

measured). The thermionic current was  $10 \times 10^{-6}$  amperes. On putting Mg-vapour, the current rose to  $\frac{2}{10}$  of a milliamperere, or  $200 \times 10^{-6}$  Amp. or by about 20 times, so that magnesium vapour seems to have been ionised at  $1300^{\circ}\text{C}$ .

*Calcium.*—The small furnace was maintained at  $920^{\circ}\text{C}$  (measured), but the storage cells having run down, the temperature in the big furnace F could not be increased. It was probably  $1150^{\circ}\text{C}$ . The thermionic emission was less than a microampere, but on putting Ca-vapour, it rose to 30 microamperes. This proves that Ca-vapour is appreciably ionised at  $1100^{\circ}\text{C}$ .

#### *Sodium*

*Sodium.*—The small furnace was maintained at  $470^{\circ}\text{C}$ , corresponding to a vapour pressure of about 2 mm. of mercury. The temperature in the big furnace was about  $900^{\circ}\text{C}$ . The thermionic emission amounted to 40 divisions on the galvanometer scale corresponding to a total resistance  $5 \times 10^6$  ohms. As one megohm was put in the galvanometer circuit, the resistance of the furnace-cell was approximately  $4 \times 10^6$  ohms. On putting Na-vapour the spot went off the scale at once, so that the microampere circuit was put in. Even this went off the scale. Then the milliamperemeter circuit was put in with no resistance in series. The current was  $\frac{1}{10}$  of a milliamperere, so that the

equivalent resistance with Na-vapour was only 13400 ohms. Thus at  $900^{\circ}\text{C}$  the conductivity of the space increases about three hundred times, when Na-vapour is put in.

The only objection which can be raised against the view that Na or Ca-vapour is ionised by heat is that the electrons emitted from the surface of the furnace F in falling to the central wire, produce fresh ions by collision. This possibility is excluded by the fact that the potential difference between the furnace and the central wire is only 1.34 volts, much lower than the ionisation potential of the elements investigated. But it may be contended that since the total potential fall between two ends of the furnace is from 6 to 10 volts, electrons emitted from the negative end may just slip along the surface and come out at the end with an energy corresponding to a voltage drop of 6 to 10.

Though we can think of such an eventuality, the probability of its affecting the main results seems to be rather remote. At least, in future experiments, efforts will be made to free the arrangement from the possibility of such an objection.

In conclusion, we wish to record our thanks to our colleague Mr. S. Bhargava, Reader in this University, for useful help in designing the apparatus and to Mr. K. Majumdar, Research Scholar, for help in taking observations.

## 25. ON AN ACTIVE MODIFICATION OF NITROGEN\*

M. N. SAHA AND N. K. SUR

(*Phil. Mag., Sr. VI, 48, 421, 1924*)

A few years ago Prof. Strutt (now Lord Rayleigh) performed a series of experiments on an active modification of nitrogen<sup>1</sup>, which excited a good deal of interest at the time. Nitrogen is well known to be an extremely inert gas, but Lord Rayleigh showed that if a condensed spark discharge be sent through  $\text{N}_2$ -gas, the glow persists in the gas flowing out of the region of the discharge, which shows considerable chemical and spectral activities. The spectrum of the afterglow was investigated by Fowler and Strutt<sup>2</sup> and shown to consist of the usual  $\alpha$ ,  $\beta$ , and  $\gamma$  groups of

positive bands, with a fourth group which was observed for the first time.

The object of the present paper is to show that almost the whole series of observations recorded by Lord Rayleigh can be explained on the basis of Klein and Rosseland's theory<sup>3</sup> of inelastic collision of the second type, which has been further developed by Franck<sup>4</sup> and his students. For convenience of discussion we begin with a short account of this theory.

The experiments on ionization potential and origin of

\* Communicated by the Authors.

<sup>1</sup> Strutt, Proc. Roy. Soc. Lond. lxxxv. p. 219; lxxxvi. pp. 56, 105, 529; lxxxvii. pp. 179, 302, 381; lxxxviii. pp. 110, 539.

