# THEORETICAL CONSIDERATIONS CONCERNING IONIZATION AND SINGLE-LINED SPECTRA.

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IN the following an attempt is made to give an explanation of some of the rather conflicting results on the ionization and characteristic radiation produced by the passage of electrons through gases and vapors. Most of the investigations of these phenomena were performed with mercury vapor, but the following considerations will in the main apply also to other monatomic gases and vapors.

The most important result of the experiments of Franck and Hertz[1] is that collisions of electrons with molecules of mercury vapor are elastic until the electrons have acquired energy equivalent to 4.9 volts. After having dropped through this voltage the electrons lose all their energy on collision and at the same time energy is radiated. This radiated energy Franck and Hertz identified as the single-line 2536 Å.U. This shows that the mercury atom does not take any energy from the colliding electron unless the latter has a definite minimum amount of energy to give to the atom. Furthermore, in view of the fact that, according to the Planck-Einstein relation $Ve = h\nu$, the frequency of the line 2536 corresponds to 4.9 volts, the experiments of Franck and Hertz gave evidence in favor of the quantum theory. They concluded from their experiments that when the electrons have dropped through 4.9 volts, ionization of the mercury vapor sets in. By using Lenard's[2] method of picking out the positive ions, they actually observed what appeared to be ionization at 4.9 volts. This result was later confirmed by McLennan and Henderson,[3] Goucher[4] and others. McLennan and Henderson also found that the single line 2536 was emitted when the atoms of mercury vapor were bombarded by 4.9 volt electrons, and established a similar result for cadmium and zinc.

These results presented two difficulties: Firstly, although the result that the collision of an electron with an atom of a monatomic gas is elastic when the electron collides with energy less than a certain definite

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[1] Verh. d. D. Phys. Ges., 16, 457 and 512, 1914.

[2] Ann. d. Phys., 8, 149, 1902.

[3] Proc. Roy. Soc., A, 91, 485, 1915.

[4] PHYS. REV., 8, 561, 1916.

amount is in conformity with the quantum theory, such conformity does not exist if ionization as well as radiation is produced by the transference of this definite amount of energy from the colliding electron to the atom. Secondly, the quantum theory requires that the transference of this amount of energy should give rise to the stimulation of a single line. But if, on the other hand, a stream of colliding electrons is used (as is always done) the emission of a single line is not compatible with Bohr's theory of the atom. It is because of these definite and important questions that experiments along these lines may reasonably be expected to furnish valuable evidence regarding the validity of the quantum hypothesis and particularly Bohr's theory of atomic structure.

As regards the first question, viz., the production of ionization simultaneously with the stimulation of the 2536 line in mercury, I pointed out that the ionization effect observed at 4.9 volts may, under certain conditions, not be impact ionization, but a photoelectric effect[1]: The stimulation of the line 2536 establishes a source of ultraviolet light in the discharge tube and so causes a dislodgment of electrons with the attending phenomena of ionization. On this view, what we might call the ionization voltage of mercury vapor would be 10.4 instead of 4.9 volts. This view has since been confirmed experimentally by Goucher.[2]

As regards the second question, the reality of the single-lined spectrum does not seem to have been established. McLennan[3] found that the many-lined spectrum was not produced until the colliding electrons have acquired an amount of energy equivalent to about 10 volts, this voltage, according to the quantum relation, corresponding to the line 1188 Å.U., which is the limiting line of the series of which 2536 is the first member. This result they also found with the vapors of cadmium, zinc and magnesium. On the other hand, Hebb and Millikan[4] find that the mercury arc, emitting its many-lined spectrum, can be made to strike with any voltage greater than 4.9 volts. I have been informed that at the April meeting of the Physical Society McLennan reported that by using dense electron streams as suggested to him by Millikan he had confirmed the latter's results.

