

CHAPTER I

INTRODUCTION

THE first important observation on the action of light on the discharge of electricity from conductors was that of Hertz in 1887, who found that a spark passed between metallic terminals in air more easily when light from another spark fell on the negative terminal. This effect led to a number of investigations by Hallwachs, Elster and Geitel, and others, who found that electrified metallic conductors lost electrification when illuminated by a suitable source of light. On taking precautions to avoid spurious effects, the important result was established that the illuminated metal could lose negative, but not positive charges. If the metal were initially insulated and uncharged, then it acquired a small positive charge as a result of illumination, but the potential to which it rose did not exceed a volt. With most metals, the leak of negative electricity ceased on the interposition of a plate of glass between the source of light and the metal. As the glass absorbs the ultra-violet radiation, it was thus proved that the effect in these metals was due to ultra-violet light alone.

The alkali metals, on the other hand, were very sensitive to light of wave-lengths within the range of the visible spectrum as well as to ultra-violet light. The leak of negative electricity from an illuminated plate occurred whether the metal was surrounded by a gas or was in the best vacuum obtainable, but the *rate* at which the leak took place varied considerably with the nature and pressure of the surrounding gas. Investigations were made by Stoletow and others soon after the discovery of the effect to determine the relations between the leak of electricity from the illuminated plate, and such factors as the pressure of the gas and the electric force outside the illuminated plate.

The emission of negative electricity from an illuminated plate is generally known as the photo-electric effect, or sometimes as the Hallwachs effect, Hallwachs being one of the first to investigate it. No satisfactory explanation, however, of the loss of negative charge by a metal when illuminated was given until the development of the theory of the ionisation of gases.

Gases in their ordinary state are almost perfect insulators. The simple electroscope shows this clearly. When the rod supporting the gold leaves is well insulated, the gold leaves will retain a charge for days, showing that the air, or other gas, in the electroscope has no appreciable conductivity. If now a flame, or an incandescent solid, be brought near the electroscope so that the hot gases have access to the gold leaves, or to some conductor in metallic connection with them, the leaves will immediately collapse, showing a complete loss of charge. The same thing happens if a beam of X-rays is directed into the electroscope, or if some radio-active substance is placed inside. Suitable control experiments show that the only possible explanation is that the gas, which in its normal state is an insulator, becomes conducting under the influence of these agents. From about 1896, very rapid progress was made by Sir J. J. Thomson and his pupils in elucidating the nature of the conductivity imparted to gases by various agents, and particularly by X-rays. The X-rays and other ionising agents are considered to produce a number of charged particles, or "ions," in the gas. These ions are molecules, or small aggregates of molecules, which differ from the rest in possessing electric charges, some negative and some positive. In an electric field they move towards the electrodes, their directions of motion depending on the signs of their charges. On arriving at the electrodes the ions give up their charges, and in this way the discharging effect of an ionised gas is explained.

The nature of ionisation was made still clearer by Sir J. J. Thomson's discovery of the existence of *electrons*, which are negatively charged particles whose masses are far smaller than those of atoms. The electron is now regarded as the ultimate unit of negative electricity. A positive charge, on the other hand, is not known to exist as a separate entity apart from atoms or molecules. The electrons when isolated by our experimental

methods are always moving with very high speeds, from 10^7 to 10^{10} cm./sec. The fastest electrons may collide successively with a number of molecules, and the effect of each collision is to reduce the velocity of the electron. When the velocity has been reduced to about 10^8 cm./sec., the electron sticks to any neutral molecule or atom with which it collides and forms a negative ion. Since ionisation of a gas by X-rays is known to produce equal numbers of positive and negative ions, it is natural to explain the negative ion as a neutral molecule which has acquired an extra electron, and the positive ion as the neutral molecule from which the electron was originally emitted. The atom on the electron theory is regarded as an assemblage of electrons, probably in rapid motion, together with a positive nucleus, so that the atom as a whole is uncharged. The forces keeping the electrons in position are naturally assumed to be electrical. When sudden and violent changes occur in the atomic forces through the impact of a swiftly moving electron, or through the action of an X-ray pulse, or ultra-violet light, the atomic system may be so much disturbed that one of the electrons leaves the system altogether. In this way one pictures the phenomenon of ionisation. When ionisation is confined to the surface layers of a solid or liquid substance, only the electron can escape from the substance, while the positive charge, necessarily associated with the parent atom, remains in the surface. In the presence of a gas these electrons become negative ions. The electrons or negative ions, as the case may be, can be detected experimentally through the emission of negative electricity from the surface, provided the electric field is favourable. It is a characteristic feature of surface ionisation, however, that if the field is reversed there is no emission of positive electricity.

