

LXIV.—*The Dissociation of Amine Vapours.*

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THE theory of Van t' Hoff that there is a definite relationship to space of the four bonds or affinities of the carbon-atom has received such remarkable confirmation from facts, that chemists have very naturally attempted to extend the conception to other elements, especially

tained in the higher salt-forming oxide. The acid oxides give, as a rule, a higher value of Δ , while in the case of the strongly alkaline oxides its value is usually negative.

DIAGRAM ILLUSTRATING THE PERIODIC VARIATION IN THE COMPOSITION OF THE HYDRIDES (OR METHIDES) AND OXIDES OF THE ELEMENTS.

	M. p. <i>t.</i>	<i>a.</i>	<i>d.</i>	$\frac{A}{d}$	RH _m . RMe _m . R.	A.	R ₂ O _n .	$d', \frac{(2A + n16)}{d'}$	V.			
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	
Hydrogen	< -200°	—	< 0·05 >	20	<i>m</i> = 1 H	1	1 = <i>n</i>	0·917	19·6	< -20	1	
Lithium	180	—	0·59	12	Li	7	1†	2·0	15	-9	2	
Beryllium	(900)	—	1·64	5·5	Be	9	— 2	3·06	16·3	+2·6		
Boron	(1300)	—	2·5	4·4	B	11	— 3	1·8	39	10		
Carbon	> (2500)	—	< 2·0 >	6	C	12	— 4	> 1·0	< 88	< 19		
Nitrogen	-203	—	< 0·7 >	20	N	14	1 — 3*	1·64	66	< 5		
Oxygen	< -200	—	< 1·0 >	16	O	16	—	—	—	—		
Fluorine	—	—	—	—	F	19	—	—	—	—		
Sodium	96	071	0·98	23	Na	23	1†	Na ₂ O	2·6	24	-22	3
Magnesium ..	500	027	1·74	14	Mg	24	2†	3·6	22	-3		
Aluminium ..	600	023	2·6	11	Al	27	— 3	Al ₂ O ₃	4·0	26	+1·3	
Silicon	(1200)	008	2·3	12	Si	28	— 3 4	2·65	45	5·2		
Phosphorus ..	44	128	2·2	14	P	31	1 — 3* 4* 5*	2·39	59	6·2		
Sulphur	114	067	2·07	15	S	32	2 — 4* 5* 6*	1·96	82	8·7		
Chlorine	-75	—	1·3	27	Cl	35½	1 — 3 — 5* — 7*	—	—	—		
Potassium ...	58	084	0·87	45	K	39	1†	2·7	35	-55	4	
Calcium	(800)	—	1·6	25	Ca	40	2†	3·15	36	-7		
Scandium	—	—	(2·5)	(18)	Sc	44	— 3†	3·86	35	(0)		
Titanium	(2500)	—	(5·1)	(9·4)	Ti	48	— 3 4	4·2	38	(+5)		
Vanadium ...	(2000)	—	5·5	9·2	V	51	— 2 3 4 5	3·49	52	6·7		
Chromium ...	(2000)	—	6·5	8·0	Cr	52	— 2 3 — 6*	2·74	73	9·5		
Manganese ...	(1500)	—	7·5	7·3	Mn	55	— 2† 3 4 — 6* 7*	—	—	—		
Iron	1400	012	7·8	7·2	Fe	56	— 2† 3 — 6*	—	—	—		
Cobalt	(1400)	013	8·6	6·8	Co	58½	— 2† 3 4	—	—	—		
Nickel	1350	017	8·7	6·8	Ni	59	— 2† 3	—	—	—		
