

QUANTUM EMISSION PHENOMENA IN RADIATION.

BY DAVID L. WEBSTER.

SYNOPSIS.

*Comparison of X-rays and Light; a Summary.*—This covers the best known cases of excitation of line spectra by electron impact, and the form of the Bohr theory, that is required by them.

*Comparison of Emission and Absorption.*—The above phenomena are compared with corresponding absorption phenomena, with especial reference to the accumulation of energy for photoelectrons by absorption.

*Deductions.*—Theories of the type of Bohr's appears inconsistent with these facts. The phenomena suggest that the law of the conservation of energy, as applied to atomic oscillators, holds only statistically. A set of postulates to replace it for individual oscillators is outlined.

COMPARISON OF X-RAYS AND LIGHT.

THE purpose of this paper is to compare the quantum phenomena in X-rays and light and to draw conclusions from them on the laws governing the emitting mechanism. Let us consider first the simpler

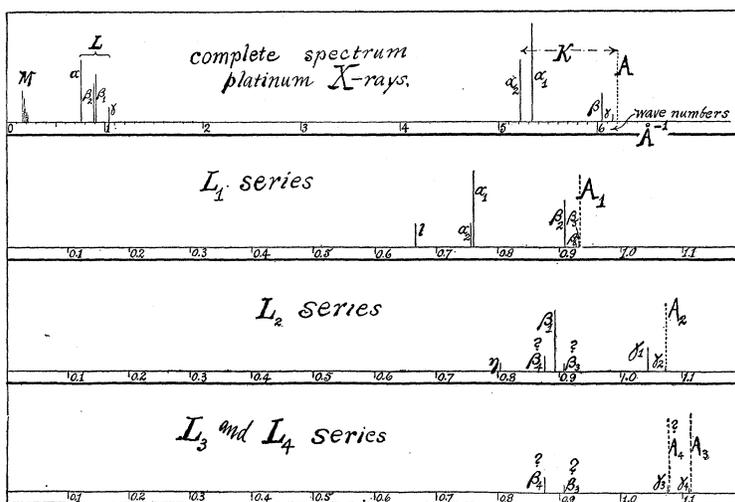


Fig. 1.

case of X-rays. In Fig. 1, we have the spectrum of platinum, on a scale of wave numbers, showing the K, L and M series. In the K series we

have the strong  $\alpha$  lines, the weaker  $\beta$  and  $\gamma$  lines and the absorption limit  $A$ . This point  $A$  is especially important, because waves of a higher frequency than  $A$  are absorbed by the element much more strongly than those of lower frequency, and also the higher frequency waves give rise to a fluorescence consisting of the  $K$  series emission lines. If now we subject a piece of platinum to cathode rays, we should find no  $K$  series emission from it unless the energy of a single cathode ray is as large as a quantum of the frequency  $A$ . (This has not been tested directly for platinum, but has been for other elements,<sup>1</sup> and we may be sure they all act the same.) For any higher value of the cathode ray energy, we

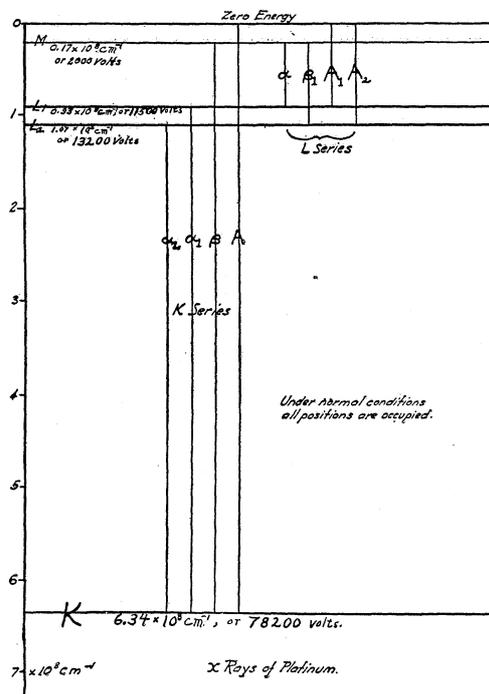


Fig. 2a.