<sup>2</sup> Fowler and Strutt, Proc. Roy. Soc. Lond. lxxxvi pp. 105-117.

<sup>3</sup> Klein and Rosseland, *Zs. f. Physik*, iv. p. 46.

<sup>4</sup> Franck, *Zs. f. Physik*, ix. p. 259; xi. p. 155. Cario, *Zs. f. Physik*, x. p. 105 and p. 166. Compton, Journal of the Optical Society of America, 1923.

spectra, which were first carried out by Franck, are now matters of common knowledge. They deal with the interchange of energy between freely moving electrons and atoms. A stream of electrons moving with a definite velocity is projected into a mass of gaseous atoms. When an electron happens to pass close to an atom, then, provided the energy of the free electron exceeds a certain limit given by the quantum condition  $eV = h\nu$ , the whole of its energy may be transferred to the valency electrons lying at the outer periphery of the atom. The valency electron is thereby lifted to higher quantum orbits. These states are not stable, and in a short time it reverts to its original position, the excess of energy being set free as monochromatic radiation. Thus the atoms abstract energy from the free electrons, and convert it to energy of its own monochromatic radiation. This process is indicated by kicks in the current-potential curves, as well as by the emission of the characteristic spectrum of the element. When the energy of the bombarding electron is sufficiently large, it may tear off the valency electron from the parent atom. This stage is known as ionization and indicated by an abrupt rise of the current in the current-potential curve.

Hitherto, attention of all workers has been confined to only one side of the problem, *i.e.*, communication of energy by the free electron to the atom. But Klein and Rosseland showed that the reverse process (*viz.*, communication of energy by the excited atom to the free electron) actually takes place in nature on a very large scale, and accounts for a large number of experimental results recorded in previous years. For example, suppose we have a mass of mercury atoms, some of which has been activated either by absorption of the light  $\lambda = 2536$  ( $1S-2p_2$ ) or by an electric discharge from the normal ( $1S$ ) stage to the next stage  $2p_2$ . If, now, an electron passes close to this mercury atom ( $2p_2$  stage), what will take place? According to older conceptions, we could think of no other process than that the electron would communicate its energy to the mercury atom, and excite it to still higher quantum states or to ionization. But Klein and Rosseland pointed out that the reverse process may also take place, *viz.*, the mercury atom may transfer its extra amount of energy corresponding to  $\lambda = 2536$  to the electron. The electron thus receives an increment in its velocity, but the transfer is "radiationless," *i.e.* the electron *chokes the emission* of the light  $\lambda = 2536$ , which would have otherwise certainly taken place. The chance of this "radiationless transfer" depends upon circumstances which are yet to be worked out, but there seems to be no doubt that it is a very general phenomenon.<sup>5</sup>

<sup>5</sup> It may be noted here that Klein and Rosseland were led to this conception from Einstein's idea of "Negative Einstrahlung" or negative absorption. A Hertzian oscillator when placed in a field of radiation may either take up the energy from the field, or give up its own energy to the field, according as the phase difference between the vibration of the resonator and the incident radiant waves is less or greater than  $90^\circ$ . The former case is positive absorption, energy being taken up by the

These considerations were further extended by Franck and his students, who showed that the excited atoms may communicate their energy not only to the electron, but also to such atoms or molecules as may come in contact with them. These atoms or molecules will therefore receive either some increment in their kinetic energy or, if the energy imparted be sufficiently large, they may be excited to their spectral emission, ionization or dissociation in the case of molecules.

These ideas, therefore, open up a very promising field of investigation, and Franck has already pointed out, and confirmed several interesting deductions. For example, a stream of mercury gas was excited by  $\lambda = 2536$ , and these activated Hg atoms were allowed to act upon the  $H_2$ -gas. It was proved that the  $H_2$ -gas was thereby dissociated into atoms. The explanation is that when a mercury atom absorbs the light  $\lambda = 2536$ , it is loaded to an energy-content of 4.9 volts. On coming into contact with the  $H_2$ -gas it delivers this energy to the molecule of  $H_2$  which is thereby broken up into atoms, as the heat of dissociation corresponds to about 3.8 volts (80000-90000 cal.).