Copper	1054	029	8·8	7·2	Cu	63	1† 2†	Cu ₂ O	5·9	24	9·8	5
Zinc	433	—	7·1	9·2	Zn	65	— 2†	5·7	28	4·8		
Gallium	30	—	5·96	12	Ga	70	— 3	Ga ₂ O ₃	(5·1)	(36)	(4·0)	
Germanium ..	900	—	5·47	13	Ge	72	— 2 4	4·7	44	4·5		
Arsenic	500	006	5·7	13	As	75	— 3 — 5*	4·1	56	6·0		
Selenium	217	—	4·8	16	Se	79	— 4 — 6*	—	—	—		
Bromine	-7	—	3·1	26	Br	80	1 — 5* — 7*	—	—	—		
Rubidium	39	—	1·5	57	Rb	85	1†	—	—	—	6	
Strontium	(600)	—	2·5	35	Sr	87	— 2†	4·3	48	-11		
Yttrium	—	—	(3·4)	(26)	Y	89	— 3†	5·05	45	(-2)		
Zirconium	(1500)	—	4·1	22	Zr	90	— — 4	5·7	43	-0·2		
Niobium	—	—	7·1	13	Nb	94	— 3 — 5*	4·7	57	+6·2		
Molybdenum .	—	—	8·6	12	Mo	96	— 2 3 4 — 6*	4·4	65	6·8		
Ruthenium ..	(2000)	010	12·2	8·4	Ru	103	— 2 3 4 — 6 — 8	—	—	—		
Rhodium	(1900)	008	12·1	8·6	Rh	104	— 2 3 4 — 6	—	—	—		
Palladium ...	1500	012	11·4	8·3	Pd	106	1† 2 — 4	—	—	—		
Silver	950	019	10·5	10	Ag	108	1†	Ag ₂ O	7·5	31	11	7
Cadmium	320	031	8·6	13	Cd	112	— 2†	8·15	31	2·5		
Indium	176	046	7·4	14	In	113	— 2 3	In ₂ O ₃	7·18	38	2·7	
Tin	230	023	7·2	16	Sn	118	— 2 4	6·95	43	2·8		
Antimony	432	012	6·7	18	Sb	120	— 3 4 5	6·5	49	2·6	8	
Tellurium	455	017	6·4	20	Te	125	— — 4 — 6*	5·1	68	4·7		
Iodine	114	—	4·9	26	I	127	1 — 3 — 5* — 7*	—	—	—		
Cæsium	27	—	1·88	71	Cs	133	1†	—	—	—		
Barium	—	—	3·75	36	Ba	137	— 2†	5·1	60	-6·0		
Lanthanum ..	(600)	—	6·1	23	La	138	— — 3†	6·5	50	+1·3		
Cerium	(700)	—	6·6	21	Ce	140	— — 3 4	6·74	50	2·0		
Didymium ...	(800)	—	6·5	22	Di	142	— — 3 — 5	—	—	—		
Ytterbium ...	—	—	(6·9)	(25)	Yb	173	— — 3	9·18	43	(-2)	10	
Tantalum	—	—	10·4	18	Ta	182	— — — 5	7·5	59	4·6		
Tungsten	(1500)	—	19·1	9·6	W	184	— — — 4 — 6	6·9	67	8		
Osmium	(2500)	007	22·5	8·5	Os	191	— — 3 4 — 6 — 8	—	—	—		
Iridium	2000	007	22·4	8·6	Ir	193	— — 3 4 — 6	—	—	—		
Platinum	1775	005	21·5	9·2	Pt	196	— 2 — 4	—	—	—		
Gold	1045	014	19·3	10	Au	198	1 — 3	Au ₂ O ₃	(12·5)	(33)	(13)	11
Mercury	-39	—	13·6	15	Hg	200	1† 2†	11·1	39	4·5		
Thallium	294	031	11·8	17	Tl	204	1† — 3	Tl ₂ O ₃	(9·7)	(47)	(4·3)	
Lead	326	029	11·3	18	Pb	206	— 2† — 4	8·9	53	4·2		
Bismuth	268	014	9·8	21	Bi	208	— — 3 — 5	—	—	—		
Thorium	—	—	11·1	21	Th	232	— — — 4	9·86	54	2·0	12	
Uranium	(800)	—	18·7	13	U	240	— — — 4 6	(7·2)	(80)	(9)		

