been deduced from straightforward quantum logic, and hence it is difficult to throw doubt on their existence. We rather discuss why the poles have not so far been discovered. According to our hypothesis the magnetic poles can never occur in free state in our universe. When two magnetic poles combine to form a neutron, nearly eighty per cent. of the energy is radiated away in the form of radiation of energy 3.7×10^9 e. volts, hence it is almost impossible to split up the neutron. It is just possible that when a neutron lying within a nucleus is bombarded by a cosmic ray of suitable energy, it is split up into free magnetic poles which produce intense disturbance in the nucleus as they are liberated. May not the mysterious phenomena of cosmic ray *bursts* be due to this cause ?

I wish to express my thanks to Dr. D. S. Kothari, and Mr. Ramnivas Rai, with whom the contents of the paper were discussed.

[Note added:—In course of a discussion on the paper, Prof. D. M. Bose raised the point that if the same mathematics were to be applied to the motion of a positron and electron about each other, we should get corresponding solutions, where 80% of the mass would be radiated away. We know of no such radiation or of particles. I have since given some thought to Prof. Bose's point but find that the electron-positron case cannot give rise to the kind of solutions contemplated by Prof. Bose. For we should have

$$\epsilon=\frac{1}{\sqrt{1+\left(\frac{\alpha/2}{\sqrt{n_r+k^2-\alpha^2/4}}\right)^2}}, \qquad \text{(A)}$$

where $\frac{\alpha}{2}$ takes the place β in (16). Now β is a large number >17, while $\frac{\alpha}{2}$ is a small fraction. The lowest allowable value of k in (A) is unity. It may be easily verified that this leads to values of $\epsilon=1-\frac{\alpha^2}{8n^2}$, $n=n_r+k$, and the radiation emitted is

$$\nu=\frac{\mathrm{Ry}}{2}\left(\frac{1}{n^2}-\frac{1}{n'^2}\right),$$

i.e., they should have double the wave-length of ordinary hydrogen lines. Such lines were looked for in the spectrum of the corona (see Observatory, 56), but none has been so far obtained.]

REFERENCES

[1] Dirac, *Proc. Roy. Soc.*, A, **133,** 60 (1931).
[2] Eddington, *Proc. Roy. Soc.*, A, **133,** 605 (1931); **134,** 524 (1931); **138,** 17 (1932).
[3] Tamim, I. *Zeits f. Phys.*, **71,** 141 (1931).
[4] Kothari, a private communication.

62. A CRITICAL REVIEW OF THE PRESENT THEORIES OF THE ACTIVE MODIFICATION OF NITROGEN

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All the existing theories regarding the phenomenon of Active Nitrogen have been criticised in the present paper and the authors have tried to show the inadequacy of each one of them. It is concluded that atomic nitrogen has nothing to do with the active modification and the experiments which establish its presence are not correctly interpreted. It is shown that the long life of the afterglow which is about 5½ hours according to the recent experiments of Lord Rayleigh throws a new complexion on the phenomenon. It is thought that in Active Nitrogen the molecule is raised to some state composed of two ^2D atoms and probably located at 9·77 volts.

The first attempt at a theoretical explanation of the phenomenon of Active Nitrogen was made by the senior author and Dr. N. K. Sur[1] of this laboratory in 1926; they thought that ordinary unexcited molecules of Nitrogen are excited by a discharge to an energy which they estimated to be about 8·5 volts. This excited molecule was supposed to have a very long life and when it collides with a foreign molecule or an atom, then it transfers this energy to the second particle by collisions of the second type. The second molecule or atom is thereby excited to emit its spectrum or become chemically reactive. In this way they attempted to explain many of the results obtained by E. P. Lewis[2], Fowler and Strutt[3].

At the time when this suggestion was made our knowledge of the energy levels of the Nitrogen atom and the molecule was practically non-existent and this suggestion stimulated an extraordinary amount of activity on the subject. All these works gave rise to further theories or modifications of Saha and Sur's theory. In view of these works, and the

great advance in our knowledge of the spectrum of the N atom and the molecule[4] it is possible now to take a critical review of these theories.

Birge[5] held that the energy of the metastable molecule was not 8·5 volts as then considered by Saha and Sur but 11·4 volts, a value which is now known to be rather wide off the mark. The next theory was that of Sponer[6] and is now known as the *triple collision theory*. In this it is supposed that by the discharge, the Nitrogen molecule is split up into free atoms. The afterglow is produced when two atoms recombine and the energy of recombination is delivered over to a third molecule which happens to be present at the point of collision. This hypothesis explains to some extent the long life of the afterglow as well as the experimentally observed fact that the decay of the afterglow is not a monomolecular, but either a bi- or tri-molecular reaction. The basis of Sponer's assumption was that the *energy of dissociation of the normal Nitrogen molecule into two ^4S atoms is* 9·5 *volts*, a value which was favoured by the knowledge of the molecular spectrum of N_2 available up to that time. It has now been found that this value is too high, for Herzberg[7] has proved that the heat of dissociation of N_2 into two ^4S atoms is 7·34 volts.