In discussing this matter at the New York meeting of the Physical Society last December I pointed out that the apparent discrepancy could be explained away on the basis of the quantum hypothesis of atomic radiation by considering three factors:

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[1] Proc. Am. Phys. Soc., Chicago meeting, Dec. 1, 1916. I wish to point out here that since the publication of this suggestion I found that Bohr had himself suggested the possibility of a photoelectric effect to explain the apparent discrepancy between the observed ionization voltage and that calculated from his theory of atomic structure.

[2] Read at February meeting of Am. Phys. Soc., 1917. Phys. Rev., 10, 101, 1917.

[3] Proc. Roy. Soc., A, 92, 305, 1916.

[4] Phys. Rev., 9, 371 and 378, 1917.

1. As soon as the gas or vapor is brought into a state of excitation the size of the atoms increases, with a resulting transformation of the atomic system into one of higher potential energy.

2. When the colliding electrons have acquired sufficient energy to displace electrons from the outermost orbit, the radiation, resulting when the displaced electrons drop back to any configuration corresponding to one of lower potential energy than that which the system has acquired by virtue of the collision, stimulates a photoelectric effect with the resulting production of dislodged electrons.

3. The apparent distribution of velocities of the colliding electrons may, under certain circumstances, produce an appreciable influence.

Let us consider these influences in succession and see in how far they are capable of lending an explanation of the observed phenomena.

1. That the atomic diameter must increase with the excitation of the gas or vapor is in strict accordance with the quantum hypothesis, and in fact, follows as a natural consequence of it. This is easily seen by considering the simplest case, namely that of hydrogen. This atom has only one electron and one positive nucleus, the electron being in the orbit corresponding to the minimum potential energy of the system. We shall call this orbit 1. Now the Balmer series is stimulated by the displacement from (and consequent dropping back to) the orbit 2; the Paschen series by the displacement from the orbit 3. Only the Lyman series is stimulated by a displacement from the first orbit. Thus, if the electron is displaced from 2 to 3 and drops back to 2 we obtain the first line of the Balmer series; 2 to 4 gives the second line of the Balmer series and so on. It is therefore evident that *in the state of excitation of the gas* there must be many orbits outside the first which contain electrons, some atoms having, at any particular moment, electrons in the first orbit, others having their electrons in the second, others in the third orbit, and so on.

It is easily seen what is the cause of this increase in the potential energy of the whole system. If there are only a few colliding electrons the chance of this happening would be very small. But if a dense stream of electrons is used, then a bound electron which has been displaced by a colliding electron to an orbit corresponding to higher potential energy stands a good chance of being knocked out again by another colliding electron before it has had a chance to drop back to its original orbit and so will emit a line which belongs to an entirely different series from that to which belongs the line it would have emitted if it had had a chance to return to its original orbit. Thus, if the electron of a hydrogen atom is displaced from orbit 1 to orbit 3, it would, if it could return to 1, emit the second line of the Lyman series; if, however, it is displaced again by another electron before getting a chance to drop further back than orbit 2, it would emit the first line of the Balmer series.

The same holds true for mercury. It follows from the experiments of Franck and Hertz that the most loosely bound electrons in the mercury atom in the normal state of its vapor are those which require a minimum amount of energy equivalent to 4.9 volts (2536 Å.U.) to displace them from their position of equilibrium. In the light of the Bohr theory this would mean the outermost stable orbit which contains electrons in the normal state of the vapor is that which corresponds to a potential energy equivalent to 4.9 volts less than the next succeeding orbit (reckoned from the center of the atom outwards) and which requires 10.4 volts to completely detach an electron from it. Now, as a matter of fact, the mercury spectrum shows many lines of much greater wavelength than this ultra-violet line 2536. These lines must be stimulated by displacements through orbits of greater potential energy than that corresponding to 2536. In other words, a smaller amount of energy than 4.9 volts is required to stimulate them, although the experiments of Franck and Hertz show that the smallest amount of energy that can cause any stimulation at all is equivalent to 4.9 volts. This all means that if the frequency of collisions of the impacting electrons with the atom is small, the line 2536 will be radiated when the colliding electrons have dropped through 4.9 volts. But if a dense stream of electrons is used some of the bound electrons that have been displaced from the outermost orbit which in the normal state of the vapor contains electrons (say orbit $n$) to the next succeeding orbit $(n + 1)$, will be displaced again by other colliding electrons before getting a chance to drop back to their original orbit $n$, and some of these may be displaced from $n + 2$ before dropping back to $n + 1$, and so on. Hence, if we got an instantaneous picture of the vapor when bombarded by a dense stream of electrons, we would see atoms of various sizes, some being several times larger than the atoms in the normal state of the vapor.

