O}\cdot\text{NO}\ldots \text{Gas}$	$\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NO}\ldots 17^\circ$	
	<hr/>	<hr/>	
Difference..	more than 101°		$97\cdot5^\circ$
	B. p.		B. p.
Nitro-compounds	$\text{C}_3\text{H}_7\cdot\text{NO}_2\ldots 131^\circ$	$(\text{CH}_3)_2\text{C}_2\text{H}_5\cdot\text{NO}_2\ldots 140^\circ$	
Nitrites	$\text{C}_3\text{H}_7\cdot\text{O}\cdot\text{NO}\ldots 44^\circ$	$(\text{CH}_3)_2\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{NO}\ldots 67\cdot5^\circ$	
	<hr/>	<hr/>	
Difference	87°		$72\cdot5^\circ$

It is also worth noticing that in the lower members of the series the difference between the boiling points is greatest; thus in the comparison of the nitrites and nitro-compounds methyl nitrite is a gas, whilst the nitro-compound boils at 101° ; with the ethyl-compounds the diff. is $97\cdot5^\circ$, in the propyl 82° , and in the isobutyl $72\cdot5^\circ$. The same thing is seen when comparing the nitrates and nitro-compounds.

The densities do not vary in the same order as the boiling points, those of the nitrates being the highest. The nitrites, however, are considerably lower than the nitro-compounds: thus—

Ethyl nitrate.....	$d_{15^\circ}^{15^\circ}$	1.1159
Nitro-ethane	„	1.0561
Ethyl nitrite	$d_{0^\circ}^{0^\circ}$	0.920
Isobutyl nitrate	$d_{4^\circ}^{4^\circ}$	1.0334
Nitro-isobutane	0°	1.0083
Isobutyl nitrite	$d_{4^\circ}^{4^\circ}$	0.8878

The boiling points and densities of nitro-compounds being so very much higher than those of nitrites, made it desirable to determine the molecular weight of a nitro-compound at a lower temperature than had been previously employed; Raoult's method was therefore used. The experiment was made with glacial acetic acid, 1.250 parts of nitroethane being added to the 100 parts of acid, the result obtained for the molecular weight was 80, the theoretical number being 75, therefore, notwithstanding the above peculiarities, when in the liquid state nitroethane has the same molecular weight as that found by Victor Meyer for its vapour.

Nitric Acid.

The specific magnetic rotation of this substance is very low, only a little more than half that of water. The small amount of water in the specimen examined would, if anything, slightly reduce the rotation, as will be seen further on, but the maximum effect it would produce could not be more than 0·004 on the molecular rotation, it may therefore be disregarded.

Hydrated Nitric Acid.

The acid examined contained 56·74 H_2NO_3 , and had the composition $\text{HO}\cdot\text{NO}_2 + 2\cdot670 \text{ mol. OH}_2$. The effect of the water is to reduce the rotation, thus—

$$\begin{array}{r}
 \text{HO}\cdot\text{NO}_2 + 2\cdot670 \text{ OH}_2 = 3\cdot656 \\
 \text{less } 2\cdot670 \text{ OH}_2 = 2\cdot670 \\
 \hline
 \text{HO}\cdot\text{NO}_2 = 0\cdot986 \\
 \text{Pure HO}\cdot\text{NO}_2 \text{ gave } 1\cdot180 \\
 \hline
 \text{Difference} = \text{reduction} = 0\cdot194
 \end{array}$$

It therefore appears that combination takes place as in the case of sulphuric acid (*Jour. Chem. Soc.*, 1886, **49**, 783). This contraction, however, is not quite so large as would be expected from the union of 1 mol. of water with the acid, and it is very probable that for the existence of H_2NO_4 a larger percentage of water may have to be present than in the acid examined, as in the case of sulphuric acid, which apparently requires at least 3 mols. of water to be added to H_2SO_4 for the conversion of all the acid into $(\text{HO})_3\text{SO}$. The calculated molecular rotation for H_2NO_4 would be about 1·930; the above result makes it 1·986. The existence of such a compound as $(\text{HO})_3\text{N}\cdot\text{O}$ cannot be regarded as improbable, as we have an analogous compound in the case of orthophosphoric acid, $(\text{HO})_3\text{P}\cdot\text{O}$, and, moreover, there are several salts which correspond to $(\text{HO})_3\text{N}\cdot\text{O}$, as—

Trimeric nitrate, $\text{Hg}_3''\text{N}_2\text{O}_8$,
 Tricupric nitrate, $\text{Cu}_3''\text{N}_2\text{O}_8$,
 Triplumbic nitrate, $\text{Pb}_3''\text{N}_2\text{O}_8$,

though there are no nitrates of the alkali metals of this type corresponding to the alkaline ortho-phosphates.

Nitric Ethers.

When nitric acid is converted into a nitric ether the change which

takes place in the rotation is very similar to that of the acids of the fatty series and shows contraction, the increase of the rotation by the alcohol radical not being equal to that required for change of composition. The best compounds to compare nitric acid and its ethers with are perhaps formic acid and its ethers, as formic acid contains the smallest amount of carbon. By subtracting the molecular rotation of the acids from the rotation of the ether, the difference obtained for the changes of composition can easily be compared—

Nitrate of methyl	2·057	Formate of methyl . . .	2·495
Nitric acid	1·180	Formic acid	1·671
<hr/>		<hr/>	
Difference for CH_2	0·877	Difference for CH_2 . . .	0·824
Ordinary value for CH_2	1·023	Ordinary value for CH_2	1·023
<hr/>		<hr/>	
Nitrate of ethyl	3·084	Formate of ethyl	3·564
Nitric acid	1·180	Formic acid	1·671
<hr/>		<hr/>	
Difference for C_2H_4 . .	1·904	Difference for C_2H_4 . .	1·893
Ordinary value for C_2H_4	2·046	Ordinary value for C_2H_4	2·046
<hr/>		<hr/>	
Nitrate of propyl	4·085	Formate of propyl . . .	4·534
Nitric acid	1·180	Formic acid	1·671
<hr/>		<hr/>	
Difference for C_3H_6 . . .	2·905	Difference for C_3H_6 . .	2·863
Ordinary value for C_3H_6	3·069	Ordinary value for C_3H_6	3·069

From these comparisons we see how similar the behaviour of nitric acid is to that of formic acid. If acetic acid and its ethers had been taken for comparison, nearly the same amount of agreement would have been observed, so that nitric acid may be said to behave in a manner similar to a fatty acid in respect to its formation of ethers.

