## Mechanism of Nitrogen Excitation in the Night Sky

THE light emitted by the night sky is a remarkable afterglow associated with recombination of atomic oxygen in the upper atmosphere[1]. Two normal atoms of oxygen could not recombine with emission of light ; the recombination occurs only in presence of a third body to satisfy the principles of conservation. If that third body is an oxygen atom ^3P, it can attain the level ^1S by the following process :

$$O(^3P) + O(^3P) + O(^3P) \rightarrow O_2(X, v = 5) + O(^1S).$$
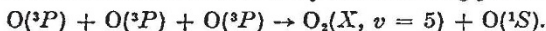
The total energy absorbed by the vibrations of the molecule and by the excitation of the atom $(0.93 + 4.18 = 5.11$ volts) agrees closely with the energy supplied by the recombination. Thus can be explained the emission of lines $\lambda\lambda$ 5577–6300 by the night sky. But if the third body is a nitrogen molecule in the normal state, the available 5.09 volts is insufficient to excite it, and we have to consider the three-body collision :

$$O(^3P) + O(^1D) + N_2(X) \rightarrow O_2(X, v_2) + N_2(A, v_2).$$
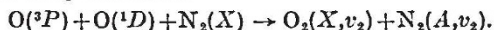
In such a collision the energy made available is $D = 7.05$ volts ; hence the possibility must be considered of emission of Vegard-Kaplan bands $N_2(A \rightarrow X)$. Only those bands the upper level of which does not exceed 7.05 volts will be emitted, and the corresponding quantum number v_2 is at most equal to 5.

Now the upper energy levels of the most intense Vegard-Kaplan bands are $v_2 = 2$ and $v_2 = 3$. To find the cause of this selection, we must consider the vibration of the oxygen molecule after collision. To bring the O_2 molecule to the v_2 level, E_1 volts are necessary ; and we have at our disposal only the difference $D - E_1$ for the N_2 molecule. Consider the necessary energy $A + E_2$ to excite the nitrogen molecule to the A state with the vibration quantum number v_2. We can admit that the excitation does not occur unless the available energy $D - E_1$ and the required energy $A + E_2$ are very close, calling in a resonance effect. The following table gives, on this hypothesis, the probability of emission of the Vegard-Kaplan bands.

	Energy available	Energy required	Difference
I	$v_1 = 0$ $D - E_1 = 7.05$ volts	$v_2 = 5$ $A + E_2 = 6.99$ volts	$+0.06$
II	1 6.89	4 6.83	$+0.06$
III	2 6.67	3 6.66	$+0.01$
IV	3 6.48	2 6.49	-0.01
V	4 6.30	1 6.32	-0.02
VI	5 6.12	0 6.14	-0.02

The transitions III and IV should be the most probable, thus explaining the intensity of the Vegard-Kaplan bands $v_2 = 3$ and $v_2 = 2$ in the spectrum of the night sky.

The probability of a collision of the second kind has been studied for a long while. It is granted that the probability increases as the difference between the exchanged energies decreases. Kaplan[2] quotes, in confirmation of this, the experiments of Bonhoeffer and Mohler on the fluorescence sensitized by atomic hydrogen. Following Kaplan, the formation of a molecule H_2 on vibration level v_1 requires a triple collision with a metallic atom capable of absorbing very exactly the liberated energy $D - E_1$ ($D = 4.34$ volts). Whence the possibility of emission from certain atoms (Na, K, Cd), whilst others (Zn, Mg) do not emit light.

Unfortunately the value of the dissociation potential of hydrogen accepted to-day is no longer 4.34, but 4.46 volts, and the coincidences that Kaplan thought he observed have disappeared. Also Kaplan has not apparently considered the rotation of hydrogen molecules. The total energy absorbed by a molecule is $E = E_v + B_v J(J + 1)$, where J designates the rotation quantum number. It would be sufficient, for the excitation of metallic atom to occur, that the required energy should be very near one of the possible values of $D - E$. But we multiply thus the theoretical possibilities of excitation, and metallic atoms, such as Zn or Mg, which have given nothing in the experiments quoted above, ought to emit the resonance radiation. The resonance potential of Zn is equal to 4.01 volts ; that of Mg is 2.70 volts. Now, in the formation of a molecule H_2 ($v = 2$, $J = 7$), the liberated energy is 4.05 volts ; it is 2.75 volts in the formation of a molecule H_2 ($v = 3$, $J = 7$). But perhaps the differences $4.05-4.01 = 0.04$ and $2.75-2.70 = 0.05$ volts are already too large to show excitation.

However, we observe also in the night sky spectrum a selection of the bands of the first positive system of nitrogen. The band $\lambda\lambda$ 6500–6550 emitted in the transition $B (v = 7) \rightarrow A (v = 4)$ is much the most intense. Now the excitation of the normal nitrogen molecule on the level $B (v = 7)$ requires 8.71 volts, an energy which we do not find in the night sky. We must therefore consider the two consecutive transitions $X (v = 0) \rightarrow A (v = 2)$ and $A (v = 2) \rightarrow B (v = 7)$. The second absorbs 2.22 volts, which is only a little less than the 2.23 volts supplied by the O (^1S) atom in returning to the ^1D level. We can thus explain the enhancement of the 6500–6550 band in the sky by collision of the nitrogen $A(v = 2)$ molecules and oxygen ^1S atoms. In these collisions, the absorbed energy is equal (at about 0.01 volt) to the available energy.

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[1] Chapman, *Phil. Mag.*, **10**, 369 (1930) and **23**, 657 (1937).
[2] Kaplan, *Phys. Rev.*, **31**, 997 (1928).

Carbonic Anhydrase

IT was shown by Henriques[1] that the rate at which carbon dioxide is evolved in the reaction $H_2CO_3 \rightleftharpoons CO_2 + H_2O$ is greatly accelerated by the presence of laked blood, mere traces of which are sufficient to catalyse this reaction[2]. That this acceleration is not due to hæmoglobin was clearly demonstrated by Meldrum and Roughton[3,4] who have separated from the red blood corpuscles a new enzyme capable of catalysing both phases of the above reaction. They described this enzyme under the name of carbonic anhydrase and gave a detailed account of its properties. Their purified preparation of this enzyme was a colourless substance, very active and sensitive to KCN, H_2S and NaN_3. The amount of this enzyme-preparation was, however, very small and scarcely sufficient even to recognize it with certainty as a protein compound. In the course of our study of metallo-protein compounds[5] present in the red blood corpuscles, we have found that the fractions of our preparations left after the complete removal of hæmocuprein had a very high content of zinc and a high carbonic anhydrase activity. By adapting our methods of purification to preparations on larger