In 1929, the above theory was modified by Cario and Kaplan[8] who assumed that Active Nitrogen contains a mixture of metastable molecules of Nitrogen in the A $^3\Sigma$ state, and metastable atoms in ^2P and ^2D states, whose excitation energies are 3·56 and 2·37 volts respectively. It was thought that molecules in A $^3\Sigma$ state are excited to B $^3\Pi$ state with $v'=10$, 11, and 12 by collisions with ^2P and to the state $v'=6$ by collision with the metastable atom ^2D. This point is well illustrated in table 1.

Table 1. *Energy in volts of the vibrational levels of the States A $^3\Sigma^+_g$ and B $^3\Pi_g$ of N_2.*

A-level				B-level	
v	V_A in volts	$V_A+{}^2D$ in volts	$V_A+{}^2P$ in volts	v	V_B in volts
0	0·00	2·37	3·56	0	1·18
1	0·18	2·55	3·74	1	1·39
2	0·35	2·72	3·91	2	1·59
3	0·52	2·89	4·08	3	1·70
4	0·68	3·05	4·24	4	1·99
5	0·84	3·21	4·40	5	2·19
6	1·01	3·38	4·57	6	2·38
7	1·16	3·53	4·72	7	2·57
8	1·31	3·68	4·87	8	2·76
9	1·46	3·83	5·02	9	2·94
				10	3·12
				11	3·29
				12	3·46
				13	3·63

From table 1, it will be seen that in the zero vibrational level of the A $^3\Sigma$ metastable state will be raised to the B $^3\Pi$ state with $v=6$ or 12 by coming in collision with ^2D and ^2P atoms respectively. Thus these bands will be enhanced, as was actually found to be the case in the experimental work of Kichlu and Acharya,[9] Herzberg Sponer and others.

At the time when this theory was propounded, the energy value of the A-level was supposed to be 8·1 volts, so that the energy of the level B_{12} to which the nitrogen molecule was raised by collision with the nitrogen ^2P atom was 11·56 volts, that of the B_6 level which is produced by collision with the ^2D atoms would be 10·48 volts. Now, the energy content of the Nitrogen molecule which by collision of the second type excites atoms to the emission of their characteristic light has been determined with great care by Okubo and Hamada.[10] They find this energy to be 9·51 volts. The active molecules present in active modification of Nitrogen in the original theory of Cario and Sponer are

$$8{\cdot}1\ (A\ ^3\Sigma),\ 10{\cdot}48\ (B_6\ ^3\Pi)\ \text{and}\ 11{\cdot}56\ (B_{12}\ ^8\Pi).$$

In none of the atomic reactions so carefully observed by Okubo and Hamada special excitation of any line corresponding to any of the above energy values is noticeable[11].

It is now known from the discovery of Vegard-Kaplan[12] bands that the energy of excitation of A $^3\Sigma$ state is 6·14 volts. When this became known Cario[13] modified his theory. The energy values of the molecular states now come to be 6·14 (A $^3\Sigma$), 9·60 (B_{12} $^3\Pi$), produced by collision with ^2P atoms and (B_6 $^3\Pi$) produced by collision with ^2D atoms. The authors pointed out that the energy of the B_{12} state is just the same which is obtained in the experiments of Okubo and Hamada.

They further pointed out that the metastable atoms $^2P_{\frac{1}{2}}$ would be generated even in the absence of a discharge by impact of two A $^3\Sigma$ molecules as shown below:—

$$N_2\ A\ ^3\Sigma + N_2\ A\ ^3\Sigma - N_2\ ^1\Sigma + 2\ N\ ^2P_{\frac{1}{2}}$$
$$6{\cdot}14+6{\cdot}14=7{\cdot}34+2\ (2{\cdot}37)$$
$$12{\cdot}28=12{\cdot}18.$$

But ^2D atoms cannot be produced by this process, and the authors suppose that there are more ^2P atoms in the active modification than ^2D atoms.

In support of this theory Cario and Kaplan argue that the presence of atomic nitrogen in the active modification is supported by the experiments of Wrede[14] and Broadway and Jackson.[15] We wish, however, to point out that a critical review of these experiments shows that proper

interpretation has not been put on them. A short account of these experiments which is given below will illustrate this point.