The only other oxygenated inorganic acid which has been examined is sulphuric acid, and this also behaves like the fatty acids in reference to its methyl ether—the only ether yet examined (*Jour. Chem. Soc.*, 1886, 49, 785)—thus :—

	Mol. rotation.
Sulphate of methyl	4·013
Sulphuric acid	2·315
	<hr/>
	2) 1·698
	<hr/>
CH_2	0·849
Ordinary value for CH_2	1·023

Ethylene Nitrate. Nitroglycol, C₂H₄(O·NO₂)₂.

The density of this substance is higher than that of ethyl nitrate, as might be expected; the difference at 15° is 0·3801 for d_{15}^{15} ; its specific rotation is slightly lower. The following comparison shows the variation between their molecular rotations :—

Ethylene nitrate	3·768
Ethyl nitrate.....	3·084
<hr/>	
Difference for displacement of H by $\text{—O·N} \begin{smallmatrix} \text{O} \\ \ll \end{smallmatrix} \text{O}$	0·684

Nitroglycerin, C₃H₅(O·NO₂)₃.

The sp. gr. differs from that of propyl nitrate at 15° by 0·5378 for d_{15}^{15} . The relationship of the molecular rotation of this compound to a mono- and di-nitrate will be best seen if the rotation of dinitrotrimethylene be calculated from that of dinitroethylene, and used with propyl nitrate for comparison—

		Diff.
Propyl nitrate.....	4·085	} 0·684
Trimethylene nitrate (calc.)	4·769	
Nitroglycerin	5·407	} 0·638

From this we see that the introduction of the second NO₂ has not produced quite such a large increase in the rotation as the first. This is strictly in accordance with displacements by hydroxyl (*Jour. Chem. Soc.*, 1884, **45**, 559), where the influence on the rotation gradually diminishes with the introduction of successive groups, so that the behaviour of these compounds is normal, and the results agree with the constitution usually assigned to them. Had nitroglycerin contained its nitrogen in any other combination of oxygen than as $\text{—O·N} \begin{smallmatrix} \text{O} \\ \ll \end{smallmatrix} \text{O}$, as it might if its constitution were represented as C₃H₂(NO₂)₃(OH)₃, the rotation when compared with that of propyl nitrate would be abnormal.

In the case of isobutyl nitrate, the influence of the iso-group is found to assert itself. This may be seen by comparing it with the calculated rotation of the normal nitrate:—

Butyl nitrate (iso)	5·180
Butyl nitrate (normal).....	5·108
<hr/>	
Difference for iso-group ..	0·072

This difference is somewhat less than that usually obtained. Thus in the case of the alcohols it is about 0·144, and for paraffins, aldehydes, and ethers about 0·112 (*Jour. Chem. Soc.*, 1884, **45**, 550—551).

Nitrites.

The only compound of this class examined is isobutyl nitrite.* This was selected as being more stable and less volatile than the lower numbers of the series. The nitrogen of this substance being united to the hydrocarbon radical by oxygen as in a nitrate, it may be considered in relation to isobutyl nitrate, thus—

	Mol. rotation.
Isobutyl nitrite	5·510
Isobutyl nitrate.....	5·180
	<hr/>
Difference +	0·330

The fact that isobutyl nitrite, although containing less oxygen than isobutyl nitrate, and consequently of a smaller molecular weight, has a higher molecular rotation, is very interesting, as showing that nitrogen when in an unsaturated condition affects the rotation of a substance in a similar manner to unsaturated carbon, by considerably increasing it (*Jour. Chem. Soc.*, 1884, **45**, 561). This point will be referred to again further on.

One of the reasons why nitrites have a much lower boiling point than nitrates may be due to their being unsaturated compounds, because we find in many cases that these have lower boiling points than saturated compounds. For example, vinyl chloride is a gas; ethyl chloride boils at 12·5°; dichlorethylene boils at 37°; ethylene chloride at 84°, &c.

Nitro-compounds.

These have the same empirical composition as the nitrites, but their rotations are very different, thus—

Propyl nitrite (cal.)	4·387
Nitropropane.....	3·819
	<hr/>
Difference —	0·568

At first sight this might be thought to be simply due to the nitrogen in nitropropane being saturated and in the nitrite unsaturated, and no doubt this is the *chief* cause of the variation; but it must be borne in mind that the structures of these two compounds

* Since writing the above some other nitrites have been examined, which give rotations confirming that of isobutyl nitrite.

differ, the nitrogen of the nitropropane being in direct union with the carbon, whilst that of the nitrite is attached to it by the intervention of oxygen, is sufficient to account for a small part of the difference between the rotations of these bodies.

The influence of the group $\text{—N}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ when displacing the hydrogen in paraffins is very small, thus—

Nitropropane	3·819
Propane (cal.)	3·590
Difference	<hr/> 0·229

With compounds of larger rotation than the above, it acts very curiously, actually reducing them, thus chloroform has a larger rotation than nitrochloroform (ehloropicrin)—

Chloroform	5·559
Nitrochloroform	5·384
Difference	<hr/> 0·175

The same thing is seen to a greater extent in the aromatic series when the nitro-compound has a much lower rotation than the hydrocarbon it is made from, and in nitroparaffins it probably reduces the value of the hydrocarbon radical.

As noticed on several occasions, the magnetic rotation of the first and second members of a series of carbon compounds do not give numbers which bear the same close relationship to each other as those of the higher members, which differ regularly by 1·023. This is also seen in the case of the nitro-compounds which vary by only 0·98, and in the nitrates, which vary first by 1·025 and then by 1·00, as the following diagram will show (Fig. 1), where they are compared with the formates and acetates. The circles on the dotted lines show the positions they would occupy if they had the ordinary relationships. The ordinates in this diagram are the decimal numbers only of the molecular rotations.

Observations on the Rotation of the Bases.

As the values for the rotation of ammonia were obtained from its solutions in water and in alcohol, it might be objected that they are not trustworthy, as probably combination of the ammonia and the solvent might take place. It was for this reason that two different solvents were employed; alcohol being taken as one, the probability of the combination of ammonia with this liquid being less than with water. The quantities of the solutions prepared were considerable, so that on taking out samples for examination no appreciable change

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FIG. I.

of composition would take place in the bulk from loss of ammonia. It will be observed that both solutions gave practically the same rotations for ammonia, viz., 1·818 and 1·826.

It would appear, therefore, that when ammonia is absorbed either by water or by alcohol, the product simply consists of the solvent and ammonia. This is confirmed by the rotations of its nitrate and acid sulphate. I hope, however, to examine ammonia liquefied by pressure at some future time, and also other easily liquefiable gases.

The displacement of an atom of hydrogen in ammonia by an alcohol radical increases its rotation, as would be expected, but not to the full extent usual for a change of composition, which is 1·023 for every CH_2 in the homologous series. This, however, is not a case quite comparable with the homologous series.