have all the  $K$  series lines emitted with constant intensity ratios under all conditions. Evidently the mechanism used in the production of  $K$  series rays by cathode rays is such as to demand the same energy quantum as that used in fluorescence, and presumably it is the same mechanism.<sup>2</sup>

In the  $L$  series we have a similar state of affairs, except that the series must be divided into three or four sub-series, each with its own absorption

<sup>1</sup> For rhodium see D. L. Webster, *PHYS. REV.*, 7, 599-613, June, 1916. For molybdenum and palladium see B. A. Wooten, *PHYS. REV.*, 13, 71-86, Jan., 1919.

<sup>2</sup> D. L. Webster, l.c.

limit and corresponding critical potential. The exact status of the series marked  $L_3$  and  $L_4$  in the diagram is not settled, but  $L_1$  and  $L_2$  are definitely known to behave exactly like the  $K$  series as shown by evidence described elsewhere.<sup>1</sup> In every case the energy required is represented by many thousands of volts.

In light, however, conditions are different. For example, in sodium vapor, studied by Tate and Foote,<sup>2</sup> if the energy of the bombarding electrons is gradually increased there is no radiation till we reach 2.1

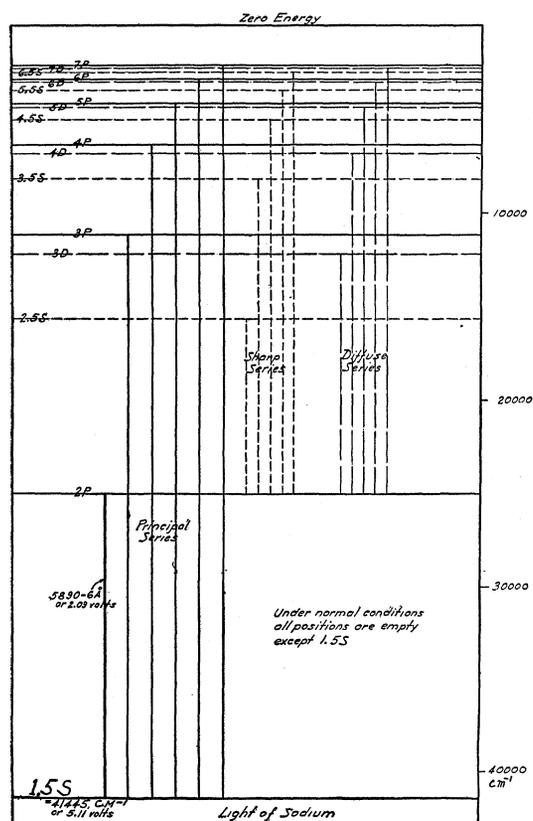


Fig. 2b.

volts, when the well-known  $D$  lines appear, alone, as a so-called “single-line spectrum.” Now 2.1 volts corresponds exactly to the quantum of their frequency. But they are the first lines of a series, like the  $K \alpha$  lines; and the limit of the series, corresponding to the point  $A$ , is at a

<sup>1</sup> D. L. Webster and H. Clark, Proc. Nat. Acad., 3, 181-5, March, 1917, and D. L. Webster, *ibid.*, Jan., 1920.

<sup>2</sup> J. T. Tate and P. D. Foote, Phil. Mag., 36, 64-75, July, 1918.

frequency more than twice as high. The  $D$  lines are the lines  $1.5S-2P$ , and the limit,  $1.5S$ , corresponds to a voltage of 5.1 volts. When this voltage is reached, we get the whole series  $1.5S-mP$ , and with it the subordinate series, some of whose lines have lower frequencies than the  $D$  lines. The important difference from the X-ray case is the existence of the so-called "single-line spectrum," at voltages between 2.1 and 5.1 volts. Such a phenomenon is unknown in X-rays.