Wrede passes through a discharge tube a steady stream of Nitrogen so that the pressure is maintained constant. There are a number of side-tubes and through a diffusion plug inserted in one of these, the gas in the discharge tube is allowed to diffuse to another tube where, if no discharge passes, the pressure would have the same value as in the discharge tube. If the discharge is allowed to pass, the pressure and temperature on the two sides of the diffusion space varies. The change in pressure can only be due to the fact that some of the molecules are broken up by the discharge into atoms and diffuse faster into the other tube where they recombine to form moleucles. Let p_0, T_0 be the pressure and temperature in the absence of the discharge and p_e, T_e the corresponding quantities when the discharge is passed. Then it can be shown that the partial pressure of atomic Nitrogen in the discharge tube is given by

$$\frac{p_A}{p_E}=\frac{1-\frac{p_0}{p_e}\sqrt{\frac{T_e}{T_0}}}{0.293}.$$

Wrede actually found that about 20 to 30% of atomic nitrogen is produced in the discharge tube under favourable conditions. We accept this result, but wish to remark that the experiment merely proves that, molecules are broken up into atoms in the discharge space. It does not, however, prove that free atoms persist in the afterglow space. In fact, recent experiments of Lord Rayleigh,[16] which show that active nitrogen, segregated in a discharge-free space can continue to glow for 5½ hours, absolutely disprove that atomic nitrogen is responsible for active nitrogen phenomena. Any free atom produced in the excited state will die out in course of 10^{-8} sec. and a metastable atom will revert to the normal ^4S state at most in 10^{-1} sec. Free Nitrogen atom in ^4S state cannot remain uncombined for more than a few seconds and even when they combine, the amount of energy set free is too small to produce any of the characteristic reactions. We therefore conclude that production of atomic nitrogen is of course prompted by the same discharge which produces Active Nitrogen phenomenon, but the two phenomena are not connected as cause and effect.

The same remarks apply to the experiments of Broadway and Jackson[15]. They performed Stern and Gerlach's experiment with molecules and atoms from the discharge space and observed the splitting of the beam on a specially sensitised screen. They obtained traces which were interpreted to be due to N $2p^3$ $^2P_{\frac{1}{2}}$ atoms, but this experiment only proves that such atoms are produced in the discharge space. It does not prove that the atoms persist in their free existence when we consider the afterglow space. Hence the presence of $^2P_{\frac{1}{2}}$ atoms on the plate show that atoms are produced in the discharge and have a pretty long life, of the order of 10^{-2} second.

Thus Cario and Kaplan's theory of Active Nitrogen in which the presence of atomic nitrogen plays such a fundamental part cannot be regarded as valid unless atomic nitrogen is found in the real afterglow, quite separate from the discharge space.

Further no atomic lines of N or N^+ have so far been observed in the spectrum of the afterglow. Kichlu and Acharya[9] failed to obtain lines of the Nitrogen atom due to transition N $2p^2$ ($3s$-$3p$), $2p^2$ ($3p$-$3d$) which are at about λ 8200. No attempt has yet been made by anybody to obtain in the active modification the resonance lines of Nitrogen ($2p^3$—$2p^2$ $3s$, $2p^2 3d$) which are in the Schumann region below λ1700. So the presence of atomic nitrogen in the afterglow has not yet been spectroscopically confirmed. The experiment would be difficult to perform for only an absorption experiment with a fluorite spectrograph can decide whether atomic nitrogen in the ^4S,^2D, and ^2P states is present in the afterglow, or definitely absent.

We therefore conclude that in spite of numerous experiments the presence of atomic nitrogen in any form in the active nitrogen has not yet been established.

Another point which goes against their theory is regarding the dark modification of Nitrogen which Okubo and Hamada[17] have tried to attack. According to Cario and Kaplan's theory when Active Nitrogen is heated or the active gas is allowed to pass through a heated tube, the metastable molecules alone survive while the metastable atoms are destroyed. In the absence of the metastable atoms the metastable molecules will no longer be excited to the B $^3\Pi$ state to emit the well-known α-bands of the afterglow. If this is so, then the total energy-content of the molecule in the "dark modification" should be much less than in the normal activated state. The best way of estimating the energy of the excited molecule is to make them collide with the vapours of such elements whose energy levels are completely known, and which do not chemically react with Active Nitrogen. Okubo and Hamada[17] found that the line of highest excitation even in the case of the so-called dark modification was λ2654.52 ($6s6p$ ^3P—$6s8d$ ^3D); in the case of Mercury, corresponding to the excitation energy of 9·51 volts.

Okubo and Hamada[11,18] try to explain the enhancement of certain bands by the application of the Frank-Condon principle. The details of their paper are not available but from a short account of their work which appeared in *Physical Review* before the values of the triplet terms was known, it appears that they consider that by a discharge the Nitrogen molecule has a tendency to be excited to that particular vibration level of the B or the A state where the normal distance between the atoms (for X $^3\Sigma$, r_0=1·09 A.U.) remains the same for the near-turning point of the

Frank-Condon diagram. Thus, there is a concentration of the atoms A $^3\Sigma^{8,11}$ as the details have not been published, it is difficult to form an accurate judgement of the value of this hypothesis.