In the displacement of a second atom of hydrogen in ammonia, the rotation is increased proportionally more than by the first, and in diethylamine it is about the usual amount for the homologous series. In dipropylamine it is only a little less.

When, however, we come to the displacement of the third hydrogen, a very remarkable increase of the rotation takes place, marking out a clear distinction between diamines and triamines.

The effect of displacing a fourth atom of hydrogen by an alcohol radical in ammonium chloride is still greater than for the displacement of the third in ammonia, or, what is the same thing, in ammonium chloride; this will be seen by the following comparison:—

Tetrethylammonium chloride	13·624
Triethylamine hydrochloride (cal.)	10·005

Difference for C_2H_4	3·619
---	-------

The following are the results obtained with the ethylamines and propylamines, showing the differences resulting from the displacements and between the variations of rotation. The displacement of hydrogen by C_2H_5 , C_3H_7 , and C_4H_9 is, of course, as far as composition is concerned, practically the same as the addition of C_2H_4 , C_3H_6 , and C_4H_8 .

		Molecular rotation.	Diff. for C_2H_4 .	Difference between rotations for each C_2H_4 .
Ammonia	N { H H H	1·818	1·791	0·262
Ethylamine	N { Et H H	3·609		
Diethylamine	N { Et Et H	5·662	2·053	
Triethylamine	N { Et Et Et	8·518	2·856	

			Molecular rotation.	Diff. for C_3H_6 .	Difference between rotations for each C_3H_6 .
Ammonia.....	N	$\begin{Bmatrix} H \\ H \\ H \end{Bmatrix}$	1·818	2·745	0·241
Propylamine.....	N	$\begin{Bmatrix} H \\ Pr \\ H \end{Bmatrix}$	4·563		
Dipropylamine	N	$\begin{Bmatrix} H \\ Pr \\ H \end{Bmatrix}$	7·549	2·986	1·129
		$\begin{Bmatrix} Pr \\ H \\ Pr \end{Bmatrix}$		4·115	
Tripropylamine	N	$\begin{Bmatrix} H \\ Pr \\ Pr \\ Pr \end{Bmatrix}$	11·664		

So that, whilst the variation of the rotations for C_2H_4 between ethylamine and diethylamine differs by only 0·262, those between diethylamine and triethylamine differ by no less than 0·803; between propylamine and dipropylamine, the variation of the rotation for C_3H_6 is only 0·241, yet between dipropylamine and tripropylamine it amounts to 1·129.

The relationships of the rotations of the ethylamines and propylamines amongst themselves and to each other will be more clearly understood by reference to Fig. 2, where they are represented graphically.

In case of the displacement with *isobutyl*, the examination of the first two only have been made, but they give results much the same as in the other cases. They are, however, interesting as showing that the iso-radicals, as compared with the normal, still exert their peculiar influence on the rotation. The following is a comparison of the results obtained with these substances:—

			Molecular rotation.	Diff. for C ₄ H ₈ (Iso).	
Ammonia.....	N	$\left\{ \begin{array}{c} H \\ H \\ H \end{array} \right.$	1·818	3·874	0·370
Isobutylamine.....	N	$\left\{ \begin{array}{c} Bu \\ H \\ H \end{array} \right.$	5·692		
		$\left\{ \begin{array}{c} H \\ Bu \\ H \end{array} \right.$	4·244		
Diisobutylamine.....	N	$\left\{ \begin{array}{c} Bu \\ Bu \\ H \end{array} \right.$	9·936		

To get the true effect of the iso-group on the rotations of these bases, it would be necessary to compare them with the normal butylamines, but these have not been examined; it can be shown, though not very accurately, by comparing them with the propylamines, in which case the difference between them should be greater than that for the value of CH_2 ; this will be found to be the case, thus—

FIG. 2.

CURVES FORMED BY THE ROTATION OF ETHYLAMINES AND
PROPYLAMINES.

Isobutylamine	5·692
Propylamine	4·563
	<hr/>
Difference for CH ₂	1·129
	<hr/>
Difference for iso-group.	0·106
Diisobutylamine	9·936
Dipropylamine	7·549
	<hr/>
	2·387
Difference for CH ₂ × 2.....	2·046
	<hr/>
Difference for two iso-groups	0·341

These numbers are as close as could be expected by this method of comparison, and clearly show that this iso-group influences the rotations of amines in the same manner as it does other classes of compounds.

The results produced by the displacement of the hydrogen of ammonia by alcohol radicals stand alone; the only other analogous cases occur in the displacement of the hydrogens in water by ethyl, when the rotations increasingly rise with each, much as in the two first displacements in ammonia, thus—

		Molecular rotation.	Difference.	
Water	O { $\begin{matrix} \text{H} \\ \text{H} \end{matrix}$	1·000	1·780 } 1·997 }	0·217
Ethyl alcohol	O { $\begin{matrix} \text{Et} \\ \text{H} \end{matrix}$	2·780		
Ethyl oxide.....	O { $\begin{matrix} \text{Et} \\ \text{Et} \end{matrix}$	4·777		

And when the hydrogen in the methyl of methyl alcohol is displaced by methyl, but although we at first get an increase in the rotation of this group for the first and second displacements, the analogy with ammonia then fails, as the introduction of a third atom of methyl does not increase the rotation to the same extent as the others do.

		Molecular rotation.	Difference.	
Methyl alcohol.....	HOC { $\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \end{matrix}$	1·640	1·140 } 1·239 }	0·099
Ethyl alcohol	HOC { $\begin{matrix} \text{Me} \\ \text{H} \\ \text{H} \end{matrix}$	2·780		
Isopropyl alcohol.....	HOC { $\begin{matrix} \text{Me} \\ \text{Me} \\ \text{H} \end{matrix}$	4·019	1·103 }	-0·136
Tertiary butyl alcohol....	HOC { $\begin{matrix} \text{Me} \\ \text{Me} \\ \text{Me} \end{matrix}$	5·122		

In *allylamine* we have an example of an unsaturated radical displacing the hydrogen of ammonia; as in the other cases, this being a first displacement, the radical does not increase the rotation to the same extent it usually does in other classes of compounds, thus—

			Increase due to C_3H_5 .
Ammonia.....	N	$\left\{ \begin{array}{l} H \\ H \\ H \end{array} \right.$	1·818
Allylamine	N	$\left\{ \begin{array}{l} Al \\ H \\ H \end{array} \right.$	5·587
			3·769
Allylacetic acid.....			6·426
Acetic acid.....			2·525
			<hr/>
Increase due to C_3H_5 ..			3·901
Ethyl allylacetoacetate			10·382
Ethyl acetoacetate			6·501
			<hr/>
Increase due to C_3H_5 ..			3·881
Ethyl allylmalonate			11·281
Ethyl malonate			7·410
			<hr/>
Increase due to C_3H_5 ..			3·871

If compared with propylamine, the increase due to the radical being unsaturated will be seen—

Allylamine	5·587
Propylamine.....	4·563
	<hr/>
Difference.....	1·024

This is about the usual difference, although it is a little larger than is usually found for compounds containing allyl.