#### *Transference of energy to atoms.*

Hg atoms activated by  $\lambda = 2536$  were allowed to act upon vapours of thallium and silver. Only such lines of these vapours were excited for which the energy required is less than 4.9 volts.

#### *Choking Effect of Inert Gases on Luminous Mercury Vapour.*

Wood<sup>6</sup> carried out years ago a number of very interesting experiments on the luminescence of mercury vapour excited by an electric discharge. He found that if inert gases like  $N_2$ ,  $He_2$ , A were added to the luminous Hg-vapour, the luminosity was quenched, the decrease in luminosity being roughly proportional to the amount of gas added. The explanation according to Franck is as follows:—When an activated Hg atom comes into collision with an atom of A or He, then in some cases energy is communicated to the latter. This results simply in an increase of the kinetic energy of the A or the He atom, as the amount of energy transformed (4.9 volts) is quite insufficient to lift the vibrating electron of A or He to the higher orbit. The net result is, therefore, the quenching of the line  $\lambda = 2536$  Å.U. or other lines of the Hg spectrum.

The phenomenon is therefore quite general. If to a mass of luminous gas another gas is added of which the radiation potential is higher than that of the luminous gas, the luminosity is choked.

resonator from the field. The latter case is negative absorption, energy being given to the field, just as in alternate current instruments, if the phase difference between the current and potential is  $>90^\circ$ , the work done by the instrument  $EI \cos\phi$  becomes negative, *i.e.*, work has to be done on the instrument.

<sup>6</sup> Wood, *Phys. Zs.* xiii. p. 353 (1912).

To those who have followed the work of Lord Rayleigh on active nitrogen, the foregoing discussion would seem to hold out promises of a very satisfactory explanation. But all is not plain sailing as the following discussion will show. We begin with a concise statement of our explanation.

When a moderately condensed discharge is sent through  $N_2$ -vapour it is converted into an excited state, falling just short of dissociation into its constituent atoms. The amount of energy to which the molecule is loaded lies between 8.2 and 8.5 volts. The average life of such an excited atom is of the order of  $10^{-8}$  second. When the excited nitrogen molecule falls back to the original state, it emits a band-spectrum lying between  $\lambda=1600$  and  $\lambda=1200$ .<sup>7</sup>

This band may be called the primary band, and the usual bands lying in the visible region (the positive bands) stand to this in the same relation as the subordinate series of an element stand to the lines of the principal series.

The arguments in favour of this view are as follows:—The spectrum of active nitrogen was investigated by Fowler and Strutt<sup>8</sup>, and found to consist of the  $\alpha$  and  $\beta$  groups of positive bands, which according to the canal-ray method of Wien<sup>9</sup> are due to the  $N_2$  molecule. None of the lines of the familiar line-spectrum (attributed by Fowler to  $N^+$ ) were observed. (It is still a moot point whether the lines due to  $N$  atom, recorded by Stark and Hartdke<sup>10</sup>, were present, as the above-mentioned investigations did not extend up to this region). None of the negative bands, which according to Wien are due to  $N_2^+$ , were present.

The evidence is thus fairly conclusive that  $N_2$ -gas in the afterglow region simply consists of excited  $N_2$  molecules. The experiments of Lord Rayleigh<sup>11</sup> to detect whether charged particles were present in the afterglow were entirely negative.

It is also clear that the afterglow bands cannot be the primary bands, for unexcited  $N_2$ -gas is completely transparent to this region. It has got an absorption band lying between  $\lambda=1600$  Å.U. and  $\lambda=1200$  Å.U. That the primary band lies in this region is also proved by the experiments of Brandt<sup>12</sup>, who, using the bombarding electron method of Franck, found an abrupt rise of current in the neighbourhood of 8.2 volts. Several kicks were observed in the current-potential curve between 8 and 9 volts, and these were shown by Brandt to be of the nature of band-emission. The primary emission bands therefore lie between  $\lambda=1600$  and  $\lambda=1200$  Å.U., and are present in the afterglow region. But the glass of the quartz vessels in which these experiments are carried out completely masks them.