Now, the energy necessary to displace an electron from the orbit $n + 1$ to $n + 2$ is much less than that necessary to cause a displacement from $n$ to $n + 1$, the energy decreasing with the number of the orbit. This follows from Kossel's[1] frequency relations:

$$\begin{array}{llllll}
\nu_{\beta_n} = & \nu_{\alpha_n} + & \nu_{\alpha_{n+1}}, & & & \\
\nu_{\alpha_n} = & \nu_{\alpha_n} + & \nu_{\alpha_{n+1}} + & \nu_{\alpha_{n+2}} = & \nu_{\alpha_n} + & \nu_{\beta_{n+1}}, \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
\nu_{\infty_n} = & \nu_{\alpha_n} + & \nu_{\infty_{n+1}}, & & &
\end{array}$$

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[1] Verh. d. D. Phys. Ges., 16, 953, 1914.

where $\alpha$, $\beta$, etc., represent the number of the lines in the several series and $n$ and $n + 1$, etc., the different series corresponding to the successive stable orbits $n$, $n + 1$, etc. For the $K$-series of characteristic $X$ radiations, according to Kossel, $n = 1$, the series thus resulting from displacements from the innermost orbit; for the $L$-series, $n = 2$, etc. It is interesting to note that a displacement even from the outermost orbit which in the normal state contains electrons, does not, for the elements investigated, give rise to visible radiations; the lowest frequencies that the normal mercury vapor atom, for example, can give are the ultra-violet series 2536···1188. According to these views the Lyman series of hydrogen are nothing else than Barkla's $K$-series of characteristic $X$-radiations for hydrogen; the Balmer series the $L$-series of Barkla.[1]

The above frequency relations are general and have been tested by Kossel for $X$-radiations and recently by Millikan[2] for ultra-violet radiation from mercury vapor. Kossel deduced these relations from general considerations of the manner in which energy transformations are supposed to take place in the Bohr atom. But they also follow directly from Bohr's equation:

$$\nu = N\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right),$$

of which a number of spectral series have been found to be special cases. According to this equation $\nu_{\alpha_n}$ is given by

$$\nu_{\alpha_n} = N\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right).$$

Similarly,

$$\nu_{\beta_n} = N\left(\frac{1}{n^2} - \frac{1}{(n+2)^2}\right),$$

$$\nu_{\alpha_{n+1}} = N\left(\frac{1}{(n+1)^2} - \frac{1}{(n+2)^2}\right).$$

Hence,

$$\nu_{\alpha_n} + \nu_{\alpha_{n+1}} = N\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right)$$

$$= \nu_{\beta_n},$$

which is Kossel's relation.

From the above consideration of the increase in atomic diameter it follows that one would not expect to obtain a single-line spectrum unless the stream of colliding electrons is very attenuated. In such case the

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[1] Other strong evidence for this conclusion is presented in Millikan's recent presidential address to the American Physical Society.

