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LUMINESCENCE.[1]

By Ernest Merritt.

THE past twenty years have been remarkable in the history of physics on account of the large number of fundamental discoveries that have been made, each of which has opened up an entirely new field of investigation, and each of which has exerted a profound influence on the trend of speculation. I refer particularly to the discovery of X-rays and its modern development in the high frequency spectra, the discovery of the electron, and of radioactivity. But many other subjects of scarcely less importance might be included in the list; such, for example, as the photoelectric effect; and, on the theoretical side, the hypothesis of quanta. In each of these cases the original discovery not only appealed to physicists at once on account of its obvious importance, but possessed also the charm of complete unexpectedness. And in each case the subsequent development of the new subject was so rapid as to be almost spectacular.

In looking over the ground from our present point of advantage it is interesting to observe how these different subjects have supplemented one another, and how in some subconscious way we have been proceeding by seemingly accidental steps toward a definite goal,—toward the solution of the problem of the structure of the atom, which is now so generally recognized as the most important of the outstanding problems of our science.

On account of its important bearing upon this problem of atomic structure the subject of luminescence, in my opinion, deserves a place in the group of subjects just mentioned. In some respects, in fact, it offers a more direct line of attack than any of these. The chief purpose of my address to-day is, therefore, to make a plea for the more extended study of the phenomena and the theory of luminescence.

Luminescence is not a new subject. It cannot attract investigators by its novelty. If none of its phenomena were known, and if the phosphorescence of Sidot blende or the fluorescence of anthracene were to be shown at this

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[1] Presidential address delivered at the Philadelphia meeting of the Physical Society, December 29, 1914.

meeting for the first time, I am confident that half of this audience would be investigating luminescence within a week. But the first discovery was made three hundred years ago. The fascinating phenomena of luminescence have to a large extent lost the appeal of novelty, for in a superficial sort of way they are well known; but so far as the theoretical interpretation of the phenomena is concerned we have made only the barest beginning. The original discovery was made too soon—before the scientific world was ready for it. Important progress has indeed been made, especially on the experimental side; but it has been made slowly and with great effort. Until very recently the position of the subject has been like that of an isolated outpost of an army: it lacked support on the two wings. But the great advance of Physics during the past twenty years has at last furnished the much needed support, and it seems to me that the time has come for the outpost to advance.

Having in mind the general question of the bearing of the phenomena of luminescence upon the problem of atomic and molecular structure, the various subdivisions of our subject may be roughly grouped in two classes. The first class includes such subjects as phosphorescence, chemiluminescence, and the influence of temperature upon these phenomena. The interpretation of the phenomena of this class involves a consideration of the relations between molecules, but does not necessarily require any hypothesis regarding the mechanism by which the light is actually emitted. We have a somewhat analogous case in the subject of magnetism, where important progress was made by the assumption that each molecule is a magnet, even before any serious attempt was made to explain the peculiarities of molecular structure to which the assumed magnetic property was due.

The second class of subjects, which bears more directly upon the problem of atomic structure, includes such matters as the detailed study of luminescence spectra, the relations between luminescence and absorption, and the influence of the wave-length of the exciting light, or more generally the influence of the mode of excitation, upon the character of the light emitted. No progress toward a theoretical interpretation is possible in these cases without some hypothesis regarding the mechanism of emission and absorption. I need hardly point out that it is often difficult, if not impossible, to entirely separate the two classes of problems.

As an illustration of important progress made by purely empirical experimentation, without the help of even the crudest theory, we have the development of the methods now used in preparing phosphorescent materials artificially. In the early days the results of attempts to make phosphorescent materials were very uncertain. Preparations made by the same method and from the same materials were in some cases brilliantly phosphorescent and in other cases entirely inactive. The color of the phosphorescence and its duration also seemed to be largely a matter of chance. An important step toward an understanding of the reasons for these uncertainties was taken by Lecoq,[1]

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[1] See Kayser, Handbuch der Spectroscopie, Vol. IV., p. 741. The chapters on Phosphorescence and Fluorescence in Kayser's Handbuch contain so complete and valuable a

who was led to believe that in most cases phosphorescence was due to the presence of impurities. Thus $CaSO_4$ gives very weak phosphorescence and $MnSO_4$ none. But if we mix the two we get a mixture which is brilliantly phosphorescent. Lecoq was the first also to suggest that phosphorescent substances were to be looked upon as solid solutions, a view which is now very generally accepted. Thus Sidot blende consists of a small amount of copper or manganese dissolved in zinc sulphide. Balmain's paint is a solid solution of bismuth in calcium sulphide. The usual method of preparation is by the calcination of the mixed dry salts.