The visible bands which are actually observed are simply secondary. Their final orbit is also unstable, just as the

final orbits corresponding to the Balmer-lines of H are the diquantic unstable orbits. These bands will therefore be emitted only when these orbits have a certain amount of stability.

According to this view, active nitrogen simply consists of the excited nitrogen molecule loaded to the energy of about 8.5 volts (corresponding to about  $1.9 \times 10^5$  calories). Its great activity is due to the ease with which the particle can part with this amount of energy. When foreign atoms or molecules are not present or present only in small amounts, the excited molecule reverts to the normal state after emission of the primary and the secondary (the usual positive) bands. The average life of the excited atom when it suffers no collision is about  $10^{-8}$  sec.<sup>13</sup>, but this may be lengthened when the number of collisions is large. This point will be discussed later on.

When foreign substances are present, the energy is mostly communicated in a radiationless transfer. The foreign substance is thereby stimulated either to luminescence or to chemical activity. The following few selected examples will bring out the point clearly.

(1) Active nitrogen, when passed over sodium, causes not only the  $D_1$  and the  $D_2$  lines, but also the subordinate series lines to flash out.

The amount of energy required for the excitation of the yellow lines is only 2.1 volts, so that the energy delivered by active nitrogen is sufficient, not only for exciting its entire line-spectrum, *but may probably also suffice to ionize it*, as well as the other alkali elements. Lord Rayleigh found that the maximum emission is at the second line of the principal series 3303. This is probably due to the fact that the energy transferred is very large compared with the excitation potential of Na.

(2) Action on mercury.

Active nitrogen, passed over Hg-vapour, excites the fundamental line  $\lambda=2536$  ( $1S-2p_2$ ) and lines belonging to the triplet group of the first subordinate and second subordinate series. The  $2P-3D$  line ( $\lambda=5790$ ) and  $2P-3d'_2$  line ( $\lambda=5769$ ) are not excited, hence probably an upper limit to the energy transferred is obtained by assuming that it just fails to excite the  $3D$  level in the Hg-atom. This is 9.4 volts, which is in accordance with our theory.

(3) Action on magnesium.

Many arc-lines are developed, but neither the line 4481

<sup>13</sup> Wien's method of determining the charge on luminous atoms may be noted here. He allowed a stream of luminous gas to flow out of a canal-ray tube into a space where a vacuum of the order of  $10^{-8}$  to  $10^{-4}$  mm. is continuously maintained by a number of diffusion pumps. In this space, the gas is allowed to pass between two parallel plates which are maintained at a small distance apart at a constant difference of potential. The spectrum of the luminous slit-like region is photographed. Particles which are uncharged show straight spectral lines, while lines due to charged particles are bent one way or the other. The vacuum in the space is so high that no collision takes place amongst the particles. In this way Wien proved that the  $\beta$  groups of positive bands are due to the uncharged  $N_2$  molecules, whereas the bands in the negative glow are due to  $N_2^+$  molecules.

<sup>7</sup> Lyman, 'The Spectroscopy of the Ultra-Violet,' p. 63.

<sup>8</sup> Proc. Roy. Soc. Lond. lxxxvi. pp. 105-117.

<sup>9</sup> Wien, *Ann. d. Physik*, lxix.

<sup>10</sup> Stark and Hartdke, *Ann. d. Physik*, lvi. p. 303.

<sup>11</sup> Strutt, Proc. Roy. Soc. Lond. lxxxviii. p. 183.

<sup>12</sup> Brandt, *Zs. f. Physik*, viii. p. 32.

nor any other spark-line was excited. The arc-line  $\lambda=4703$  (1P-4D) was either not excited at all or excited very feebly.

The ionization potential of magnesium is 7.65 volts, and thus active nitrogen would just suffice to ionize magnesium. Active nitrogen passed over Ca, Ba, or Sr, would excite, besides their arc spectrum, also the spark spectrum.