The experimental evidence, hitherto considered, indicates that the photo-electric effect is localized in the surface of the metal, that is to say, ionisation occurs in the surface itself—a phenomenon distinct from gaseous ionisation produced by X-rays. This view was firmly established by the experiments of Sir J. J. Thomson¹ and Lenard² who found that a metallic plate in vacuo,

¹ Sir J. J. Thomson, *Phil. Mag.* XLVIII. p. 547, 1899.

² Lenard, *Ann. d. Phys.* II. p. 359, 1900.

illuminated by ultra-violet light, emitted electrons. These electrons have velocities of the order of 10^7 cm./sec., and thus are much slower than ordinary cathode or β rays. It is convenient to refer to the electrons emitted from illuminated metals as photo-electrons, thus indicating their mode of production, but it must not be taken as implying that they are in any way different from other electrons. This discovery of the emission of electrons from illuminated surfaces made it possible to formulate much more definite views about the whole subject of ionisation by light. The primary action of the light is to ionise atoms in the surface, that is, to cause them to emit electrons, some of which get away from the surface and can be detected experimentally.

It may seem somewhat strange that ionisation by ultra-violet light manifests itself as a surface effect in solids and liquids, while ionisation by almost all other agents appears most evident in gases. Yet there is no fundamental distinction on this account. Ultra-violet light—provided extremely short wave-lengths are used—does ionise gases just as readily as X-rays. But with the ordinary sources of ultra-violet light, the surface effect is the only one observed, and the methods of investigating it differ considerably from the methods employed in studying gaseous ionisation.

With the progress of experimental knowledge, it has become clearer that each substance has a definite wave-length at which its photo-electric effect starts. Wave-lengths longer than this are incapable of causing the emission of photo-electrons, while all wave-lengths shorter than this are effective. The critical wave-lengths for the alkali metals are in the visible spectrum, for the other metals they are between $\lambda 2500$ and $\lambda 4000$, and for the non-metals they lie beyond $\lambda 2200$, the wave-lengths being measured in Ångström units (10^{-8} cm.). The critical wave-length for oxygen is about $\lambda 1350$. There is considerable experimental difficulty in working with such short wave-lengths, and this has seriously hampered the study of ionisation of gases by ultra-violet light. In general, the more electro-positive an element is, the longer is the wave-length at which the ionisation begins. The critical wave-length at which the photo-electric effect starts has recently acquired an important significance, for on certain theories we can

immediately calculate from it the work that is necessary to take an electron away from its parent atom. This is a quantity of fundamental importance in the electrical theory of atomic structure, for it measures the potential energy between the electron in its equilibrium position and the rest of the atomic system. For this reason I have endeavoured to indicate, wherever possible, the wave-length at which the photo-electric effect starts for the substance investigated. Unfortunately there is often much uncertainty in arriving at a correct estimate, since many experimenters have approached the subject from quite a different point of view, and explicit information as to the effective spectral region is wanting. We may almost say that the critical wave-length at which the photo-electric effect starts completely characterizes the photo-electric behaviour of a substance so far as the fundamental process is concerned. Of course, the actual experimental photo-electric currents are influenced by a number of secondary effects such as the absorption of the active light and of the electrons by matter.