Pentamethylenediamine is a useful example of the successive displacements of hydrogen by NH_2 in paraffins. This can be seen by comparing its rotation with that of amylamine and then again with pentane.

		Difference for displacement of H by NH_2 .
Pentane	5·638	} 0·971
Amylamine (calculated) .	6·609	
Pentamethylenediamine..	7·492	} 0·883

From this it is seen that the second displacement produces rather

less effect on the rotation than the first; this we find to be the case in other displacements in the paraffins, as in the hydroxyls of glycerin previously referred to, &c.

Before considering the rotations of piperidine and pyridine, it will be as well to consider those of the two nitriles, propionitrile and glutaric nitrile (cyanide of trimethylene). To compare these compounds it will be the simplest plan to add 1·023 to the rotation of propionitrile, which will give the value of butyronitrile, viz., 1·023 + 3·331 = 4·354, and both numbers will then be related to compounds of the same hydrocarbon; we then get the following comparisons:—

Propane (calculated)	3·590	}	0·764
Butyronitrile (calculated).	4·354		
Glutyronitrile	5·136	}	0·782
Average			0·773

In this case the first and second displacements by CN give nearly the same numbers, the second being slightly the higher; this is exceptional in compounds of this class, and may possibly be due to some slight impurity in the glutyronitril: the numbers, however, cannot be far from the truth.

Piperidine.—The magnetic rotation of this base is very low, showing clearly that it is a saturated compound. The following is a comparison of it with amylamine, which contains two atoms more hydrogen:—

Amylamine	6·609
Piperidine	5·810
	<hr/>
	0·799

This is a rather larger difference than is usually found between a saturated fatty compound and a saturated *ring* compound, and is more than the value of $H_2(0·508)$ by which they differ.

A number of ring compounds discovered by my son have had their magnetic rotation determined, and will show this; those containing a methyl group will require to have the usual amount deducted from them, as it has been shown that this increases the rotation by about 0·111, as in iso- and secondary compounds.

Valeric acid, $C_5H_{10}O_2$	5·513
Tetramethylenecarboxylic acid, $C_5H_8O_2$	5·049
	<hr/>
Difference	0·464

Enanthylic acid, $C_7H_{14}O_2$	7.552
Methylpentamethylenecarboxylic acid, $C_7H_{12}O_2$..	6.928
	<hr/>
Less	0.624
	<hr/>
Difference	0.513
Caprylic acid, $C_8H_{16}O_2$	8.565
Methylhexamethylenecarboxylic acid, $C_8H_{14}O_2$..	7.974
	<hr/>
Less.....	0.591
	<hr/>
Difference	0.480
Ethyl propylmalonate, $C_6H_8O_4Et_2$	10.370
Ethyl tetramethylenecarboxylate, $C_6H_6O_4Et_2$...	9.940
	<hr/>
Difference	0.430

The average of these differences is 0.471, not very far from the value of H_2 by which they differ, but only a little more than half the difference found between amylamine and piperidine; in this case, however, we are dealing with a base, and it has been seen that substances of this class are somewhat exceptional in their behaviour; this, therefore, may be the cause of the variation.

Pyridine has also a very low rotation if considered in relation to aniline, from which it differs only by CH_2 , thus—

Aniline.....	16.162
Pyridine	8.761
	<hr/>
Difference....	7.401

in fact, it is lower than benzene, from which it differs only by having N substituted for CH, and the value of this element as N''' is not very different from that of CH (see p. 738).

Benzene	11.297
Pyridine.....	8.761
	<hr/>
	2.536
Less for H	0.254
	<hr/>
Difference.....	2.282

This is very remarkable, especially when we find that the introduction of NH_2 into benzene increases its rotation so much.

Aniline	16·162
Benzene	11·297
	<hr/>
Influence of NH_2	4·865

By comparing pyridine with piperidine the effect of the difference of H_2 , by which they vary in composition, will be seen.

Pyridine	8·761
Piperidine	5·810
	<hr/>
	2·951

This shows how much the higher of the two the rotation of pyridine is, through being an unsaturated compound, although of less molecular weight than piperidine. This is not very far from three times the difference existing between saturated and unsaturated compounds differing from each other by H_2 .

Isobutylamine with Water and Alcohol.—As aqueous and alcoholic ammonia appear to be simply solutions of NH_3 in these solvents, it was thought that it would be well to see if a monamine acted in the same way. Solutions consisting of equal volumes of isobutylamine and water, and isobutylamine and alcohol, at 15° , were therefore made; in both cases heat was evolved and contraction took place; the latter will be seen by a comparison of the found and calculated densities of these mixtures.

Water and Isobutylamine.

Density found	0·9002
Average density	0·8681
	<hr/>
Difference due to contraction ...	0·0321

Alcohol (absolute) and Isobutylamine (the mean of two preparations).

Density found	0·7791
Average density.....	0·7656
	<hr/>
Difference due to contraction....	0·0135

On comparing the magnetic rotations of these mixtures, it will be found that a small amount of combination is indicated.

Equal Volumes of Water and Isobutylamine.

Molecular rotation of mixture calculated	
from constituents	11·200
Molecular rotation of mixture found	11·099
	<hr/>
Difference	0·101

Equal Volumes of Alcohol and Isobutylamine.

Molecular rotation of mixture calculated	
from constituents.....	10·459
Molecular rotation of mixture found.....	10·361
	<hr/>
Difference.....	0·098

Piperidine and Water.—This base has a great attraction for water, and considerable heat is evolved on mixing these two substances.

The mixture examined had the composition $C_5H_{11}N + OH_2$. The following is a comparison of the average and found densities of the mixture:—

Density found	0·9133
Average density	0·8897
	<hr/>
Difference due to contraction ...	0·0236

This is a considerable contraction for the small quantity of water used, viz., 17·07 per cent. The magnetic rotation of this also shows a small amount of combination.

Molecular rotation of mixture calculated	
from constituents.....	6·810
Molecular rotation found	6·724
	<hr/>
Difference	0·086

The rotation of isobutylamine with water and alcohol, and of piperidine with water, therefore indicates that these mixtures contain a small quantity of unstable compounds, of the composition—

the amount most probably varying with the temperature, as was found in the examination of mixtures of aldehyde with water and alcohol (*Jour. Chem. Soc.*, 1887, **51**, 815—819), and of course may be the case with solutions of ammonia, but, if so, the amount entering into combination at the temperatures at which the rotations were observed was too small to appreciably affect them.