(4) Hydrogen and the inert gases have no other influence on active nitrogen except a mere dilution of the glow. This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active energy.

On the other hand, when helium is activated by an electric discharge, it is capable of storing a large amount of energy ( $e=20.4$  volts) and hence would be found to be an extremely active substance. This view is supported by an interesting observation of Lord Rayleigh<sup>14</sup> in a recent paper, who found that activated helium on coming into contact with  $N_2$ -gas (unexcited) excites the afterglow. If the present view is correct, it would excite not only the positive bands but also the line-spectrum due to N. This point ought to be further investigated.

We now come to the most formidable difficulty confronting the above explanation, viz., chemically pure nitrogen shows no afterglow at all. This matter forms the subject matter of a very interesting paper by Lord Rayleigh in vol. xci. of the P. R. S. London. Following experiments by Tiede and Domcke, who found that chemically pure nitrogen, prepared by heating barium and potassium azide, and carefully freed from all impurities, shows no afterglow at all, Lord Rayleigh showed that nitrogen purified by prolonged standing over the liquid alloy of Na and K gave an afterglow, which was however very faint. On introducing small impurities of oxygen, or almost

any easily excitable gas (1 in 1000 parts), the glow was restored to full brilliancy. This observation has also been confirmed by recent experiments of Pirani<sup>15</sup>, who claims for his nitrogen a purity of  $5 \times 10^{-5}$  per cent. Pirani finds that perfectly pure  $N_2$  shows no luminescence at all, though admixture of electronegative gases like  $O_2$ ,  $H_2O$ ,  $I_2$  in concentration of  $1.5 \times 10^{-3}$  give a maximum after-luminescence. Large admixtures, say from 6 to  $8 \times 10^{-3}$ , choke the luminescence. In all these experiments, the authors seemed to have looked only for the after-luminescence of the chemically pure gas as a test of activity. They did not evidently apply the chemical tests. This point is of some importance, because the afterglow is simply the sign of the return of the molecule from the higher quantum states to one of the intermediate unstable states; it does not indicate the reversion to the normal state. Hence, if under certain conditions the intermediate orbits (*i.e.* final orbits of the afterglow band) be not stable, these will not be emitted at all, though the gas will exhibit all the chemical and spectral activity recorded by Lord Rayleigh.

It seems to be a general phenomenon that the activated atom, when left to itself, has always a tendency to fall to the lowest quantum state, without stopping at the intermediate stages. Hence only the primary bands would be emitted. This is confirmed by an interesting investigation of Wood<sup>16</sup>, who finds that in his discharge-tubes, Balmer lines of H (for which the final orbit is an unstable orbit) are always rendered very brilliant if  $H_2O$  vapour is present as an impurity. The subject is, however, well worth further investigation.

Our explanation of the absence of afterglow in active nitrogen, if true, would mean that nitrogen may be loaded to an energy of about 8.5 volts without being luminous, and therefore will still possess all other properties associated with active nitrogen.

<sup>14</sup> Lord Rayleigh, Proc. Roy. Soc. Lond. vol. cii. p. 454.

<sup>15</sup> Pirani, 'Chemical Abstracts,' 1923, ii. p. 157.

<sup>16</sup> Wood, Phil. Mag. xliii. p. 729.

## 26. THE PRESSURE IN THE REVERSING LAYER OF STARS AND ORIGIN OF CONTINUOUS RADIATION FROM THE SUN

(*Nature*, **114**, 155, 1924)

There seems to be at present a wide divergence of views regarding the magnitude of pressure in the "reversing layers" of stars. While earlier investigators assigned to it a pressure of one to ten atmospheres, on the basis of pressure shift of lines to the red, these experiments do not appear to carry much weight at present. Fowler and Milne (Monthly

Notices R.A.S., vol. 83, p. 415, 1923) actually assign to it a pressure of the order of  $10^{-3}$  to  $10^{-4}$  atmospheres.

The following speculations will show that probably an accurate method of determining the pressure may be developed from the limit of series absorption of elements in the Fraunhofer spectrum. To introduce the subject, let