[2] Loc. cit., p. 378.

lines of longer wave-length will be so weak that they will not show on the photographic plate. As the density of the stream of electrons is increased the intensity of the long wave-length lines will increase. If the electron stream is very dense, as in the case of the mercury arc, the long wave-length lines will become very intense. Furthermore, on account of the increase in potential energy when the atom "swells" the energy required to completely detach an electron from the atom becomes less than 10.4 volts. In fact, from Kossel's relation it is seen that the necessary amount of energy for this may be as low as 4.9 volts and even less. And hence ionization by successive impacts may take place even at these low voltages. In general the ionization at these low voltages may not be great, but in the case of a dense stream of electrons as in the mercury arc, it may be considerable.

2. The second point to be considered is the photoelectric effect due to the light radiated from the atoms in their attempt to regain their original configuration after having been disturbed by the impacting electrons. In the case of devices like Lenard's, in which a third electrode in the form of a screen is interposed between cathode and plate, most of the effective excitation, when the applied voltage is about 5 volts, takes place between the screen and the plate. It is therefore to be expected that a great part of the photoelectric effect would act on the plate. The positive ions formed by collision ionization would not have an appreciable influence on the distribution of potential between the cathode and the screen, because they are drawn to the plate, which, it will be remembered, is always maintained at a negative potential with respect to the cathode. In the case of a two-electrode device the photoelectric effect on the plate, which is now anode, will not have any influence, since the photoelectrons cannot come out of the positive plate, or will at least be returned to the plate when they do come out. The photoelectric effect can, however, also manifest itself by its action on the neighboring atoms and, as we shall see below, also on the cathode. Millikan has recently applied the photoelectric effect produced by the line 2536 on the neighboring atoms to explain the appearance of the lines of longer wave-length than 2536 on his photographic plates, on the basis that the observed photoelectric long wave-length limit of mercury is 2800 Å.U. He has pointed out, however, that so far as his argument is concerned it is immaterial whether the photoelectrically liberated electrons come from the mercury vapor, from condensed films of mercury or from the substance of the cathode, and he accordingly leaves the question of their origin entirely open, insisting only on their being produced photoelectrically. With respect to this question, it must be remembered that the photoelectric effect

will exert an influence in producing positive ions from the atoms at low voltages only in virtue of the swelling of the atoms when the vapor is brought into a state of excitation. As stated above, it follows directly from the experiments of Franck and Hertz that the normal mercury vapor atom does not generally contain electrons in orbits greater than that corresponding to the series 2536···1188, and hence, if there were no swelling, that is, no increase in potential energy by successive impacts by electrons or successive stimulation by light, the least amount of energy that could stimulate any radiation from that atom would be that which is equivalent to 4.9 volts. And therefore the photoelectric effect due to the stimulation of the line 2536 by an atom could only cause the absorption and reëmission of this line by another atom, and would not assist in the direct multiplication of positive ions.

The emission of electrons from atoms of the vapor cannot be determined by the photoelectric long wave-length limit of the substance itself. This quantity is a different thing from the long wave-length limit of the photoelectric effect on the atoms in the gaseous state of the substance. In the latter case this quantity is determined by the energy necessary to completely detach an electron from the atom, whereas in the former case the energy necessary to detach an electron from the atom must be very small because of the frequent collisions of the atoms in the solid state of the substance and the effect of the electrons in the neighboring atoms, and therefore the photoelectric long wave-length limit of the solid or liquid is mainly determined by the work which an electron must do in order to escape from the surface of the substance. The following table shows the difference between these two quantities for a few substances. The long wave-length limits of the solids and of the atoms in the gaseous state of the substance respectively are denoted by $\lambda_0$ and $\lambda_c$, and the equivalent voltages by $V_0$ and $V_c$. The values of $V_0$ are taken from photoelectric and thermionic measurements, while the values of $V_c$ are calculated from the convergence wave-lengths $\lambda_c$ of the principal series, and are assumed, for reasons developed in this paper, to represent the ionization voltages of the substances.