Value of Nitrogen.

From the foregoing results it is possible to get an estimate of the amount of influence nitrogen has on the magnetic rotation of bodies. In the first place, it will be as well to consider it as it exists in

nitrates, where it is in a pentavalent condition. If these bodies have the composition $\text{RO} - \text{N} \ll \text{O}$, it will be necessary to subtract from a nitrate, the value of the radical, also that of one oxygen as found in the hydroxyl of acids, namely, 0.137, and for the two oxygens which are fully saturated with nitrogen, that is the values which this element has when fully saturated with carbon, viz., 0.261, which is probably the same as if saturated with nitrogen. We then get from ethyl and propyl nitrates the following results:—

Ethyl nitrate	3.084	
Ethyl	2.300	} 2.959
O ₂ saturated by N.....	0.522	
O in hydroxyl of acids..	0.137	
<hr/>		
N ^v	0.125	
Propyl nitrate	4.085	
Propyl	3.323	} 3.982
O ₂	0.522	
O	0.137	
<hr/>		
N ^v	0.103	

These numbers are not far apart, and show that the value of nitrogen when saturated is very low, namely, about 0.114.

This method of calculation cannot be satisfactorily applied to nitro-compounds, because we have no very definite information as to the effect produced on the rotation when $-\text{N} \ll \text{O}$ is in direct union with the carbon of an alcohol radical, except that it appears to reduce the value of the hydrocarbon radical to a small extent.

In the *nitrites* the nitrogen is trivalent. We can get a value for it in a similar manner to that used with nitrates, taking the constitution to be

It will be more simple, and perhaps more correct, if the rotation of propyl nitrite be used in this estimation; this is easily obtained from that of isobutyl nitrite, by adding to the rotation of propyl nitrate the difference found between isobutyl nitrite and nitrate; this is 0.330. Propyl nitrite will therefore be 4.085 (propyl nitrate) + 0.330 = 4.415.

Propyl nitrite	4.415
Propyl	3.323
O saturated with N.....	0.261
O as in hydroxyl of acids.....	0.137
	<hr/>
N'''	0.694

The rotation of nitrogen in bases can be found approximately by subtracting the rotation of a paraffin from a base and then the value of H from the remainder.

Amylamine (calculated)	6.609
Pentane	5.638
	<hr/>
NH.....	0.971
Less H	0.254
	<hr/>
N'''	0.717

The cyanides also can be used to give a value, thus—

Ethyl cyanide	} 3.331
Isopronitryl	
Less ethyl	2.300
	<hr/>
CN	1.031
Less C	0.515
	<hr/>
N'''	0.516

Taking trimethylene cyanide we get—

Trimethylene cyanide	5.136
Trimethylene, $\text{CH}_2 \times 3$	3.069
	<hr/>
$(\text{CN})_2$	2.067
Less C_2	1.030
	<hr/>
N_2 '''.....	1.037
N'''	0.518
Average value of N''' = 0.611.	

In the cyanides the value comes a little lower than in the other products, but it is possible that the value of carbon subtracted is not quite correct, as we do not know its true value when three-fourths saturated with nitrogen; though of course in all the values found for the elements they are only approximate and not absolute, as they are found to vary slightly in different series of compounds, and in some instances they vary considerably. These numbers, however, show the

interesting fact that unsaturated nitrogen (N''') has a very much greater influence on the magnetic rotation of compounds containing it than when it is saturated (N^V); this is about 0.5, taking the average of all the values given, and practically half the amount of the difference usually found between saturated and unsaturated carbon compounds (differing by H_2).

The clearest evidence of this is, perhaps, after all, best seen in the comparison between a nitrite and nitro-compound, where both have the same composition, the variation due to difference of constitution probably not reducing the rotation of the nitro-compounds by more than about 0.1; this would then leave 0.468 between these compounds in favour of N''' over N^V .

Hydrochloric, Hydrobromic, and Hydriodic Acids.

When studying the magnetic rotations of the aqueous solutions of these acids, one striking fact is noticed, and that is the magnitude of the numbers as compared with those deduced from the rotations of the chlorides, bromides, and iodides of the alcohol radicals. The latter, however, refer to the acid in combination, and not in the free state, but the addition to them of about 0.2 will make the necessary correction for this. The numbers are as follows:—

		In combina- tion.	In free state.
Hydrochloric acid ..	Cl	$1.733 + H\ 0.254 = 1.987$	2.187
Hydrobromic ,, ..	Br	$3.562 + H\ 0.254 = 3.816$	4.016
Hydriodic ,, ..	I	$7.757 + H\ 0.254 = 8.011$	8.211

Concentrated aqueous solutions of these acids were first examined, and these gave molecular rotations for the pure acids nearly twice as large as the above; a more dilute solution of one of the acids was then examined, and this gave a still higher result, and it soon became evident that acids in different states of concentration gave different results; it appears necessary, therefore, to examine a graduated series of each acid, commencing with very concentrated and finishing with dilute solutions. The following are the results obtained:—

				Mol. rotation of HCl.
Hydrochloric acid	41.70	per cent.	HCl	4.045
,, 	36.5	,, ,,		4.215
,, 	30.86	,, ,,		4.303
,, 	25.60	,, ,,		4.405
,, 	15.63	,, ,,		4.419

				Mol. rotation of HBr.
Hydrobromic acid		65.59	per cent. HBr	7.669
"		56.00	" "	8.061
"		39.71	" "	8.415
"		24.60	" "	8.547
"		15.47	" "	8.519
				Mol. rotation of HI.
Hydriodic acid		67.02	per cent. HI	17.769
"		65.10	" "	17.868
"		61.97	" "	18.117
"		56.78	" "	18.308
"		42.70	" "	18.403
"		31.77	" "	18.451
"		20.77	" "	18.428

In all these series it is seen that the molecular rotations found for the pure acids first rise as the solution is diluted, and then become practically stationary, the variations of the last two numbers in each series not being more than might be expected from experimental errors.

These results have been graphically represented on Fig. 3; in this, two curves start from the calculated values of each acid, one representing the rotations in reference to the percentage of the acids, the other in reference to the molecular composition of the solution. The registers for these are both given on the top of the diagram, whilst those for the rotations are given in three columns, one on the left side and two on the right side, each headed with the formula of the acid it refers to. This arrangement was adopted to get the three sets of curves as nearly as possible in juxtaposition. It will be noticed how great a similarity there is in the character of these curves, especially those corresponding to the molecular proportions; each rising rapidly from the calculated rotations of the acids and then gradually turning off to a horizontal line. The difference of the highest rotation, represented by the horizontal lines, from the calculated is in all cases more than twice as large as the latter, thus—

	HCl.	HBr.	HI.
Highest number	4.412	8.533	18.435
Calculated number	2.187	4.016	8.211
Difference	2.225	4.517	10.224

All the rotations of these acids closely approach the horizontal line,

and therefore their highest rotations, when they contain from 6 to 7 mols. of water.