Now this difference between the two cases is readily explained by the diagram in Fig. 2. According to Kossel's<sup>1</sup> modification of the Bohr theory, the  $K$  series is produced by removing an electron from the innermost ring, called the  $K$  ring, and allowing one to fall into its place from another ring, the  $L$ ,  $M$  or  $N$ . While I think there is ample evidence against the idea that the Bohr rings actually exist, it may be that the stable positions that do exist will act in much the same way. I have therefore drawn the diagram giving the  $K$  position at the bottom, indicating that a potential of 78,200 volts is required to lift the electron from it to the surface of the atom, where its energy would be zero. The energy required to do this is the quantum of the absorption limit,  $A$ , of the  $K$  series. Similarly the energies required to lift an electron from the  $L_1$  and  $L_2$  positions are the quanta of the absorption limits  $A_1$  and  $A_2$  respectively; and the  $K \alpha$  lines are produced by removing an electron from the  $K$  position to infinity and replacing it by one falling from  $L_1$  or  $L_2$ . By such considerations Bohr<sup>2</sup> predicted the fact that the critical potential for emission of the  $K$  series would be that which gives an electron a quantum of the frequency  $A$ , and Kossel, in 1914, predicted the relation  $\nu_{K\alpha} = \nu_{KA} - \nu_{LA}$  which he tested as accurately as he could, and he also predicted some relations between emission line frequencies. An essential point for this explanation of the critical potential by Bohr and Kossel is that the electron removed from the  $K$  position *must* go to infinity, and cannot be allowed to come to rest in the  $L$  or  $M$  positions. That is, *in the normal atom all positions involved in X-ray processes are full.*

In light, on the other hand, we have a set of stable positions, shown in Fig. 2 as  $1.5S$ ,  $2P$ ,  $2.5S$ ,  $3P$ ,  $3D$ , etc., and the process of exciting the single line spectrum is evidently to lift an electron from  $1.5S$  to  $2P$  and let it fall back. If the electron is lifted to infinity, or zero energy, we shall excite the whole system, including the subordinate series. As van der Bijl<sup>3</sup> has suggested, the existence of the "single-line spectrum" means simply that *in the normal atom no position is filled above  $1.5S$ .*

<sup>1</sup> W. Kossel, Verh. d. D. Phys. Ges., Nov. 30, 1914.

<sup>2</sup> N. Bohr, Phil. Mag., 26, 1-25, July, 1913.

<sup>3</sup> H. J. van der Bijl, PHYS. REV., 10, 546-556, Nov., 1917. Van der Bijl does not call it the  $1.5S$  ring, but describes it in terms equivalent to that.

In mercury, which has been studied by Frank and Hertz, McLennan and Henderson, Davis and Goucher and others, we have a more complex state of affairs indicated in Fig. 3. The lines  $1.5S-2p_2$  and  $1.5S-2P$  both appear at the potentials given by the quantum law, applied to their

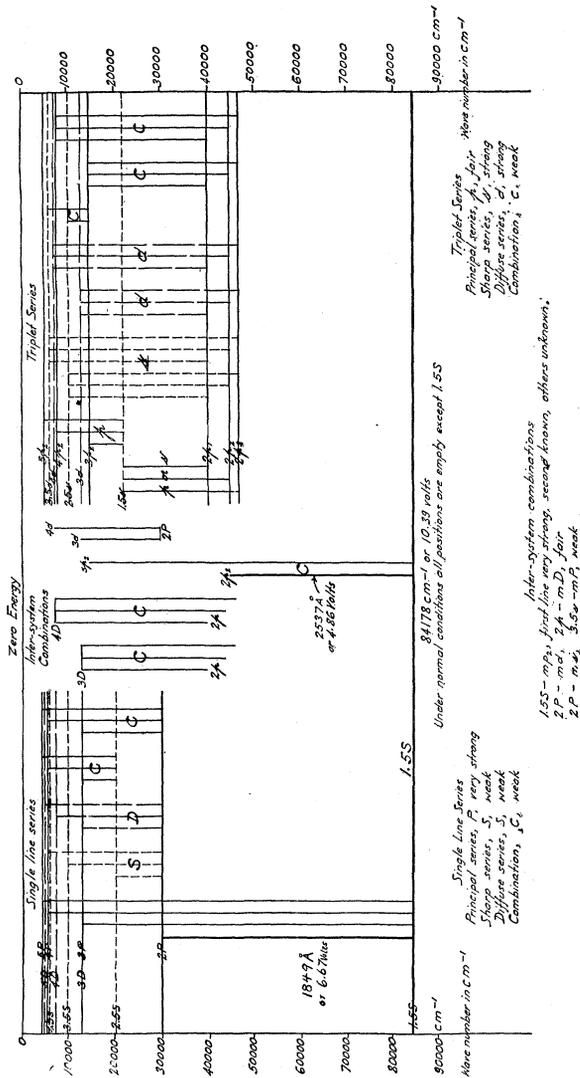


Fig. 3.

