

When both the discharge and flow of gas are stopped, the solid deposit was found to glow deep green for several minutes. The half-life was influenced by impurities in the nitrogen, being 37 sec. for pure nitrogen and 20 sec. for nitrogen contaminated with oxygen. This phosphorescence following the discharge is called the *afterglow*. The spectrum of the afterglow shows only α , α' , and α'' lines. The α lines are blue-green, while α' and α'' are single lines at 5943.8 Å. and 4683 Å. respectively.

When the afterglow has ceased, the dark solid can be made to phosphoresce at a later time by removing the helium and allowing the ice to warm up. Somewhere between 10° K. and 16° K., the α emission is observed. This consists of five lines between 5214 Å. and 5240 Å. This is followed shortly by β emission (5549 Å., 5616 Å. and 5657 Å.). These lines increase in intensity and reach a maximum near 30° K. The B band emission (3000 Å. to 4700 Å.) begins just a few degrees below this, thereby adding a blue cast to the glow. They are enhanced when a small amount of oxygen is present. It seems to last longer than the green components so that between 35° K. and 40° K. the glow is predominantly blue. There appears to be no emission above 40° K. The Vegard-Kaplan bands (2300 Å. to 4450 Å.) are also seen during warm-up when an excess of argon is deposited with the nitrogen, and oxygen is less than 0.01%.

The α lines are believed to be caused by the forbidden $2d-4s$ transition of atomic nitrogen. The β group may be caused by the $1s-1d$ transition of atomic oxygen. The B band system is not thoroughly understood. It is believed to be associated with NO_2 .

Some estimated intensities of the various emissions during warm-up are presented in Table IV.

TABLE IV

Wavelength angstroms	Intense feature	System	Colour
2946	250	VK	Ultra-violet
4306	60	B	Violet-blue
4683	10	α''	Blue
5214	200	α	Blue-green
5220	500	α	
5228.5	1000	α	
5235	750	α	
5240	400	α	Yellow
5549	1000	β	
5616	750	β	
5657	650	β	
5943.8	150	α'	Orange

The relative light intensities are for a particularly good warm-up. In pure nitrogen the 5228.5 Å. line is the brightest during this period. In a very thin deposit, the green glow can be seen in daylight. The rate at which the material sublimates is very low. A fireball, consisting of a small percentage of nitrogen atoms equivalent to that responsible for the warm-up glow, would be several orders of magnitude brighter because of

the more rapid sublimation rate. The increased brightness has been observed in the laboratory. Herzfeld and Bass²⁵ state that when the phosphorescing solid was warmed suddenly from 4.2° K. to over 25° K., "it emitted a flash of blue light, which looked like a flame burning through the solid." This is how a cometoid fireball might appear but on a grand scale. The light would contain strong α and β components in the blue-green and yellow, and possibly enhanced B bands from oxygen impurities. The light of the fireball might therefore contain the strong lines in Table IV. There could also be infra-red lines which are not listed (7910 Å. and 8570 Å.). From many descriptions of green fireballs over New Mexico, it appears that the α lines come as close to the correct shade of green as can be expected, especially the bright 5228.5 Å. line. For instance, compare the painting by Mrs. La Paz in *Life* magazine where she tried to faithfully reproduce the actual colour of a green fireball with the cover of *Scientific American* where a photograph of the green nitrogen glow is shown.^{26,27}

Milligan and Pimental²⁸ in carrying out the photolysis of diazomethane, CN_2H_2 , noticed that on warm-up a red glow appeared between 20° K. and 25° K. It persisted until the temperature reached 30° K. They did not make spectral measurements nor was the excited or unstable species identified. They believe that an electronically excited state of C_2H_4 may account for the luminescence. Nitrogen might also be considered because of the similarity of temperature ranges for phosphorescence.

The aliphatic ketones, when irradiated at 77° K., have also been reported to phosphoresce in the blue and violet when warmed.²⁵ Nitrogen ice is the most brilliant by far, however.

2. ESTIMATED BRIGHTNESS OF PHOSPHORESCING FIREBALLS

Consider a sphere of frozen nitrogen which contains a small percentage of metastable nitrogen atoms, comparable to that currently achievable in the laboratory.

If n is the number of pairs of frozen atoms per N_2 molecules, then the unstable percentage, P_r , is given by

$$P_r = \frac{100n}{N+n} \quad \dots \quad (1)$$

and

$$n = \frac{NP_r}{100-P_r} \quad \dots \quad (2)$$

Similarly, if m is the mass of a nitrogen atom, then the mass of the unstable matter is given by $2nm$, or from Equation (2),

$$2nm = \frac{2NmP_r}{100-P_r} \quad \dots \quad (3)$$

The mass of the nitrogen sphere, M , is given by

$$M = 2(N+n)m = \frac{4}{3}\pi\rho a^3 \quad \dots \quad (4)$$

where ρ is the density of solid nitrogen.