| Substance. | $\lambda_0$. | $\lambda_c$. | $V_0$. | $V_c$. | $V_c - V_0$. |
|---|---|---|---|---|---|
| Mercury.... | 2800 (Millikan) | 1188 (Paschen) | 4.44 | 10.4 | 6.0 |
| Zinc........ | 3570 (Richardson) | 1320 (Paschen) | 3.48 | 9.24 | 5.8 |
| Magnesium . | 3750 (Richardson) | 1336 (Paschen) | 3.32 | 9.13 | 5.8 |
| Calcium .... | 3660 | 1246 (Lyman) | 3.4 (W. Wilson) | 9.96 | 6.6 |

The data available at present are far too meager to warrant any importance being attached to the fact that the difference between $V_0$ and

$V_c$ for the substances given here is nearly constant. If, however, this were to be found to be generally true, it would mean that if the ionization voltage of a substance is less than about 6 volts, or if the substance has a convergence wave-length of the principal series greater than about 2000 Å.U., it should be photoelectrically active in the dark.

The values given in the table show, at any rate, that there is a considerable difference between the energy necessary to detach an electron from the solid or liquid and that required to detach an electron from an atom in the gaseous state of the substance. Since, therefore, the long wave-length limit of the mercury atom in the gaseous state is 1188 Å.U. the line 2536 cannot detach electrons from the normal mercury atom. All the atom can do is to absorb the light and may reëmit it. But in absorbing it the potential energy of the electron in the atom is increased, and if it is again exposed to 2536 radiation before getting a chance to reëmit the absorbed light its potential energy will be further increased, and by a third stage of the process the electron will be knocked out of reach of the attracting forces of the atom and will be carried away by the applied electric field. Also, as explained above, the transformation of the atom into a configuration of higher potential energy will give rise to the emission of light of different wave-length from the line 2536.

The great difference between the photoelectric long wave-length limit of a substance and that of the atoms of its vapor carry weight in the explanation of the maintenance of an arc, say between mercury and iron electrodes. It means that since a great deal of the light emitted by the stimulated atoms is of shorter wave-length, and therefore of greater energy, than the minimum amount of energy necessary to liberate electrons from the surface of the substance, there must be a copious emission of electrons from the cathode under the influence of the light radiated by the atoms, and these electrons must on account of the difference between $V_0$ and $V_c$ be emitted with appreciable velocity. Thus, if they are liberated by the convergence line 1188 they will start with an initial velocity of about 6 volts; those that are liberated by the intense line 2536 will have an initial velocity of about 0.4 volt.

3. This brings out the importance of the initial velocities, even in the case in which a hot filament is used as cathode, and where the arc is seldom very intense. There is no reason why an appreciable number of electrons should not be emitted by the hot cathode photoelectrically once the gas or vapor is stimulated. If, for example, a calcium-coated platinum cathode is used the line 2536 would liberate electrons from it with an initial velocity of 1.5 volts. Adding these electrons to those that are emitted thermionically with Maxwellian velocities, we see that

the initial velocities can under certain circumstances have quite an appreciable influence in maintaining an arc at applied voltages less than that necessary to ionize the atom, and in fact less than that necessary to cause any stimulation at all of the normal atom.

It is possible that the comparatively high velocities with which electrons may be emitted from the cathode under the influence of the light from the stimulated atoms may account for the discrepancy in the experimental results on the ionization of helium. Franck and Hertz,[1] Pawlow[2] and Bazzoni[3] find the ionization voltage of helium to be about 20 volts, while Bohr's theory requires that it should be 29 volts. Bazzoni took special care to purify his helium and used a device which consisted only of a hot-wire cathode of tungsten and a cylindrical anode. His current-voltage curves show a very sharp increase at about 20 volts, thus indicating the occurrence of impact ionization. While it is true that there could not have been any photoelectric liberation of electrons from the anode in his device, it is quite possible that there might have been such electron liberation from the tungsten cathode. Remembering that the photoelectric long wave-length limit of tungsten, according to thermionic measurements of Langmuir, is equivalent to 4.5 volts, it is seen that 20-volt light, which has a wave-length of only 620 Å.U., should be capable of liberating electrons from tungsten with the high initial velocity of about 15 volts, so that when the applied voltage is 20 the energy of these electrons, on reaching the anode, would correspond to about 35 volts. The current would therefore not only be increased by the extra electrons liberated photoelectrically from the cathode, but also by the electrons dislodged from the helium atoms by these high velocity electrons. Adding to this effect the increase in potential energy by successive impacts, as explained above, we see that quite a considerable amount of ionization can take place under an applied voltage which is too low to ionize the normal helium atom.