respective frequencies, and the whole spectrum appears at the potential given by the quantum of  $1.5S$ . Again the explanation is van der Bijl's hypothesis that  $1.5S$  is the only position that is normally full. In calcium also, effects exactly like those in mercury have recently been

observed by Mohler, Foote and Stimson,<sup>1</sup> and the explanation is again van der Bijl's hypothesis. These phenomena in light show clearly the existence of empty positions of stability, and if such empty positions were present in the X-ray mechanism they ought to show in the same way, by a "single-line spectrum" in each X-ray series. The fact that such a single line spectrum fails to occur is therefore strong evidence against any theory of X-rays that assumes empty positions of stability in the normal atom below the 1.5S position, as several of the recent theories do.

#### COMPARISON OF EMISSION AND ABSORPTION.

So far the theory is good, and these elements are typical of the groups whose quantum emission phenomena are best known. When we apply the theory to absorption, referring again to Fig. 2, we see to some extent why it is possible to have sodium vapor absorb the *D* lines, and lift its electron to *2P*, and why it is impossible for any element to show selective absorption for any of its X-ray emission lines. Instead, it must absorb rays above the frequency *A*, since a quantum of such a frequency is required to remove the electron to a place where it can stay. But then the question arises, why can not the same process occur in light, and why does not sodium vapor absorb not only the *D* lines but also all frequencies above 1.5S, and give a fluorescent spectrum under such conditions similar to X-ray fluorescence? Applied to absorption, this type of theory is most unsatisfactory.

A more fundamental difficulty appears when we consider the nature of the absorption process. The electron must in some way collect energy enough from the X-rays to appear as a photoelectron. This, according to Barkla,<sup>2</sup> means the amount  $h(\nu + \nu_A)$ , where  $\nu$  is the frequency of the rays absorbed and  $\nu_A$  is that of the absorption limit. This conclusion is drawn from the observed fractions of the total X-ray energy that appear in photoelectrons and in fluorescent X-rays and the fact that the photoelectrons all appear to have the same energy,  $h\nu$ . While the evidence on this latter point does not seem quite conclusive, it is significant that the energy  $h(\nu + \nu_A)$  is exactly the amount suggested by the Bohr theory, although Barkla's evidence was not drawn at all from this theory. I say "suggested," rather than "required," because it is not certain that the electron could not be helped out of the atom by another electron falling in from an outer stable position as the first one goes out, thus neutralizing the force that would otherwise restrain the one that leaves.

<sup>1</sup> F. L. Mohler, P. D. Foote and H. F. Stimson, Bull. Bur. Stan., 1920. Abstract in PHYS. REV., 14, 534, Dec., 1919.

<sup>2</sup> C. G. Barkla, Proc. Roy. Soc., A.92, 501-4, Aug., 1916.

However that may be, the electron leaves with energy of the order of  $h\nu$  and must collect from somewhere a quantity of this order or perhaps  $h(\nu + \nu_A)$ . Millikan<sup>1</sup> has recently described experiments leading to conclusions of the same general type for photoelectrons produced by light.