Lecoq's views were confirmed by Verneuil, who found that better results were obtained if a flux such as NaCl or Na_2CO_3 was used. More recently Lenard and Klatt have developed the procedure in the case of the metallic sulphides in great detail, so that if we have pure materials to start with we are now in a position to reproduce the phosphorescent preparations of this class with considerable certainty.

Wiedemann and Schmidt have used two other methods of preparation, which, while probably not so generally applicable, sometimes have the advantage of not requiring calcination. One of these methods simply calls for the evaporation to dryness of a suitable mixture of two salts. For example, if a small amount of a solution of $MnCl_2$ is added to a solution of NaCl and the mixture evaporated to dryness, the dry salt gives a pink phosphorescence.[1] In some cases the precipitation of a metal from a solution will carry down a sufficiently large amount of some other metal present to give the proper conditions for phosphorescence in the dried precipitate.

In all these cases the essential thing seems to be the bringing into intimate association of a small amount of one substance—usually called the active substance—and a large amount of some other substance, the latter acting as the solvent in the resulting solid solution. The intensity of phosphorescence is found to vary greatly with the concentration, increasing rapidly with the concentration at first and, after reaching a sharply defined maximum, decreasing scarcely less rapidly as the amount of active material is still further increased. In the case of the solid solution of $MgCl_2$ cited above the maximum is reached for a concentration of 0.8 per cent. The sulphides studied by Lenard and Klatt usually give maximum brightness with a concentration of .01 per cent. or less.

In cases where so small an amount of active substance is required for brilliant results it is evident that the purity of the materials used is a matter of great importance. It is very difficult to obtain a salt which is sufficiently pure to be entirely free from phosphorescence, especially when tested by cathode rays. The extreme sensitiveness of certain substances to small traces of impurity is illustrated by an experience described by Waggoner.[1] After a long search

discussion of the literature down to the date of publication (1908) that I have usually not thought it necessary to cite references except in the case of work done since that date.

[1] C. W. Waggoner, Phys. Rev., XXVII., p. 209.

some cadmium sulphate had been obtained which showed only the barest trace of afterglow. This was dissolved in water that had been twice distilled, but which had stood in a glass bottle over night. When the solution was evaporated to dryness the salt was found to be brilliantly phosphorescent. The water had evidently dissolved some substance from the glass of the bottle in which it had been kept. But when 200 c.c. of the water from the same bottle was evaporated in a platinum vessel it left a residue so small that it could be seen only when the vessel was at a red heat. There are many evidences that phosphorescence may often give a test of purity which is equalled in sensitiveness only by spectroscopic examination, or by the ionization test for radium.

That luminescence in minerals is also due to impurities has been definitely proved in a large number of cases. Probably we all recall the important assistance that was given by kathodo-luminescence in the study, and in some instances the discovery, of several of the rare earths. The opinion is now generally held that impurities are present in the great majority of cases of luminescence in solids, possibly in all cases. Yet there does seem to be one exception, namely the salts of uranium. The presence of slight impurities in these salts is of course probable. But their fluorescence seems to be chiefly determined by the uranyl radical, and retains the same general character whatever may be the acid with which this radical is combined or the source of the uranium. This exception to the general rule is so striking that I have sometimes wondered whether the active substance in this case may not be one of the radio-active products of uranium, for which the salt serves as a solvent. A few experiments have been made to test this conjecture. For example the salt has been freed from Ur-X in the hope that it would lose its fluorescence thereby until new Ur-X was formed. But the results are thus far altogether negative.

On the whole very satisfactory progress has been made in developing methods of preparing phosphorescent materials. And yet we can scarcely feel content, for the knowledge gained is almost entirely empirical. We have no means of telling what substances may be used to advantage either as solvents or as active substances—except, of course, that certain materials have been tried before and have been found to work. The fact that phosphorescent substances are in most cases solid solutions is virtually the only generalization that can be used as a guide.