The photo-electric effect was among the first phenomena to receive an interpretation on the quantum theory of radiation. The characteristic feature of the quantum theory is that the transference of energy to or from the radiant form is not continuous, but takes place in small finite units. An unexplained peculiarity of the theory is the necessary assumption of the variation of the unit of energy from one wave-length to another. The unit of energy is directly proportional to the frequency of the radiant energy, and is therefore equal to hn , where n is the frequency and h a constant known as Planck's constant. Hence if the energy is completely transferred to the photo-electron when light ionises a molecule, the energy of the photo-electron should be proportional to the frequency of the light. Experiments have now shown quite definitely that this is the case. When the quantum theory was first applied to the photo-electric effect it was assumed that the light was molecular in structure, each "molecule" or unit containing an amount of energy hn which could not be subdivided, and therefore on interaction with matter was wholly transferred to the photo-electron. Although many experiments show a remarkable agreement with the predictions

of the quantum theory, it is such a radical departure from the classical views of the nature of radiant energy that many attempts have been made to explain the results on lines more in accordance with the older ideas. The view now prevalent is that the quantum theory gives the correct mathematical expression for the energy transformations, but gives no indication of the nature of the phenomena to which it is applied.

In discussing photo-electric experiments, it is often desirable to know what part of the spectrum produced the effect under consideration. As most investigators do not give any information on this point, beyond merely stating their source of light, it was thought that a short account of the various sources of light used in photo-electric experiments would be useful. This will be found in Chapter x, together with some observations on the regions of the spectrum of the light transmitted by a number of substances including quartz and fluorite.

CHAPTER II

IONISATION OF GASES AND VAPOURS BY ULTRA-VIOLET LIGHT

THE interpretation of experiments on gases is always much simpler than the interpretation of experiments on solids and liquids. This is due to the comparatively simple conception of the physical state of a gas which we have in the kinetic theory of gases. Not only is our picture of the molecular state of a solid or liquid much less defined and precise, but also the difficulty of interpreting our results is considerably increased by the necessity for taking intermolecular forces into account in any explanation which aims at completeness. A considerable amount of positive knowledge has been acquired as to the nature of ionisation by Röntgen rays, and much of this is due to the fact that the effect can be studied, with comparative ease, in gases. Thus we know indirectly from ionisation experiments, and more recently directly from C. T. R. Wilson's experiments, that ionisation by Röntgen rays consists, first of the expulsion of a number of corpuscles moving with high speeds from certain molecules, and secondly, of the ionisation of a much larger number of molecules by these corpuscles. But when we turn to ionisation by light, almost all the experiments have been concerned with the photo-electric effect at solid or liquid surfaces. The difficulties of interpreting such experiments with any degree of exactness has doubtless caused investigators from time to time to turn to the ionisation of gases by light. Unfortunately it has been extremely difficult to get any evidence of true ionisation of gases by light until comparatively recently, to say nothing of a detailed investigation of the phenomenon. The experimental difficulties are such that almost all the experiments are restricted to proving

that the ionisation exists, or does not exist, under certain conditions of illumination.

A general consideration of the photo-electric effect leads to the conclusion that the more electronegative an element, the more difficult it is to ionise it by light. In more precise terms, this means that the longest wave-length which is capable of ionising an element goes more and more into the ultra-violet as the element becomes more and more electronegative. All the gases and vapours which are convenient to use in ionisation experiments are electronegative, and it so happens that the wave-lengths which are effective in such gases can only be got experimentally with special precautions. For example, only specially selected specimens of clear fluorite will transmit the light which ionises air; all other solid substances are opaque to the light.

A few remarks on the peculiar difficulties met with in investigating ionisation by light should be useful at this point. As

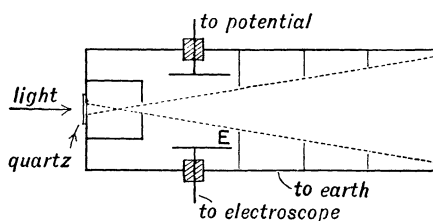


Fig. 1.

ionisation chambers usually have electrodes made of some metal or other conductor, spurious results are frequently obtained due to photo-electric action at the electrodes which give relatively big effects. The following is an example of spurious results of this kind obtained on one occasion and illustrates the care which must be taken in these experiments. An ionisation chamber of the form shown in Fig. 1 was made so that no light fell directly on the electrode *E*. The light passed in through a quartz window from a discharge in hydrogen. It is now known that this light is incapable of ionising air. Yet in this apparatus a small leak of the order 10^{-15} amp. was always obtained. Now it was found that when the same light fell upon a surface of the same nature as the inside (lamp-black surfaces) of the ionisation vessel, a leak of