From the foregoing short review it will appear that the existing theories of molecular structure are quite insufficient to explain the phenomenon. More well-planned experiments are needed to throw light on the subject. Lord Rayleigh's recent work proves that the surface has a strong catalytic action in accelerating the destruction of the glow. He finds that the poisoning action of the walls can be removed by treating the surface with Sulphuric Acid or Meta-phosphoric Acid. The glow then persists for 5½ hours at least. Unfortunately, no details have yet been published regarding the spectroscopy of the segregated glow. The total intensity of the light radiated after segregation during the whole period of decay, and the absorption spectrum of the glow should be carefully measured. It has been ascertained that the decay of the glow is either bi- or tri-molecular which proves that the emission of light is provoked by collisions of two bodies or three bodies and Lord Rayleigh prefers the two-body collision. It appears to us that the phenomenon can be explained if we suppose that two excited atoms of Nitrogen N ^{2}D or N ^{2}P form an extremely stable state of the molecule in the following way:

$$N\ ^2D + N\ ^2D = N_2\ ^1\Sigma.$$

The state produced is such that it does not easily transit to any of the levels A or X being forbidden by two or three selection principles. The energy of this stable state is very nearly 9·77 volts and when this collides with a normal nitrogen molecule it gives its energy to it raising it to the B_{12} or B_{11} state or the B_6 state. These excited molecules then make the transitions according to the Frank-Condon principle giving rise to the especially enhanced bands. When the molecule collides with foreign atoms or foreign molecules it communicates its energy to the latter in exactly the same way by collision of the second type.

Attempts are being made to verify some of the suggestions.

REFERENCES

[1] Saha, M. N. & Sur, N. K., *Phil. Mag.*, **48,** 421, 1924.
[2] Lewis, E. P., *Astrophys. Jour,*. **12,** 8, 1900; *Ibid*, **20,** 49, 1904; *Phil. Mag.*, **25,** 826, 1913; *Nature*, **111,** 529, 1923.
[3] Fowler, A., and Strutt, R. J., *Proc. Roy. Soc.*, **85,** 219, 1911; **85,** 377, 1911; **86,** 56, 1911; **86,** 105, 1911; **86,** 262, 1911; **88,** 110, 1912; **92,** 438, 1916; **93,** 254, 1917.
[4] Mathur, L. S. & Sengupta, P. K., *Proc. U. P. Acad. Sc.*, **5,** 187, 1935.
[5] Birge, R. T., *Nature*, **114,** 642, 1924.
[6] Sponer, H., *Zeits., f. Phys.*, **34,** 622, 1925.
[7] Herzberg, G. & Sponer, H., *Zeits. f. Phys. Chem.*, **26,** 1, 1934.
[8] Cario, G. & Kaplan, J., *Zeits. f. Phys.*, **58,** 769, 1929.
[9] Kichlu, P. K. & Acharya, D. P., *Proc. Roy. Soc.*, **103,** 168, 1929.
[10] Okubo, J. & Hamada, H., *Phil. Mag.*, **5,** 372, 1928.
[11] Okubo, J & Hamada, H., *Phy. Rev.*, **42,** 795, 1932.
[12] Kalpan, J., *Phy. Rev.*, **45,** 675, 1934.
[13] Cario, G., *Zeits. f. Phys.* **89,** 523, 1934.
[14] Wrede, E., *Zeits. f. Phys.*, **54,** 53, 1929.
[15] Broadway & Jackson, *Proc. Roy. Soc.*, **127,** 678, 1930.
[16] Rayleigh, Lord., *Proc. Roy. Soc.*, **151,** 572, 1935.
[17] Okubo, J. & Hamada, H., *Phil. Mag.*, **15,** 103, 1933.
[18] Okubo, J. & Hamada, H., *Astrophys. Jour.*, **77,** 130, 1933.

63. A NEW MODEL DEMOUNTABLE VACUUM FURNACE

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A vacuum graphite furnace suitable for high temperature research has been described in this paper. A special feature of the apparatus is that the parts can be taken out and set again for experimental work in a very short time. Temperatures up to 2500°C can be very quickly attained within a vacuum of 10^{-4} mms. A photograph of the apparatus and four diagrams explaining its action are given.

INTRODUCTION

For some time past we have been using in this laboratory a new model vacuum furnace of which the parts are demountable. This has been found to be extremely useful for researches on Thermal Ionisation of elements and salts and other high temperature work. With this apparatus it has been possible to attain temperatures up to 2500°C within a graphite tube very quickly. The special feature of the apparatus is that it can be taken to pieces in no time and set again for a fresh experiment. A sketch of the apparatus showing the important parts is shown in Fig. 1.

DESCRIPTION

The working of the apparatus will be clear from figures (2 and 3) which represent its horizontal and vertical