In some of the other problems of luminescence the situation is better, for a suggestion first made by Wiedemann in 1889 and since resuggested in more or less modified form by several other physicists, has proved of great utility. According to the Wiedemann theory luminescence is an accompaniment of what the chemists would call, I believe, a reversible reaction. It is assumed that the active substance is changed by the action of the exciting agency from the stable condition A into the unstable condition B. If the return of the substance to the condition A is accompanied by the emission of light we have phosphorescence. Fluorescence may be due either to vibrations set up during the change from A to B, or to the fact that the reaction B to A proceeds, with the emission of light, during excitation as well as during decay. We should expect, therefore, that the fluorescent light, that is the light emitted during excitation, would consist in part of the same wave-lengths that are present during phosphorescence, but that other wave-lengths, resulting from the reaction A to B, may also be present and in some cases predominant. An explanation is thus offered of the fact that the color of phosphorescence is often different from that of the fluorescence of the same substance with the same excitation. Thermo-luminescence is to be explained as the result of some change that is made possible by rise of temperature, during the progress of which the molecules are thrown into such violent vibrations as to emit light. In many instances thermo-luminescence seems to be nothing more than accelerated phosphorescence. In such cases the conditions at the temperature of excitation are apparently not favorable for the rapid emission of the energy stored during excitation. Phosphorescence is therefore very weak and of extremely long duration. This may be true in so marked degree that no phosphorescence can be detected at all, and the condition produced by excitation is practically permanent so long as the physical conditions remain the same. In such cases the reaction A to B can occur at the lower temperature, while the reverse reaction B to A cannot. But if the temperature is raised it becomes possible for the stored energy to be liberated and thermo-luminescence is observed. In such cases the material will not show thermo-luminescence when heated a second time until it has been reexcited, say by the light of a spark or by cathode bombardment. If all cases of thermo-luminescence are of this kind we should not expect thermo-luminescence to be shown unless there has at some time been an opportunity for excitation. In the case of certain natural minerals whose freshly exposed surfaces were found to show thermo-luminescence even when the specimen had been broken in the dark, it has been suggested that the original excitation was due to radium rays.

The theory illustrated by these few examples was first advanced by Wiedemann in his well known paper entitled "Zur Mechanik des Leuchtens."[1] It was discussed in much greater detail in a later paper by Wiedemann and Schmidt,[2] which appeared in 1895, and which in my opinion is to be regarded as one of the classics in the field of luminescence.

While the fundamental conception of the Wiedemann theory has been retained, it has been customary in recent years to make the hypothesis more definite by assuming that the change which I have referred to as the reaction A to B consists in the expulsion of an electron from a molecule of the active substance, while the recombination of the ions thus formed constitutes the reverse reaction B to A. This is the form of the theory that has been advocated by Stark, Lenard and others. Chemists I believe are still inclined to look upon the change assumed in the Wiedemann theory as a chemical reaction in the ordinary sense. My own feeling is that we must admit the existence of several distinct types of luminescence, in some of which the phenomena are

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[1] E. Wiedemann, Annalen der Physik, 37, p. 177, 1889.

[2] E. Wiedemann and C. C. Schmidt, Annalen der Physik, 56, p. 177, 1895.

explainable in terms of electron dissociation alone, while in others chemical changes form the predominant factor. Although it may later be possible to bring all cases of luminescence into one category as regards the process which leads to the emission of light, I doubt whether we are yet in a position to do this.

In support of the Wiedemann theory in its general form we have several well established facts. For example when fluorescence is excited in liquids or in isotropic solids the light emitted is unpolarized, regardless of the condition, as regards polarization, of the exciting light. Apparent exceptions are noticed when the fluorescent surface is observed at an oblique angle, since the light from the interior is partially polarized by refraction when it passes into the air. But a study of such cases by Millikan has shown that there is nothing to indicate any polarization in the light before it reaches the refracting surface. The absence of polarization is one of the strongest arguments against any theory which assumes that the vibrations causing emission are set up by some process analogous to resonance. On the other hand it is just what we should expect from the Wiedemann theory, since the light emitted during the change B to A cannot be affected by the manner in which the condition B was established. The argument is equally strong whether the process B to A consists in the recombination of ions or in a chemical reaction. In the case of the fluorescence of vapors, Wood has found that the fluorescence light is partially polarized.[1] This fact offers support to the view that the processes of excitation and emission are essentially different from the corresponding processes in solids and liquids, and justifies the term resonance radiation which Wood has applied to this type of fluorescence.

