

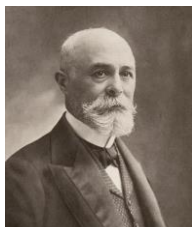
Henri Becquerel and the intensity of phosphorescent light

In April 1892, the *Journal de Physique* published an article from the great French physicist Henri Becquerel about phosphorescent light and the laws that can describe its intensity. Becquerel is best known for the discovery of radioactivity, which won him a share of the third Nobel Prize for Physics to be awarded, in 1903; he gave his name to the SI unit for radioactivity, the becquerel.

Here, Becquerel first highlights how luminous phenomena – including phosphorescence – allow physicists an insight into the structure of matter. The first physicist who studied the light emitted by phosphorescent bodies was his own father, Alexandre Becquerel. He showed that, after a short while, the intensity of this light (i) can be described by the equation of exponential decay: $i = i_0 \exp(-\alpha t)$ where t is the time elapsed since the intensity was i_0 and α is a coefficient specific to each substance. Indeed, this relationship was verified by examining a body in a phosphoroscope. But he also noticed that this law is not verified for phosphorescent bodies that emit light for periods of minutes or hours. Then, it should be replaced by the empirical formula $i_m(c + t) = c i_0^m$ where m and c are specific constants. However, even this empirical formula was still not a completely satisfactory way of describing the observed intensities because c and m were to be given different values during the same experiment with the same body if the experiment is quite long.

At about the same time, M. Wiedemann analysed further the various alternatives of light excitation and extinction in the phosphoroscope, admitting that the exponential law is exact and using it to establish various theoretical considerations on phosphorescence (*Ann der Physik und Chemie*, t. XXXIV, 1888).

Henri Becquerel, also assuming that the exponential law is true, established that the intensity of light emitted by a body in a phosphoroscope is defined by several exponential decays with the parameter α . But he encountered the same problem: the different observed values of the intensity do not lead to a constant value for α . While announcing that the detailed methods of calculation and his numerical tables will be published later, he gives the values obtained with alumina. Here, α grows from 0.2216 to 0.4577 depending on the duration of light exciting the sample. He highlights that the regular increase of α leads him, by simple mechanical considerations, to postulate a relationship between the intensity of emitted light and the time elapsed since the excitation light ceased. As Becquerel thought that the emitted light is the result of intermolecular vibratory movements, he considered that its extinction and the resulting decrease of the movement's amplitude are due to an intermolecular damping force that is a function of the speed of the vibrating particles. However, a



damping force that is proportional to the speed leads to the exponential relationship for intensities and that is not observed experimentally.

In this paper, he exposes a new assumption: the damping force may be proportional to the square of the speed, as occurs when a solid body moves in a resistant environment. He then calculated the differential equation of the movement and, for the displacement of the vibrating particle u , he established a relationship between the amplitude of the n^{th} half-period u_n and the initial amplitude u_0 :

$$u_n = \frac{u_0}{1 + \frac{4}{3} n \gamma u_0}$$

Noticing that the number of half-periods is proportional to the time and that the amplitude is proportional to the square root of the intensity, he finally establishes Equation (1):

$$u = \frac{u_0}{1 + u_0 b t} = \sqrt{i} = \frac{1}{a + b t} \quad (1)$$

This formula is similar to the empirical formula given below, where $m = \frac{1}{2}$.

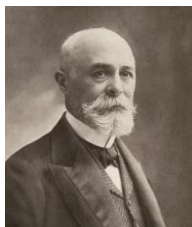
$$i^m (c + t) = c i_0^m$$

Henri Becquerel highlights that, in his father's experience, the value of m was always near $\frac{1}{2}$ and could even be exactly $\frac{1}{2}$ for some bodies, especially for particular preparations of sulphide, of calcium and of strontium. This formula seems to be unsuitable for other bodies but, as these may be considered as mixtures of different substances or of different compounds of the same substance, each emitting a glow with a different law of extinction, he therefore deduces that the total intensity is the sum of the partial intensities:

$$i = \frac{1}{(a + b t)^2} + \frac{1}{(a' + b' t)^2} + \dots \quad (2)$$

He describes this as "A remarkable way to describe the intensities of the glow emitted by long-lasting phosphorescent bodies".

To reinforce his theory, he reports comparisons with observations published by his father in the *Annales de Chimie et de Physique*, t. LX.1, (1860). Here, the



intensities were deduced from the distance – named y – that a lamp had to be moved away to obtain an intensity on a transparent surface that was equal to that of the glow emitted by the phosphorescent body. This led, apart from a constant factor, to

$$i = \frac{I}{y^2}$$

He deduces that formula (1) becomes, in this case, simply the equation for a straight line ($y = a + bt$): this was experimentally verified with the few bodies mentioned above. For mixtures of substances such as the preparation of calcium sulphide, or for strontium and barium sulphides, the curve has a convex shape near the y axis.

Observations for the blue calcium sulphide¹ are very well represented by the relation

$$i = \frac{I}{y^2} = \frac{I}{(57 + 0,09t)^2} = \frac{I}{(7,97 + 0,65t)^2}$$

and Henri Becquerel provides a table of very close observed and calculated values of y from 0 to 1725 seconds. He deduces that the intensity fits the formula during half an hour (= 1800s) and he estimates that during this period the differences between observed and calculated values are within the experimental errors of measurement.