The fact that ionization does not set in until the applied voltage is 20 volts gives, when we consider the effects that manifest themselves here, a rather striking confirmation of Bohr's theory, because it follows from his theory that this is just the voltage necessary to displace an electron from the orbit, which in the normal state contains the two electrons, to the next succeeding orbit. According to the theory of Bohr the energy radiated in the formation of single orbit atoms is given by

$$W = W_0 \Sigma F^2,$$

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[1] Verh. d. D. Phys. Ges., p. 34, 1914.

[2] Proc. Roy. Soc., 90, 398, 1914.

[3] Phil. Mag., 32, 566, 1916.

where $W_0$ is the ionization energy of the hydrogen atom and $F$ is given by

$$F = N - \frac{1}{4} \sum_{s=1}^{s=n-1} \operatorname{cosec} \pi \frac{s}{n},$$

$N$ being the number of nuclear charges and $n$ the number of electrons in the orbit. Since for helium $N = 2$ and $n = 2$, this gives for the formation of the helium atom an energy dissipation equivalent to 6.12 $W_0$ and for the binding of only one electron with the double nucleus, 4 $W_0$. Hence the ionization energy of helium is $(6.12 - 4)W_0 = 2.12\ W_0$ and the energy necessary to displace an electron to the next stable orbit

$$2.12 W_0 \left(1 - \frac{1}{4}\right).$$

Since $W_0$ is $2.16 \times 10^{-11}$, this gives 21 volts. It is therefore to be expected that ionization in helium should start at about 20 volts, because this is the minimum voltage necessary to cause the swelling of the atoms and the liberation of the photoelectrons.

It is seen, therefore, that a consideration of the three factors: the increase in atomic potential energy by successive impacts, the photoelectric effect of the light emitted by the stimulated atoms and the initial velocities of the electrons emitted from the cathode affords an explanation of the results obtained by workers in this field. In particular, the recently published results of experiments of Millikan and Hebb are just what is to be expected from these considerations. The fact that Franck and Hertz and McLennan obtain single-line spectra is due, as Millikan also pointed out, to their probably not having used dense electron streams.

It is now evident that the quantity which can be called the ionization voltage of a gas or vapor is not necessarily the minimum voltage required to ionize the gas or vapor. This latter voltage, we have seen, depends more on extraneous conditions than on the nature of the substance, and can therefore not be considered a property of the substance. According to the views postulated above ionization voltage must be defined as the equivalent of the minimum energy necessary to completely detach an electron from the *normal atom,* and is therefore the least voltage through which one electron must drop to ionize the normal atom. This quantity is a property of the substance only and does not depend on extraneous influences. It is determined by the equation

$$V = \frac{h\nu_c}{e},$$

where $\nu_c$ is the convergence frequency of the principal series, $h$ is Planck's constant and $e$ the elementary charge.

In view of the disturbing influences discussed above it would seem that the experimental determination of the ionization voltage is not a simple matter. The observed ionization at voltages below that required by the Bohr theory does not necessarily invalidate this theory. On the contrary, the fact that ionization is observed to start at the voltages necessary to cause the minimum displacement of an electron from the outermost orbit of the normal atom, seems, on the basis of the interpretation given here, to lend support to the Bohr theory.

RESEARCH LABORATORY, WESTERN ELECTRIC CO.,
NEW YORK,
May 30, 1917.