It is very difficult to form a conception of the meaning of these results, so far as experiments have gone. Acids when diluted with water either combine with it, and thus cause a reduction in the rotation, as sulphuric (*J. Chem. Soc.*, 1886, **49**, 782—784) and nitric acids, or are not influenced by it, as in the case of formic, acetic, propionic (*J. Chem. Soc.*, 1886, **49**, 778—781), glutaric acids, &c., but in no case does an increase take place; such a result would indicate dissociation. It was thought that something of this kind might take place, the very concentrated acids possibly containing complex molecules built up of several molecules of the acids, and breaking down on dilution; thus the highest rotations would be the correct ones for the simple acids, but the difficulty in the way of this is that in compounds in which the halogens must exist in single atoms the rotations of the acids deduced from them are only half those found in the examination of the dilute solutions. On account of the difficulty of finding an explanation, experiments were made to see if the solvent played any part in this matter; it was, however, found very difficult to get a liquid which would dissolve these acids in sufficient quantity, and at the same time not to be affected by them. Acetic anhydride, for example, was found to change rapidly into acetic acid and acetyl chloride, or bromide, according as it was saturated with hydrochloric or hydrobromic acids. Heptane was found to be only capable of dissolving about 1 per cent. of hydrochloric acid. At last isoamyl oxide was tried, and this dissolved about 18 per cent. of hydrobromic acid and 13 per cent. of hydrochloric acid. Unfortunately hydrobromic acid was found to gradually act upon it, so that it could not be examined in this solvent. Hydrochloric acid, however, has no influence upon it. Its solution in this substance was therefore examined. Two preparations were made, and these gave the following results:—

	Mol. rotation. HCl.
I. Containing 10·68 per cent. HCl gave	2·211
II. ,, 12·82 ,, ,, 	2·265
	<hr/>
Average.....	2·238
Calculated rotation	2·187
	<hr/>
Difference	0·051

These two results are very interesting, as they are quite different from those obtained on the examination of aqueous solutions, and are

as close to the calculated as could be expected, considering the small percentage of acid contained in the specimens measured. No doubt if hydrobromic and hydriodic acids could have been examined in the same way analogous results would have been obtained. It appears therefore that the calculated numbers for the halogen acids are practically the correct ones, and that the high results obtained from the aqueous acids are *abnormal*, and in some unaccountable way caused by the presence of water, though, as already mentioned, chemical union with water would not increase, but reduce the rotations of the acid, according to all previous experiments.

G. Lemoine (*Ann. Chem. Phys.* [5], **12**, 239), as well as Bertholet, have noticed the peculiar fact that, whilst gaseous hydriodic acid is decomposed by light the aqueous solutions are not, this seems to indicate that water has some peculiar influence upon this acid.

Salts of Ammonia and Compound Ammonias.

The results of the examination of the solutions of the salts of ammonia and the compound ammonias containing hydrochloric, hydrobromic, and hydriodic acids are not less remarkable than those of the acids themselves, except that the effect of various degrees of dilution does not influence the molecular rotation of the salts; this will be seen from the results of the examination of the four aqueous solutions of ammonium iodide and the two of ammonium bromide, as given in the following tables:—

					Mol. rotation. NH ₄ I.
I.	NH ₄ I,	60.44	per cent.		19.936
II.	„	58.46	„		20.032
III.	„	54.64	„		19.971
IV.	„	30.50	„		20.049
Average					19.996

					Mol. rotation. NH ₄ Br.
I.	NH ₄ Br,	40.42	per cent.		10.159
II.	„	25.00	„		10.196
Average					10.177

From these it will be seen that although the solutions vary very considerably in strength, yet they give numbers which are practically the same in both instances. This fact should be borne in mind when

considering the results of the examination of the aqueous solutions of other salts referred to in this paper.

On considering the rotations obtained with solutions of the different salts formed by ammonia and the compound ammonias with the halogen acids, it will be useful to find what their calculated rotations are, so as to compare them.

The rotation of the acids taken in this place will have to be those found for them in combination, already given on page 739, then, as ammonia and the compound ammonias contain unsaturated nitrogen which will become saturated on their union with the above acids, this, as shown elsewhere, will reduce the rotation by about 0·5. The rotations of these salts may then be calculated thus :—

			Calculated.	Found.
N_4HCl	$= \text{HCl } 1\cdot987 + \text{NH}_3$	$1\cdot818 - 0\cdot5$	4·305	6·096
NH_2EtHCl	$= \text{HCl } 1\cdot987 + \text{NH}_2\text{Et}$	$3\cdot609 - 0\cdot5$	6·096	7·997
NHEt_2HCl	$= \text{HCl } 1\cdot987 + \text{NHEt}_2$	$5\cdot662 - 0\cdot5$	8·149	9·896
NEt_3HCl	$= \text{HCl } 1\cdot987 + \text{NEt}_3$	$8\cdot518 - 0\cdot5$	11·005	11·739
$\text{C}_5\text{H}_{11}\text{NHCl}$	$= \text{HCl } 1\cdot987 + \text{C}_5\text{H}_{11}\text{N}$	$5\cdot810 - 0\cdot5$	8·297	10·034
NH_4Br	$= \text{HBr } 3\cdot816 + \text{NH}_3$	$1\cdot818 - 0\cdot5$	6·134	10·177
NH_4I	$= \text{HI } 8\cdot011 + \text{NH}_3$	$1\cdot818 - 0\cdot5$	10·329	19·996

From the above it will be seen that the experimental results are greatly in excess of the calculated, and on examining them they are found to be nearly equal to those which would result from simply adding together the rotations of the bases, and the highest or *abnormal* rotations of the acids, no allowance being made for combination or saturation of nitrogen :—

	Abnormal rotation.		Calculated.	Found.
NH_4Cl	$= \text{HCl } 4\cdot412 + \text{NH}_3$	$1\cdot818$	6·230	6·096
NH_2EtHCl	$= \text{HCl } 4\cdot412 + \text{NH}_2\text{Et}$	$3\cdot609$	8·021	7·997
NHEt_2HCl	$= \text{HCl } 4\cdot412 + \text{NHEt}_2$	$5\cdot662$	10·074	9·896
NEt_3HCl	$= \text{HCl } 4\cdot412 + \text{NEt}_3$	$8\cdot518$	12·930	11·739
$\text{C}_5\text{H}_{11}\text{NHCl}$	$= \text{HCl } 4\cdot412 + \text{C}_5\text{H}_{11}\text{N}$	$5\cdot810$	10·222	10·034
NH_4Br	$= \text{HBr } 8\cdot533 + \text{NH}_3$	$1\cdot818$	10·351	10·177
NH_4I	$= \text{HI } 18\cdot436 + \text{NH}_3$	$1\cdot818$	20·253	19·996