10^{-10} amp. was obtained. The first leak of 10^{-15} amp. might be accounted for by a trace of light finding its way to the electrode after several reflections. An amount only 10^{-5} of the incident light would be sufficient, and it is difficult to be certain that this is not the true explanation of the leak. A decisive test was the following. A surface effect would decrease continuously as the pressure of the gas increased (assuming no ionisation by collision). A volume effect on the other hand would, at some stage or other, increase with the pressure. As the leak decreased with increasing pressure, it was concluded that the small effect obtained was merely a surface effect at the electrode.

Perhaps the best method of testing for ionisation by light is to illuminate a stream of gas and then to pass it through an ionisation chamber where the conductivity can be tested. If proper precautions are taken to prevent the entry of any light into the ionisation chamber, the presence of *positive* ions as well as negative ions in the stream of gas can be taken as conclusive evidence of the ionisation of the gas. Further tests must be made to determine whether the gas, or some impurity in it, is ionised, but at all events the effect is not due to a spurious surface effect. The presence of negative ions alone simply points to a photo-electric effect at the surfaces on which the light falls, in the neighbourhood of the window. The disadvantage of this method is that very large quantities of gas are required to sweep through the apparatus and the difficulties of ensuring a large supply of pure gas are considerable. This is the method which has been adopted by practically all investigators on ionisation of gases by light.

Experimental Results for Air and similar Gases.

The earliest experiments of any importance on ionisation of gases by light were those made by Lenard¹. The light was obtained from an intense spark between metallic terminals. Air illuminated by this light was found to discharge both positively and negatively charged bodies, hence ions of both signs must have been present in the air. Most of the experiments were carried out with the unfiltered air of the room, though some experiments

¹ Lenard, *Ann. d. Phys.* i. p. 486, 1900; iii. p. 298, 1900.

were made on dust-free gases. Ionisation of the same order was obtained in air, carbon dioxide and oxygen, a smaller effect in coal gas and a very small effect in hydrogen. The ionising light was found to be strongly absorbed by air, carbon dioxide and oxygen, and more strongly still by coal gas. In the case of the filtered gases, appreciable effects were only obtained when the spark was within a few mm. of the quartz window. This indicates that the ionising light is located far in the ultra-violet. One peculiar result was that the ionisation was more powerful in fresh air than in air which had been illuminated for some time. Again, the mobilities of the ions produced in unfiltered air were measured and found to be 3·13 cm./sec. for the negative ion and ·0015 cm./sec. for the positive ion—the latter being of quite a different order from the mobility of the positive ion produced by Röntgen rays, etc. These two observations point very strongly to the explanation that the conductivity observed is due to the presence of dust particles, or other nuclei, which emit electrons like ordinary surfaces when illuminated and remain positively charged. Their low mobility is explained by their great mass relative to that of the molecules and the fatigue-like effect is due to the removal of the positively charged particles by the electric field. Mobility experiments were not made with the filtered gases, hence it is not certain that the conductivity of the gases indicates that an ionisation of the gases themselves takes place, since ultra-violet light may produce in filtered gases nuclei which are photo-electric (p. 19).

Bloch¹ showed that the ionisation obtained by Lenard was really due to a photo-electric effect of the minute dust particles suspended in the air. On filtering the air, the number of positive ions produced was reduced to zero. It should be mentioned however that in a few experiments of Lenard the light had to traverse shorter distances than in Bloch's, and so Bloch's conclusions are not strictly applicable to these. However, when the light has to traverse 5 cm. of air or more and a quartz plate, Bloch's experiments show that filtered air is not ionised.

The method of studying ionisation by means of condensation nuclei as developed by C. T. R. Wilson² is the most sensitive

¹ Bloch, *Le Radium*, p. 240, 1908.

² C. T. R. Wilson, *Phil. Trans. A.* cxii. p. 403, 1899.