Throughout the table the values included in brackets are estimated values.

The melting points of the elements are given in the first column (1) of numbers; column (2) contains the mean coefficient α of linear expansion between 0° and 100° of solid elements expressed in millionth parts, *e.g.*, in the case of bismuth the mean expansion of one metre for 1° is $\alpha = 0\cdot00014$.

In column (3) the relative densities of the elements in the solid or liquid state are indicated; whilst column (4) contains the corresponding atomic volumes.

The number of hydrogen-atoms in the hydride or of methyl-groups in the methide is indicated in column (5), the composition of the methides being represented by small figures, that of the hydrides by larger thick figures.

The composition of the oxides referred to the type R₂O_n is shown in column (7). The * indicates that the oxide is markedly acid, the † that it is markedly basic. Small figures denote comparatively unimportant or less common oxides and those which only exist in combination; the large figures important and more common oxides, known in a separate condition. Oxides such as CO and H₂O₂, which do not directly form salts are excluded. The figures in columns (8), (9), and (10) respectively denote the relative density of the higher salt-forming oxide, its molecular volume and the "volume" of an equivalent of oxygen in the oxide; the negative values apply to those cases in which the volume of the oxide is less than that of the element contained in it. The number of the period is indicated in column (11). The number of missing elements is indicated by bracketed figures in the column of symbols: thus between Didymium and Ytterbium 14 elements are wanting.

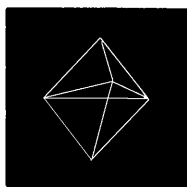
those which enter into the composition of the so-called organic substances.

In making this extension, we are bound to keep in mind the principles of the original conception, namely, that the four valencies of the carbon-atom are directed to the four angles of a tetrahedron of which the atom occupies the centre. In this hypothesis, as we understand it, the equality of the valencies, *inter se*, is represented by the symmetry of direction and the equal length of the vectors from the centre to the four angles. The consistent development of such an hypothesis appears to us to lead to difficulties of two kinds, the first arising out of the geometrical conceptions involved in it, and the second being met with in the attempt to extend it to other elements. It ascribes a perfectly distinct existence to these four bonds, so that in all carbon compounds we have to deal with neither more nor less than that number, unless we make the additional assumption that in certain cases the carbon-atom may lose its tetrahedric character.

And farther, if the tetrahedric relation of the valencies is unvarying, it is difficult to conceive in what way the atom can be united by more than three of its bonds to one atom of any other element.

We meet then with the difficulty of having to explain the existence of such compounds as carbonic oxide, in which carbon appears to be no longer quadrivalent, or of certain cyanogen compounds, as for example the isocyanides in which the carbon-atom is either combined by more than three bonds to a single nitrogen-atom or is bivalent, $R \cdot N \equiv C$ or $R \cdot N \equiv C$; so that in attempting to remove the one objection, we are brought face to face with the other, namely, that *ex hypothesi* we conceive the valency of each element to be constant. Such instances are rare in comparison with the number of bodies which fall in with the hypothesis of Van t' Hoff, but they are well known and well defined. We do not, however, dwell further on this subject, hoping to attack it experimentally later, merely stating here that results we have obtained with the nitrogen-atom bear also on this matter.

Willgerodt has brought forward the view that the nitrogen-atom may be regarded as having a configuration represented by a double tetrahedron. We have given some attention to the question of the



configuration of the atoms possible in the case of several elements and among them more particularly of nitrogen, and we have come independently to the same conclusion and have endeavoured to put the hypothesis to the test of experiment.

Starting from the consideration that a nitrogen-atom combined with four or five different groups should give a compound capable of isomerism, and that among these isomers there are two possible, the form of one of which is the non-superposable image of the other, we have attempted to obtain such a body containing what is in fact an "asymmetric nitrogen," and capable, one would suppose, of rotating the plane of polarisation to the right or to the left. The separation of these isomers, if they exist, we have not yet succeeded in effecting.

Attacking the problem from another point of view we find that a space configuration such as that given above requires that we consider nitrogen as essentially a quinquivalent or pentad atom. We have then to reconcile with this view the fact that nitrogen in a large number of cases appears to be triad.

We have endeavoured to find an explanation in the supposition that one atom of nitrogen in its apparently triad condition may combine by its two available affinities with another similar atom to form a condensed molecule, and that such molecules are readily dissociated by heat into the ordinary molecules containing quasi-triad nitrogen.