It is thus seen how little the numbers obtained in this manner vary from those found, except in the case of triethylamine hydrochloride, which will be referred to further on. The hydrochloride of piperidine, which is analogous to a diamine, behaves in the same way as salts of that class. The only explanation I can find for these remarkable results is, that these salts when in solution are almost

entirely dissociated into their acids and bases, the acids, owing to the presence of water, acquiring the high or abnormal values; the slight difference between the calculated and experimental numbers being due to the presence of a very small quantity of undissociated salt. In the case of triethylamine, the amount of dissociation is evidently considerably less than in the other salts, the third molecule of ethyl it contains adding to its stability. This is only what might be expected, as the addition of a fourth molecule yields the remarkably stable chloride of tetrethylammonium. This has also been examined, and probably does not dissociate when in solution, or only to a small extent. The rotations obtained from the chloride of tetrethylammonium and the hydrochlorides of ethylamine and ammonia have been plotted out side by side with the calculated numbers in Fig. 4. From this it will be seen that the calculated numbers form a curved line (similar to the ethylamines, Fig. 2, facing p. 730), but straightens a little between triethylamine hydrochloride and triethylammonium chloride, whilst the experimental form a straight line; the latter, owing to the dissociation of the salts, is considerably far apart from the curved line in the lower portion of the figure, but both meet at the top, at a point representing tetrethylammonium chloride. It will also be seen that the distance between the curved and straight lines is less at the points representing triethylamine hydrochloride than at those representing the other hydrochlorides, thus showing a smaller amount of dissociation.

From the different results obtained from solutions of hydrochloric acid in two kinds of solvents, it appeared desirable to examine some of these salts in solvents other than water. Solutions of diethylamine hydrochloride, and ammonium iodide in absolute alcohol were therefore employed, as no other suitable solvent could be found, but from the rotations obtained dissociation evidently takes place, though not to quite so large an extent as when water is used, as the following numbers show:—

	Mol. rotation. Alcoholic solution.	Mol. rotation. Aqueous solution.	Calculated.
Diethylamine hydrochloride...	9·674	9·896	7·149
Ammonium iodide	18·955	20·032	10·409

All these results made it important to study the behaviour of some other salts of ammonium when in solution, and for this purpose aqueous solutions of the nitrate, acid sulphate, and neutral sulphate of ammonium were employed. Nitrate of ammonium is not supposed to dissociate to any appreciable extent, nor is it likely that the acid sulphate would; the neutral sulphate, however, is known to do so to

FIG. 4.

CURVES SHOWING ROTATIONS INDICATING DISSOCIATION
OF HYDROCHLORIDES WHEN IN SOLUTION.

some extent, as it gives off some of its ammonia when its solution is boiled.

The calculated rotations for these salts compared with the experimental rotation are as follows :—

Nitrate of Ammonium.

HNO ₃	1·180
NH ₃	1·818
<hr/>	
Less 0·2 reduction due to combination and	} 2·998
0·5 for the nitrogen being saturated =	
0·7	
	<hr/>
	2·298
Found	2·320
	<hr/>
Difference	0·032

Acid Sulphate of Ammonium.

H ₂ SO ₄	2·315
NH ₃	1·818
<hr/>	
	4·133
Less 0·7 as above	0·700
	<hr/>
	3·433
Found	3·455
	<hr/>
Difference	0·022

Neutral Sulphate of Ammonium.

H ₂ SO ₄	2·315
(NH ₃) ₂	3·636
<hr/>	
	5·951
Less 0·7 as above × 2	1·400
	<hr/>
	4·551
Found.....	4·980
	<hr/>
Difference	0·431

From this it is seen that the nitrate and acid sulphate of ammonium give results very nearly identical with those calculated. This is valuable in two ways—first, inasmuch as it shows the method of calculating the rotation of these salts to be trustworthy; and, secondly,

that the very high numbers obtained by the halogen acids and their salts with ammonia and compound ammonias are abnormal.

The rotation of the neutral sulphate of ammonium is rather higher than the calculated, probably the latter is a little low, as the introduction of a second ammonia would most likely be attended with a slightly smaller amount of change than that represented by 0.7; it would not, however, nearly account for all the difference found, which is no doubt due to a certain amount of dissociation of the salt.

It is very probable that the determination of the magnetic rotations of salts in solution may be of value in distinguishing between those salts that do and those that do not dissociate in the presence of water, as well as to give an idea of the extent of dissociation.

With regard to the foregoing results, it was thought that the numbers obtained for the heat of neutralisation of the salts under consideration might in some way correspond with those of the magnetic rotations; they do not appear, however, to bear in the least upon this subject, chloride of ammonium, and the hydrochlorides of the ethylamines giving numbers close to those obtained for the nitrate and sulphate of ammonium. Triethylamine hydrochloride is also a further exception, as it gives a very low number for its heat of neutralisation; this is quite contrary to the results of the magnetic rotation, which show that this salt exists in a less dissociated condition when in solution than the other hydrochlorides, and therefore would be expected to give higher numbers.

The following table gives the numbers obtained for the heat of neutralisation of most of the salts examined:—

The principal results of this research may be briefly summed up as follows:—

Nitric acid when diluted with water combines with it, forming an acid, $\left. \begin{matrix} \text{HO} \\ \text{HO} \\ \text{HO} \end{matrix} \right\} \text{N}:\text{O}$, corresponding to orthophosphoric acid, $\left. \begin{matrix} \text{HO} \\ \text{HO} \\ \text{HO} \end{matrix} \right\} \text{P}:\text{O}$.

Nitric acid forms ethers in an analogous way to sulphuric and the fatty acids, that is, with condensation.

Unsaturated nitrogen, N''' , acts in a manner analogous to unsaturated carbon, the rotations of compounds in which it exists being considerably higher than those containing the saturated element.

The low rotations of nitro-compounds as compared with those of the nitrites is chiefly due to the former containing saturated and the latter unsaturated nitrogen.

That aqueous and alcoholic ammonia, at the ordinary temperature, appear to consist of solutions of NH_3 only; but in the case of aqueous and alcoholic solutions of isobutylamine and aqueous solutions of piperidine a small amount of combination takes place with these solvents at ordinary temperatures.