Experiments made with excitation by light of different wave-lengths, by X-rays, and by cathode bombardment indicate that the distribution of energy in a fluorescence spectrum is the same for all of these modes of excitation.[2] It often happens that not all of these exciting agencies are effective; or that the substance tested possesses several independent fluorescence bands, which are excited by the different agencies to a different extent. In such cases the color of the total light emitted may vary with the mode of excitation. But if we direct our attention to some one band it is found that if this band is excited at all the distribution of intensity throughout the band is the same for all modes of excitation thus far tested. This result is of course what the Wiedemann theory would lead us to expect, for the phenomena connected with the change from the condition B to the condition A will not depend upon the means by which the change from A to B was produced. Or, speaking in terms of the modern form of the theory, the effects produced when an electron reunites with the positive nucleus will be the same no matter what method was used in bringing about its dissociation.

Similar reasoning based on the Wiedemann theory would lead us to expect that the distribution of energy in a phosphorescence band will remain the same throughout the period of decay. On account of the faintness of phosphores-

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[1] R. W. Wood, Philosophical Magazine, 26, p. 846, 1913.

[2] E. L. Nichols and E. Merritt, PHYS. REV., XXVIII., p. 349.

cence spectra this conclusion is difficult to test with any high degree of accuracy; but in so far as it has been possible to test it the conclusion is confirmed.[1]

Studies of the law of decay of phosphorescence, while leading in many cases to confusing and even contradictory results, on the whole lend support to the Wiedemann theory. If the exciting light produces a separation of the active material into two parts—and if this is its only effect—then we should expect the recombination to occur in accordance with the laws that apply to bimolecular reactions. It can readily be shown that in this case the law of decay should be

$$I = 1/(a + bt)^2 \quad \text{or} \quad 1/\sqrt{I} = a + bt$$

where I is the intensity of phosphorescence at any time t.[2] The law can be conveniently tested by plotting the reciprocal of the square root of I against t, in which case, if the law is obeyed, a straight line is obtained.

In the case of the afterglow in gases Trowbridge has found this law to hold with great exactness.[3] It also applied during the early stages of decay in the case of a number of solids, for example in the case of Sidot blende. Usually, however, when $I^{-1/2}$ is plotted against t the resulting curve is found to consist of two parts, each of which is nearly straight, separated by a region of rather sharp curvature.[4] Such curves suggest that the decay involves two processes, which have been called by Lenard the Momentan-prozess and the Dauer-prozess, the former being predominant during the early stages of decay and the latter during the period of slow decay which follows. In Lenard's experiments the first or Momentan-prozess has been found to follow a law of the exponential type.

Ives and Luckiesch[5] have found that in some cases even the second process does not give a linear relation, but shows considerable curvature, sometimes curving up and sometimes down.

The question of the decay of phosphorescence is complicated by two considerations, both of which are neglected in the derivation of the simple linear law. In the first place phosphorescent solids are very far from being homogeneous, and it has been shown that lack of homogeneity is in itself sufficient to account for most of the observed deviations from the simple law.[6] In the second place we have no reason to feel sure that a separation of the active material into two parts is the only effect of excitation. Secondary changes, possibly chemical in their nature, may in many cases follow this primary change. Both of these disturbing factors may perhaps be removed by working at low temperatures.

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[1] E. L. Nichols and E. Merritt, Phys. Rev., XXI., p. 247, 1905; C. W. Waggoner, Phys. Rev., XXVII., p. 220; C. A. Pierce, Phys. Rev., XXX., p. 663, XXXII., p. 115; H. E. Ives and M. Luckiesch, Astrophysical Journal, XXXIV., Oct., 1911.

[2] E. L. Nichols and E. Merritt, Phys. Rev., XXII., p. 279, 1906.

[3] C. C. Trowbridge, Phys. Rev., XXVI., p. 515; XXXII., p. 129.

[4] E. L. Nichols and E. Merritt, Carnegie Publication, No. 152.

[5] H. E. Ives and M. Luckiesh, Astrophysical Journal, Vol. XXXVI., p. 330, 1912.