Now where does the electron get this energy? If in light or X-rays the energy is all concentrated in a point of the wave front, the electron might get at once as much as the energy  $h\nu$  of the primary cathode ray, but no more. But energy is the ability to do work; and to produce coördinated motions of electrons in different parts of a crystal, a train of waves of X-rays must have this ability at points widely scattered over the wave front and perpendicular to it. And in a reflected or scattered train of waves the whole energy is very much less than the quantum emitted from the primary radiator, according to any reasonable theory of these phenomena, so that the amount of energy coming within reach of any one atom exposed to this beam must be correspondingly reduced. In light, as shown by the diffraction pattern at the focus of a high-power microscope objective, the ability to do work must be distributed over practically a whole hemisphere of the wave front if not more, thus indicating a distribution of energy in light even wider than any we have definite evidence of in X-rays. It would be most unreasonable to assume that X-ray waves are not constructed like those of light, and probably the energy is distributed as widely in one case as in the other. If now the X-rays have passed through a slit, the wave train thus limited contains but a small fraction of a quantum, and if they are then reflected from a crystal it contains even less. The same is true of light subjected to such treatment. But in either case the photoelectron has as much energy when produced by the weakest beam as when produced by the strongest. And in X-rays photoelectrons can be obtained easily, as shown by ionization methods, when the heads of the successive wave trains are as far apart, on the average, as many millions of wave-lengths. One might perhaps attempt to explain the accumulation of energy by the coincidence of a large number of wave trains. But it is well known that this would not lead to a photoelectric current proportional to the intensity of the rays; and so it is evident that the absorption of energy by the photoelectron is not dependent upon coincidence. If not, then it must be by a process of gradual accumulation. According to the electromagnetic theory it would be very gradual indeed and, even in a strong monochromatic beam a resonating electron should take many weeks to acquire the energy  $h\nu$ . But aside from such theoretical considerations, the practical reasons given here seem sufficient to show the gradual nature of the process.

<sup>1</sup> R. A. Millikan, Am. Phys. Soc. meeting, Dec. 31, 1919.

Now let us suppose an electron from the  $K$  ring is absorbing X-rays and has lifted itself half way to the position of zero energy, and then is struck by a cathode ray. One would expect that if the cathode ray has only energy enough to lift the electron the rest of the way to the surface, it will produce the  $K$  series lines. But no. It must have a whole quantum of the critical frequency and no less. The same difficulty appears also in light, as one may see by reference to the phenomena described above.

In such a theory as I have just described there seems to be no way to distinguish the energy stored by absorption from the energy acquired from a cathode ray, and prevent them from being combined as suggested above. In a theory of heat radiation that I proposed in 1915,<sup>1</sup> based on Parson's magneton theory, the distinction might be made, because the energy accumulated by absorption was stored in a rotary form not readily affected by the impact of a cathode ray. But even here, there is some difficulty. The X-ray absorption spectrum is continuous, and it is hard to see how we can avoid the assumption that the natural absorption frequency of an electron is different at different times. Certainly it is not fixed by Bohr's energy considerations, because a larger quantum than  $h\nu_A$  could not be collected continuously: the electron would escape as soon as it has the energy  $h\nu_A$ . Some other determining factor must be present. In light also, in solids and liquids, especially metals with free electrons, there must be continual changes and readjustments of the electron's frequency.

If now such a change of frequency occurs when an electron has nearly finished collecting a quantum, and the change is to a lower frequency, for which the energy already stored is more than a quantum, one would expect photoelectric action even if no rays happen to be falling on the electron when the change occurs. In this or some such way, one would expect some evidence of the stored energy to appear. Thus the magneton hypothesis, while distinctly better than the other, is still unsatisfactory, because evidence of stored energy fails to appear. The stored energy causes trouble, and perhaps more trouble than it is worth.

After all, what is it worth? As Poincaré<sup>2</sup> has said, every time we deal with a new type of phenomenon, we find or invent a new quantity that we can call energy, and define it so as to make the total energy of the system a constant. As both he and Ritz<sup>3</sup> have said, the law of the conservation of energy is not a law, but a postulate. Some time, a phe-

<sup>1</sup> D. L. Webster, Proc. Amer. Acad., 50, 131-145, Jan., 1915; see also *PHYS. REV.*, 8, 66-9, July, 1916.

<sup>2</sup> H. Poincaré, *Science and Hypothesis*, Paris, 1901, Chapter VIII.