That in the displacement of the hydrogen in ammonia by alcohol radicals the rotation is not increased by the usual amount due to the change of composition for the first, but it increases for the second, and becomes very large for the third displacement, and in the displacement of the fourth hydrogen in ammonium salts it is still larger. The introduction of iso-radicals increases the rotation more than the normal ones to quite the usual extent.

Allylamine behaves like other unsaturated compounds, giving a considerably higher rotation than the corresponding saturated base, propylamine.

Pentamethylenediamine shows that the effect of a second displacement of hydrogen in paraffins by NH_2 is to produce slightly less influence on the rotation than the first.

Piperidine has a rotation showing that it is a saturated compound; it is, however, slightly lower than that usually found for saturated ring-compounds when compared with paraffin-derivatives.

Hydrochloric acid, when examined in its solution in amyl oxide, gives a rotation practically the same as that found for its elements when in compounds, that is H in paraffins and Cl in the chlorides of the alcohol radicals, with the addition necessary to represent it in the free state, 2.238 being found and 2.187 calculated.

The solutions of hydrochloric acid in water give abnormally high rotations for this acid, increasing up to certain limits with the *dilution* of the solution, the highest rotation being more than double that of the calculated.

Aqueous solutions of hydrobromic and hydriodic acids also behave in an abnormal manner, like those of hydrochloric acid, the results being rather more strongly marked. This cannot be explained on the assumption that the acids combine with water, such a result would lower instead of increase the rotation.

The rotation of ammonium salts when in aqueous solution is not influenced by the strength of the solution.

The salts of ammonia and the compound ammonias with hydrochloric, hydrobromic, and hydriodic acids when in aqueous solutions give very high rotations, which can only be explained on the assumption that they are almost entirely in a state of dissociation. Their

acids, on account of the water present, would then possess the abnormal rotations referred to above, and this would give the solutions their high values. Alcoholic solutions of ammonium iodide and diethylamine hydrochloride behave like the aqueous, but the rotations are not quite so high, showing less dissociation.

Triethylamine hydrochloride does not dissociate nearly so much as the other hydrochlorides, and the chloride of tetrethylammonium is thought not to dissociate at all, or only very slightly, when in aqueous solution.

Aqueous solutions of the nitrate and of the acid sulphate of ammonium give normal rotations, showing no appreciable amount of dissociation. The neutral sulphate, however, gives slightly high rotations, clearly indicating that it does dissociate to a small extent when dissolved in water.

The following is a list of the substances examined, with their molecular rotations, and the numbers of the pages where they are referred to in this paper:—

Substance.	Molecular rotation.	Page.
Nitric acid	1·180	680, 724, 725
Orthonitric acid	1·930	681, 724
Methyl nitrate	2·057	682, 722, 725
Ethyl nitrate	3·084	682, 722, 725
Propyl nitrate	4·085	683, 722, 725
Isobutyl nitrate	5·180	683, 722, 726
Ethylene nitrate	3·768	684, 726
Nitroglycerin	5·405	685, 726
Isobutyl nitrite	5·510	686, 723, 727
Nitromethane	1·858	687, 722, 723
Nitroethane	2·837	687, 722, 723
Nitropropane	3·819	688, 722, 727
Chloropierin	5·384	689, 728
Ammonia (aqueous solution)	1·810	689, 728
Ammonia (alcoholic solution)	1·826	690, 728
Ethylamine	3·609	691, 728
Diethylamine	5·662	691, 728
Triethylamine	8·518	692, 728
Propylamine	4·563	692, 730
Dipropylamine	7·549	693, 730
Tripropylamine	11·664	694, 730
Isobutylamine	5·692	694, 730
Isobutylamine (aqueous solution)	5·567	695, 735
Isobutylamine (alcoholic solution)	5·593	696, 735
Diisobutylamine	9·936	697, 730

Substance.	Molecular rotation.	Page.
Allylamine.....	5·587	697, 732
Pentamethylenediamine	7·492	698, 732
Piperidine	5·810	699, 733
Piperidine (aqueous solution).....	5·724	700, 736
Pyridine.....	8·761	700, 734
Propionitrile	3·331	701, 733
Trimethylene cyanide	5·136	702, 733
Ammonium chloride.....	6·096	712, 743
Ethylamine hydrochloride (in aqueous solution).....	7·997	713, 743
Diethylamine " " "	9·896	713, 743
Diethylamine " " (in alcoholic solution)	9·674	714, 744
Triethylamine " " (in aqueous solution)	11·739	715, 744
Tetrethylammonium chloride " "	13·624	715, 729
Piperidine hydrochloride " "	10·034	716, 743
Ammonium nitrate " "	2·320	721, 745
" acid sulphate " "	3·455	721, 745
" sulphate " "	4·980	722, 745
Sulphuric acid	2·315	725, 745
Ammonium bromide (NH ₄ Br 40·42 per cent. sol.)	10·159	716, 742
" " (NH ₄ Br 25 " ")	10·196	717, 742
Ammonium Iodide (NH ₄ I = 60·44 " ")	19·936	718, 742
" " (NH ₄ I = 58·46 " ")	20·032	718, 742
" " (NH ₄ I = 54·64 " ")	19·971	719, 742
" " (NH ₄ I = 30·5 " ")	20·049	720, 742
Ammonium Iodide in alcohol (NH ₄ I = 21·10 per cent.)	18·955	720, 744
Hydrochloric acid (HCl = 41·70 per cent. sol.)	4·045	702, 739
" " (HCl = 36·5 " ")	4·215	703, 739
" " (HCl = 30·86 " ")	4·303	703, 739
" " (HCl = 25·6 " ")	4·405	704, 739
" " (HCl = 15·63 " ")	4·419	704, 739
Hydrochloric acid in isoamyl oxide (HCl = 12·82 p. c.)	2·265	705, 741
" " (HCl = 10·68 " ")	2·211	705, 741
Hydrobromic acid (HBr = 65·59 per cent.)	7·669	706, 740
" " (HBr = 56·0 " ")	8·061	706, 740
" " (HBr = 39·71 " ")	8·415	707, 740
" " (HBr = 24·6 " ")	8·547	707, 740
" " (HBr = 15·47 " ")	8·519	708, 740
Hydriodic acid (HI = 67·02 per cent.)	17·769	708, 740
" " (HI = 65·1 " ")	17·868	709, 740
" " (HI = 61·97 " ")	18·117	709, 740
" " (HI = 56·78 " ")	18·308	710, 740
" " (HI = 42·7 " ")	18·403	710, 740
" " (HI = 31·77 " ")	18·451	711, 740
" " (HI = 20·77 " ")	18·428	711, 740