[6] E. L. Nichols and E. Merritt, Carnegie Publication, No. 152, Chapter XV.

At the temperature of liquid air secondary chemical changes could scarcely occur. While if an amorphous phosphorescent substance is formed by freezing a homogeneous solution we should expect that the material would be approximately homogeneous. Experiments along this line by Kennard[1] are encouraging, since in the case of paraffin and frozen kerosene the decay, at the temperature of liquid air, was found to follow the linear law.

The study of phosphorescence is also complicated by the fact that in many substances the effect produced by a given excitation is largely affected by the previous history of the specimen. After a substance has been excited and then allowed to decay until no trace of phosphorescence can be detected its condition is usually not the same as it was originally. If subjected for a second time to the same excitation, even after a rest of several days, its phosphorescence is found to be brighter and of longer duration. In many cases also the substance is found to be thermo-luminescent. In studying the decay of phosphorescence this residual change must be taken account of, and in the more recent work the substance has usually been brought back to a standard condition by heating, or by brief exposure to infra-red radiation. But the cause of the residual change and the methods for its removal are so little understood that we cannot feel at all certain that the disturbances due to it are really eliminated.

Another source of disturbance,—which is at the same time a very interesting phenomenon in itself—is the effect of the red and infra-red rays upon the decay of phosphorescence. In the case of Balmain's paint the longer rays cause a considerable increase in the brightness of phosphorescence, which, however, is only temporary and is followed by more rapid decay. In Sidot blende it has usually been thought that the effect is simply to increase the rapidity of decay without any preliminary increase in brightness. But Ives and Luckiesch[1] have found that while this is true during the early stages of decay, a temporary flashing up of phosphorescence can also be observed in Sidot blende if the exposure to infra-red takes place after the decay has proceeded for several minutes.

It is clear that the phenomena of phosphorescence are extremely complex. And unfortunately the complexity appears to be especially great in the case of the substances that are most common and therefore most frequently studied. The problem has not yet been reduced to its lowest terms. In the further study of the subject it appears to me of the greatest importance to choose the conditions of observation, if this is possible, so as to eliminate some of the sources of disturbance. The work of Kennard[2] at low temperatures appears to be a promising step in this direction.

Let us consider now the problems of luminescence which are more obviously and directly connected with the question of atomic structure. Take for example the question of the relation between the wave-length of the exciting light in the case of fluorescence or phosphorescence and that of the light emitted.

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[1] Kennard, E. H., PHYSICAL REVIEW, IV., p. 278, 1914.

[3] Ives and Luckiesch, Astrophysical Journal, Vol. XXXIV., p. 173, 1911.

[3] Kennard, E. H., PHYSICAL REVIEW, IV., p. 278, 1914.

Since excitation cannot occur without absorption this question is closely connected with that of the relation between the luminescence spectrum of a substance and its absorption spectrum.

The law, first enunciated by Stokes, that the wave-length of the fluorescent light is always longer than that of the exciting light has led to extended discussion and experiment. Probably more papers have been published dealing with Stokes' law than on any other topic connected with luminescence. The fact that there are many cases where the law is violated seems to be now well established. The most striking exceptions to the law are probably those found by Wood in the case of fluorescent vapors. But even in these cases the longest wave-length that will excite luminescence is only a little longer than the shortest wave-length in the light emitted. As a general statement of what appears to be a fundamental relation the law still retains its value.

For a long time Stokes' law was thought to be exact, and attempts were made to base it upon thermodynamic reasoning. Fluorescence was thought of as a case of degradation of energy, the transformation of the short wave energy of the exciting light into the long wave energy of fluorescence being looked upon as somewhat analogous to the passage of heat from higher to lower temperature. I think that the attempts to base Stokes' Law on the Second Law of Thermodynamics are now generally regarded as unsound. Nevertheless this view has many attractive features, and it does not seem to me that it should be finally dismissed until, with the aid of the more recent methods of thermodynamics, it has been again considered.