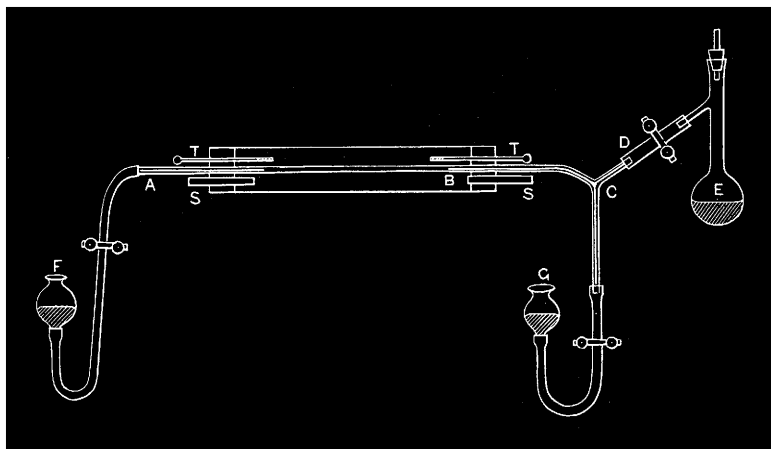
To test the hypothesis, we measured the expansion of a known quantity of amine vapours when the temperature was raised from that of the laboratory to 100°, the pressure remaining constant.

The apparatus used consisted of a horizontal tube, AB, about 700 mm. long and 2.5 mm. in the bore, to which was attached the T-piece C of the shape shown in the figure. To A and C were fitted rubber tubes with mercury bulbs, F and G, which could be raised or lowered as required. To the end D was attached the distillation bulb E containing the substance to be experimented upon in the liquid state; and this again was connected with a Sprengel pump. The tube AB was enclosed in a glass jacket provided with two thermometers, T, and tubes, S, for the supply and exit of steam.

The apparatus having been partially exhausted, the mercury was caused to fill the tube AB completely by raising the reservoirs F and G. The clamp on F having been tightened, G was lowered and raised repeatedly, so as to ensure the expulsion of the air from the connections and the replacement of it by the amine vapours.

Then G having been lowered till the mercury stood just below the bend of the T-piece, F was lowered so as to draw over some of the vapour into the tube AB. Then F was clamped, and the Sprengel pump worked till the mercury from G rose up the branch D.

When this was done, the clamp at D was screwed tight, and F lowered until the mercury from C reached a convenient fixed point, B, in the horizontal tube within the steam jacket.



Thus any possible condensation of the saturated vapour was avoided, the pressure on the enclosed gases being less than when they were drawn in. To make sure of this, however, the length V_0 of the column of gas was finally increased by about 50 per cent. by simultaneously lowering F and G. It may be noted here that condensation was at once evident on increasing the pressure after the gas was enclosed. Lastly, the clamp on F was tightened, and the volume of the gas taken by measuring the length V_1 of the column enclosed in the horizontal tube, the thermometers being read at the same time.

Next, steam was passed into the jacket. During the heating, the mercury bulb F was lowered, and the clamp slackened to permit the gases to expand; when the temperature was again steady, the pressure was finally adjusted so as to bring the column at B to exactly the same mark as before, all the adjustments being performed with F, so that neither the bulb C, nor the clamp upon its tube, was touched during the whole experiment. After measuring the volume V_2 at this higher temperature, as a further check upon the results the pressure in G was again lowered in some experiments, and the mercury brought back by means of F to its original position at B, and the increased volume V_3 once more taken.

Lastly, the steam was turned off, the apparatus allowed to cool, and a final measurement of the volume V_4 at the temperature of the laboratory was made.

It will be observed that the horizontal direction of the column of mercury at its upper extremity, and the fixed position of the bulb G, enabled us to secure with great accuracy the same pressure for each pair of measurements. The smallness of the volume operated upon is, however, an objection which will be remedied in our next apparatus.

Several blank experiments were first made with air to test the accuracy of the method, and the average error was found not to exceed 0·5 per cent. in the expansion between 17° and 100°.

Then we introduced various amines into the bulb E, and now obtained on heating an expansion of 5 or 6 per cent. above the normal.

Next, we substituted ether vapour for the amines when the abnormal expansion to a great extent disappeared—though not completely. This we ascribed to the difficulty of freeing the apparatus of the amines, the scent of which hung about the rubber connections in spite of repeated exhaustions. Finally, we operated on a solution of pure monethylamine in ether dried over potash, when the abnormal expansion re-appeared.

The equivalence of V_0P_0 to V_1P_1 at the temperature of the laboratory, and of V_2P_2 to V_3P_3 at 100° proved that at each of these temperatures the vapour of the amines obeys Boyle's law; while the equivalence of V_1P_1 to V_4P_4 showed that the heating caused no permanent increase of volume. But a comparison of V_1, P_2, t_1 and V_2, P_2, t_2 showed that there was an increased expansion of the amine vapours which was not observed in the case of air or ether.