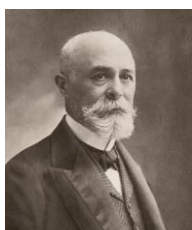
He then calculates the total quantity of emitted light, Q , as

$$Q = \int_0^{\infty} i dt = \int_0^{\infty} \frac{dt}{(a + bt)^2} = \frac{1}{ab}$$

and applies this calculation to each of the materials that make up the blue light mixture. Noticing that $57 \times 0.09 = 5.13$ and $7.97 \times 0.65 = 5.18$, he deduces that the total amount of light emitted by each of them is the same, despite their unequal extinction speed.

He also highlights that there is another way to demonstrate that substances are mixtures of materials with different extinguishing times. The temporary projection of the sun's spectrum on a screen made of powdered material shows phosphorescence to have been excited in particular spectral regions. These

¹ This is what Becquerel wrote, although we know calcium sulphide today as CaS, a white solid.



form the absorption spectrum of the substance concerned because the rays have to be absorbed to be active.

To prove this, he studied the preparation of calcium sulphide and observed an absorption spectrum consisting of two active bands: α for the wavelengths 400-455 nm (a dark blue glow) and β from 340 to 365 nm (as Becquerel wrote, a light blue-greenish glow²). However, if the excitation action lasts a little longer, a lighter glow appears and quickly disappears on the most refractory half of α , from 400 to 405. This glow may then justify the presence of a third term in the formula, although this term would have very little influence.

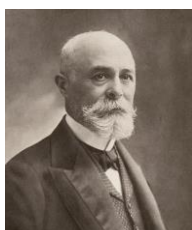
The glows emitted by the α and β bands have unequal persistence durations and Becquerel describes how to make this inequality more visible. He describes heating the material and observing that the phosphorescence is momentarily bright and then diminishes while the green β band disappears rapidly and the blue α is visible for a long time. If the spectrum is projected onto the substance for a long time or if the substance is at a temperature higher than 100°C, the α band appears alone and the body appears dark blue (instead of light blue at ordinary temperatures).

Through experiments with other preparations of phosphorescent sulphides of calcium, of strontium, and of barium, Becquerel observed that similar phenomena occur: some appear free of mixtures and show only one excitation band in the spectrum, a sulphide of calcium gives only the β band, a luminous strontium sulphide gives only one band and the intensity of the light emitted almost exactly follows formula (1) above. He also noticed that different materials mixed together lead to colour changes in the emitted light which are similar to those he studied in fluorides of calcium, either when they are made phosphorescent by heating or when they are examined with a phosphoscope with different speeds of rotation.

He explains that studying the decreasing light emitted by phosphorescent bodies should therefore isolate radiation of a given wavelength, emitted under the excitation influence of monochromatic radiation of an equally determined wavelength. However, the experiments he reported convinced him that formula (1) has a high probability of properly describing the variation of its intensity.

Trying to understand the physical foundations of his observations, Becquerel suggested a relationship between intensity of the phosphorescent light and the duration of exposure to excitatory radiation. He reminds his readers that he already demonstrated that, for certain bodies such as the uranium compounds, the absorbed radiation corresponds to vibratory movements that are harmonics

² Becquerel's remark here is odd, because the wavelengths quoted are in the near ultra-violet part of the electromagnetic spectrum.



of those of the radiation emitted by phosphorescence. He then assumes that vibratory movements are produced in the bodies, either permanently or due to the incident radiation. By an extension of Kirchhoff's law, Becquerel supposes that the absorbed radiations would be those whose vibrations are either synchronous with or harmonics of the intermolecular vibrations.

In the case of a body subjected to light and becoming phosphorescent because the intermolecular ether³ takes a vibratory movement synchronous with the one that will constitute phosphorescence, he expresses the amplitude of the ether as $U = A \cos kt$ ($t = \text{time}$) and the amplitude of the movement which produces phosphorescence as $u = u_0 \cos kt$. Writing down the relative speed of the phosphorescence movement in relation to the vibrating medium, and assuming that the damping is proportional to the square of this speed, the differential equation of the movement leads to the relation

$$u = A - \frac{A - u_0}{1 + (A - u_0)bt}$$

However, Becquerel concludes that this is “a formula that needs to be verified by new ongoing experiences”.

Finally, Becquerel highlights that this paper gives a fairly accurate account of the reduction of the intensity of light emitted by phosphorescent bodies and that this is due to his assumption: namely, that the intermolecular movements that produce phosphorescence are damped in proportion to the square of the speed of the vibrating particles.

Original article:

[Influence d'un champ magnétique sur le rayonnement des corps radio-actifs](#), Henri Becquerel, J. Phys. Theor. Appl. 9, 71-78 (1900)

[Journal de Physique archives](#)

We are pleased to offer this commentary in collaboration with [SciencePOD](#).

³ When he wrote this paper, Becquerel, like all late 19th century physicists, would have believed the ether (or aether) to be the medium through which light was meant to propagate. This theory was finally disproved in the early 20th century.