Another explanation of Stokes' law has been based upon the theory of quanta. If excitation is due to the emission of electrons under the influence of the exciting light, in other words to a process analogous to that of the ordinary photoelectric effect—the velocity with which the electron leaves the active molecule will be determined by the wave-length of the exciting light. Similarly the wave-length of the light emitted when the electron returns will be determined by its energy at the time of recombination. Owing to collision with other molecules, however, a portion of the energy of the electron will generally be lost before an opportunity for recombination occurs. On the whole, therefore, the frequency of the light emitted will be less than that of the exciting light. This explanation has the advantage of accounting for the deviations from Stokes' law, for there will always be some electrons, although relatively a small number, which gain energy by collision before returning, and the light emitted during recombination will in such cases have a shorter wave-length than the exciting light. This view leads us to expect also that the deviations from Stokes' law will be less marked at low temperatures; and the small number of experiments which bear upon this question are in agreement with the theory. This explanation of Stokes' law, which is due to Einstein, is interesting in being almost the only case in which the theory of quanta has been applied to luminescence.

In the case of solids and liquids the fluorescence spectrum usually consists of one or more bands, shaded in both directions from a well defined maximum, and rarely less than one or two hundred Ångström units in width. In some cases the band may extend nearly throughout the visible region. In a large class of cases, but apparently not in all, the region of most intense excitation is immediately adjacent to the fluorescence band, on the short wave side. This region of excitation corresponds, of course, to a region of absorption; and in a large class of substances, of which fluorescein and eosin are typical, a certain symmetry is noticeable when we compare the curve of intensity in the fluorescence spectrum with the curve which gives the absorption coefficient as a function of wave-length. The fluorescence curve is steep on the short wave side and dies away gradually toward the red; while the absorption curve is steep on the long wave side and dies away gradually toward the violet. In cases where the two curves overlap, and this is usually the case, Stokes' law is violated.

Although the region of maximum excitation occupies the position just described, the substance is usually excited to some extent also by light of shorter wave-lengths. This fact is very beautifully illustrated by throwing a spectrum from a quartz prism upon the surface of a solution of one of the fluorescent dyes, such as fluorescein. The brightness of the fluorescence excited by the relatively weak ultra-violet rays is often such as to suggest that the energy of the light is more efficiently utilized for excitation when in the form of short waves. There has been no experimental test of this conjecture in the case of ultra-violet excitation. But throughout the principal absorption band the reverse has been found to be true.[1] The specific exciting power, that is the fluorescence excited by a given amount of absorbed energy, is greater for light at the long wave side of the band than in the middle, and still greater than for light on the violet side. I am inclined to think that we have here a promising case for the application of the theory of quanta, which by the aid of plausible hypotheses may be made to give at least a qualitative explanation of the facts.

While most substances possess a luminescence spectrum in which the bands are few in number and quite broad there are several exceptions, and the number of exceptions is increasing as the study of luminescence proceeds. In the case of anthracene there are four or five bands, which are narrow even at ordinary temperatures and become quite narrow as the temperature is lowered. A still more notable case is that furnished by the uranium salts, which have played so important a part in the history of luminescence as well as in the history of radioactivity.

The fluorescence of these salts is not only remarkable because of its brilliancy, but still more so on account of the structure of its spectrum, the manner in which the energy is distributed among the different bands, and the striking and significant relation that is found to exist between fluorescence and absorption. Brilliant fluorescence is shown only in the uranyl salts, *i. e.*, the salts in which the uranium occurs in the radical UO_2. At ordinary temperatures seven or eight bands are usually visible, the width of each being in the neighborhood of 100 Ångström units. Although the different uranyl salts give bands which differ

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[1] E. L. Nichols and E. Merritt, Carnegie Publication, No. 152, Chapter XIII.

somewhat in position and width the general appearance of the spectrum is much the same in all cases. The absorption spectrum of these salts also consists of a group of bands, whose width is approximately the same as that of the fluorescence bands. If plotted on the scale of frequencies the bands are found to be spaced at equal intervals, the absorption bands apparently forming a continuation of the bands of fluorescence as we proceed toward the shorter waves. It is found, however, that the regions of fluorescence and of absorption overlap, and that the bands which are common to both regions are "reversible." That is to say these bands will appear as absorption bands if the substance is observed by transmission in white light, but will appear as fluorescence bands if the substance is illuminated by ultra-violet rays only.