The following are some of the results:—

No. 1.—*Test Experiment with Air.*

Pressure = 264 mm.

Volume at 13·5°	$V_1 = 199\cdot0$
Volume at 100°	$V_2 = 257\cdot7$ observed.
	259·08 calculated.

Here the error is about $\frac{1}{2}$ per cent.

No. 2.—*Mixture of Mono-, Di- and Tri-ethylamine in Aqueous Solution.*

Pressure = 148 mm.

Volume at 15°	$V_1 = 159\cdot0$
Volume at 100°	$V_2 = 234\cdot0$ observed.
	205·9 calculated.

This experiment gave an abnormal expansion of about 12 per cent.

No. 3.—*The same as in No. 2.*

Pressure = 383 mm.

Volume at 15° $V_1 = 148.0$

Volume at 100° $V_2 = 207.25$ observed.
191.68 calculated.

Pressure lowered to 263 mm.

Volume at 100° $V_3 = 300$

$V_2P_2 : V_3P_3 = 78898 : 78900.$

The abnormal increase was about $7\frac{1}{2}$ per cent., but the pressure was not so low.

No. 4.—*The same Mixture of Amines dried over Potash.*

Pressure = 173.5 mm.

Volume at 13.5° $V_1 = 121.0$

Volume at 100° $V_2 = 167.0$ observed.
157.5 calculated.

On cooling, volume at 17 = 122, *i.e.*, = 120.53 at the original temperature. Abnormal expansion of 6 per cent., with return to the original volume within the instrumental error.

No. 5.—*The same as No. 4.*

Pressure not noted, but about 250 mm.

Volume at 16.5° $V_1 = 183.0$

Volume at 100° $V_2 = 250.0$ observed.
235.8 calculated.

Abnormal expansion of 6 per cent.

No. 7.—*Monethylamine in Aqueous Solution.*

Pressure 398.5 mm.

Volume at 17° $V_1 = 200$

Volume at 100° $V_2 = 272$ observed.
257 calculated.

Abnormal expansion of nearly 6 per cent.

No. 8.—*Test Experiment with Ether Vapour.*

Pressure = 389 mm.

Volume at 17° $V_1 = 195.0$

Volume at 100° $V_2 = 253.5$ observed.
250.4 calculated.

Error about 1.2 per cent.; but the mercury smelt of ethylamine.

No. 9.—*Test Experiment with Ether after Continuous Exhaustion and Heating of the Tube.*

Pressure 697 mm.

Volume at 15.0, $V_0 = 135$ $V_0P_0 = 94095$

Pressure 452 mm.

Volume at 15.5, $V_1 = 209$ $V_1P_1 = 94120$

Pressure 452 mm.

Volume at 100.5, $V_2 = 278$ $V_2P_2 = 125755$

Pressure 363 mm.

Volume at 100.5, $V_3 = 347$ $V_3P_3 = 125961$

Observed volume at 100.5 = 278

Calculated „ = 271

The error was larger than in the previous case; but after the experiment, on cooling down to 17°, the observed volume was within 1 per cent. of the calculated, and the mercury still smelt strongly of the amine.

No. 10.—*Monethylamine Dissolved in Ether, dried over Potash.*

Pressure = 379.5 mm.

Volume at 17° $V_1 = 200.0$

Volume at 100° $V_2 = 267.0$ observed.
257.2 calculated.

Pressure 291.5 mm.

Volume at 100° $V_3 = 349.5$

Volume at 18° $V_4 = 263.5$

Relation of final volume at 18° to original volume at 17° reduced to same temperature and pressure = 1 : 1013583.

The relations $V_0P_0 : V_1P_1$ at 15° and $V_2P_2 : V_3P_3$ at 100° also varied only by about 1 per cent.

The abnormal expansion was in this case nearly 4 per cent. between 17° and 100°.

The above experiments seem to show that to some extent, at least, the vapour of ethylamine breaks up when heated from 17° to 100° into a larger number of molecules. Similar abnormal expansion has been observed in bodies which must be regarded as completely saturated in the single molecule—but in all these cases polymerisation is

structurally possible, and we think that in the nitrogen compounds it is necessary, if we are to extend Van t' Hoff's hypothesis to them.