<sup>3</sup> W. Ritz, *Ann. Chim. Phys.*, XIII, 145-275, or *Collected Works*, Paris, 1911, p. 345.

nomenon may arise where this postulate is not advantageous in its most complete form. It seems to me that this time has come. Explanations of phenomena are important, but a postulate is not.

To preserve our explanations of refraction and other classical phenomena of physical optics, let us assume as usual that the oscillator is governed by an equation of the form

$$m\ddot{x} + g\dot{x} + fx = eE_x,$$

$x$  being the displacement of the electron from its equilibrium position and  $E_x$  the external electric force in the  $x$  direction. As Ritz suggested, a vibration controlled by a magnetic field or some similar agency is more probable than the elastic force  $fx$ , but as this is the usual form of dispersion equation, we may use it here. Any magnetic or similar vibration could be substituted without changing our present conclusions. This equation gives absorption at a rate  $g\dot{x}^2$ , the mean value of which through a whole period is  $\frac{g}{m} U$  where  $U$  is the energy of the oscillation. Now, instead of assuming this absorbed energy to be stored somewhere, and reëmitted some time later, *let us assume it to be simply annihilated*. Then let us assume that the electron may at any time start an emitting oscillation of large amplitude, continuing uniformly until a whole quantum is radiated, or else emit a photoelectron with a quantum of energy. And let us assume that the probability of starting such an oscillation or photoelectron during a time  $dt$  is

$$\frac{g}{m} \frac{U}{Q} dt,$$

where  $Q$  is the "accumulated energy" defined above, which may be  $h\nu$  or may be something larger. Further let us assume that transfers of energy either to or from cathode rays or other colliding particles can take place, but by quanta only.

That these hypotheses give a mathematical theory of dispersion exactly like the classical theory is evident from the fact that the dispersion theory is not concerned with what becomes of the power  $g\dot{x}^2$  after it is taken from the electron by the damping force.

To make them give a theory of heat radiation we need only an entropy condition for the oscillator. To get this we may use almost the same condition as in my heat radiation theory, referred to above, which was modelled to a great extent on Planck's. If  $Q = h\nu$ , the behavior of an oscillator in a given field of radiation is almost equivalent to what is assumed there, because the rate of absorption and mean rate of emission

are the same. To make them exactly equivalent, we have only to assume that an oscillator newly formed in an atomic readjustment will behave almost exactly like the one of the other theory, which absorbed energy continuously and stored it, radiating by quanta or multiples of quanta. The only difference is that in starting its career with its new frequency it must not start at the zero of the scale of absorbed energy, but at any point on it, the probability of starting at any one point being proportional to the density of oscillators on the scale of energy at that point; and when it changes frequency again it must not be considered to have a store of energy in it. In other words, the stored energy of the previous theory must have been merely a mathematical fiction and should not have been assumed to have any real physical existence.

If the energy  $Q$  is greater than  $h\nu$  we have a case of fluorescence, the energy  $h\nu$  appearing in a photoelectron and the rest as fluorescent rays. In this case we get into the question of the thermodynamics of fluorescent bodies, which needs a long discussion. In the absence of very definite evidence on the exact value of  $Q$ , as suggested above, the time does not seem ripe for such a theory.

#### SUMMARY.

We may summarize these conclusions as follows: The simple Bohr theory is good for explaining the phenomena of excitation of X-rays and light by impact, if we assume that in the normal atom all rings are full from the  $K$  ring to the  $1.5S$  ring, inclusive, but none outside  $1.5S$ . But the theory is quite unsatisfactory for absorption phenomena. Even if the absorbing electron is not a member of a Bohr ring, but a "magneton" of the type assumed in my previous theory, situated in a stable position similar to a Bohr ring, and having the required resonance frequency, there are still some difficulties when the frequency is subject to change with time. Consequently it seems better to assume that in postulating the existence of stored energy in the oscillator we have carried the postulate of conservation of energy a step too far. We had better abandon it at this point and postulate a system of equations that give the conservation of energy as a statistical effect only and preserve the explanations of dispersion and heat radiation intact, at the same time explaining the phenomena of excitation of radiation by impact.

ROGERS LABORATORY OF PHYSICS,  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
CAMBRIDGE, MASS.