Wurtz, who investigated methylamine and ethylamine (*Ann. Chim. Phys.* [3], 30, 467) was unable by ordinary means to determine their vapour-density.

Izarn, to whom he referred the matter, employing a new method, measured the vapour-density of the two amines at different temperatures and pressures, and found in every case a greater value than that required by theory. Thus, at 35.84° and 1128 mm., the density of ethylamine was 1.6027 observed, as against 1.5568 calculated. Izarn, however, did not experiment at temperatures lower than 27° , or higher than 56° . Our own observations made at pressures of from $\frac{1}{6}$ th to $\frac{1}{3}$ rd of that employed by him in the experiment quoted, by showing an abnormal expansion to take place on raising the temperature from 17° to 100° , seem to indicate that the specific volume of the vapour is a function not so much of the pressure as of the temperature, and it is on this that the hypothesis which we now put forward is founded.

The equality of the four valencies of carbon, which has been sufficiently established by experiment, is well represented by the symmetry of the tetrahedron, and we must suppose that a rise of temperature affects them all equally. Carbon, therefore, unless in combination with an element which is not symmetrical in its space relations, must be tetrad at all temperatures. This property it can only have in common with those elements which can be represented by the five regular solids, the valencies of which *ex hypothesi* must be 4, 6, 8, 12, and 20, corresponding to the number of the solid angles of those bodies. It is impossible, therefore, to find a geometrical representation for diad, triad, and pentad atoms which shall be symmetrical in three-dimensional space, and it becomes almost a necessary consequence of Van t' Hoff's hypothesis when we attempt to extend it to the nitrogen-group, that we should have two of the valencies different in value from the other three. Moreover, this difference would be manifested above a certain critical temperature, but would probably disappear below it, and, further, the union of an element of strong affinity with one of the valencies might render the other four equal with respect to atoms of weaker affinity.

With regard to the latter supposition, representing the pentad atom by a double tetrahedron, if we suppose one angle taken up, for instance, by chlorine, the remaining four are symmetrically situated with respect to one point within the atom, and may be saturated by four equal atoms or groups as in the ammonium, phosphonium, and arsonium salts.

The effect of certain elements in weakening the bonds of other

elements is a matter of ordinary observation (see Van t' Hoff, "La Chimie dans l'espace"). Compare, for example, the relative strength of the affinity between two carbon-atoms when combined with hydrogen, oxygen, or nitrogen, *e.g.*, $\text{CH}_3\text{—CH}_3$; $\text{CH}_3\text{—COOH}$; COOH—COOH ; $\text{CH}_3\text{—CN}$; CN—CN .

Again, the action of heat in weakening chemical affinity is also a matter of common experience. Thus, mercury, cadmium, and zinc in the gaseous state have no affinity in respect to atoms of the same kind, whilst iodine vapour exhibits the same phenomenon at high temperatures.

Now, as regards the nitrogen-atom, it appears that in contrast to carbon it is the hydrogen and hydrocarbon groups which weaken the affinity between nitrogen-atoms. Thus, we have $\text{NO}_2\text{—NO}_2$, but not $\text{NH}_4\text{—NH}_4$, nor $\text{NH}_3\text{—NH}_3$, at ordinary temperatures.

Hence, in the case of the amines, the bonds uniting the nitrogen-atoms in the double molecule will probably be extremely weak, and likely to be destroyed even at a comparatively low temperature. It is interesting in this connection to recall the fact that Hofmann (*Ber.*, **3**, 112) found that it was practically impossible to separate the three ethyl bases (mono-, di-, and tri-ethylamine) by distillation, in spite of there being an interval of some 40° between the boiling points of ethylamine and diethylamine, as well as between those of diethylamine and triethylamine. Now, it is conceivable that in such a mixture a molecule of one amine may unite with a molecule of a different amine to form a compound more stable than if both molecules were precisely similar, and capable accordingly of being volatilised to a certain extent without being dissociated.

In conclusion, we would say that, in our opinion, the nitrogen-atom is essentially pentad, and that when we find it triad we have to deal with molecules which have been dissociated, and in which the two available bonds of the nitrogen-atom are too feeble at the temperature of observation to enable two molecules to hold together.

We hope to continue our experiments as to the valency and space configuration of the nitrogen-atom and other atoms.