If we measure the intensity of the successive bands, starting with the band in the red, we find that the energy increases from band to band until a maximum is reached for a band lying in the green, after which the intensity for each succeeding band is much less than that of the one that precedes it. The distribution of energy in each band as determined by the spectrophotometer is much the same, on a small scale, as the distribution among the bands. Curves plotted to show the distribution of energy in a single band, in the group of bands, in the fluorescence band of a substance like fluorescein, and in the spectrum of a black body, are of the same type, and so strikingly similar in form that we might pass from one to the other simply by changing the wave-length scale.[1] At low temperatures each band of the uranyl spectrum breaks up into a group of lines, and I do not doubt that if the energy distribution in each line could be determined it too would be found to give a curve of the same type. One is reminded by this group of curves of an old rhyme, whose origin I do not recall, but which finds its applications in physics as well as in entomology:

> The very fleas have other fleas,
> And lesser ones, to bite 'em
> And these again have other fleas;
> And so *ad infinitum.*

Upon looking at these curves one can scarcely escape the feeling that both the fluorescence and the absorption regions in a substance like fluorescein are really made up of bands like those in the uranyl salts, but that the bands are so broad as to overlap and form single bands of fluorescence and absorption respectively, which we are unable to resolve.

At the temperature of liquid air both the fluorescence and absorption of the uranyl salts become more complex. Each fluorescence band breaks up into several extremely narrow bands, which are often as sharp as spectral lines; and new lines frequently appear in the regions that were dark at higher temperatures. In the absorption region also the bands are replaced by lines. In general appearance and in complexity these spectra suggest the spectra obtained from an arc or from a vacuum tube. They are in reality, however, much simpler, since it is possible to arrange the lines in groups or series, in

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[1] E. L. Nichols and E. Merritt, Phys. Rev., XXXIII., p. 354, 1911.

each of which the lines are spaced at equal intervals on the scale of frequencies. It often happens that the absorption lines can be most satisfactorily arranged in series for which the interval is shorter than that of the fluorescence bands. But in some cases the fluorescence series appear to be continuous with the absorption series, with the interval constant throughout, and with certain lines capable of appearing either as fluorescence or as absorption according to the method of observation.[1]

It is natural to expect that it would be possible, by a suitable choice of the exciting light, to excite one series of fluorescence lines without exciting the rest. As yet, however, no one has succeeded in doing this, although some slight indications have been found that the intensities of the different series do not change in exactly the same ratio as the excitation is changed. Light corresponding to one of the absorption bands is undoubtedly more effective in excitation than that falling in the intervals between bands. But diffuse absorption which is capable of producing excitation is present throughout the short wave region, so that any light lying on the short wave side of the first reversible band is able to excite to some extent. The whole question of the relation between the wave-length of the exciting light and the intensity and structure of the fluorescence spectrum requires further study.

In some respects the most promising field for study in the whole subject of luminescence is that opened up by Wood[2] in his work on the fluorescence or resonance spectra of vapors. Unfortunately the experimental difficulties are so great that few physicists have had the courage to undertake the work. The vapors of sodium, potassium, iodine and many other elements show fluorescence spectra consisting of a vast number of lines, so narrow that these spectra will stand analysis by the most powerful methods of spectroscopy. The absorption spectra of such vapors are equally complex. Wood estimates that the absorption spectrum of iodine contains not less than 35,000 lines in the visible region. The complexity of the phenomena would be altogether disheartening if it were not for the fact that the fluorescence can be greatly simplified by the use of monochromatic light for excitation. If a single line of some strong gaseous spectrum is used for excitation the fluorescence spectrum is found to consist of a relatively small number of regularly spaced lines. At first Wood was of the opinion that each of these fluorescence lines corresponded in position to a line in the absorption spectrum. His more recent work shows, however, that this is not in all cases true.

The lines of a given series, although spaced with great regularity, do not show constant intervals, either on the scale of frequencies or on that of wave-lengths. If plotted to a frequency scale the intervals increase slightly as we pass toward the shorter wave-lengths. In this respect therefore the series are not as simple as the constant interval series of the uranyl salts. It must remembered, however, that Wood has pushed his resolving power much further than would be possible with the uranyl spectra. If the latter could be resolved to the same

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[1] H. and J. Becquerel and H. K. Onnes, Leiden Communications, No. 110, 1909.

[2] R. W. Wood, Philosophical Magazine, 24, 673, 1912; 26, p. 828, 1913.

extent and measured with the same accuracy as was reached by Wood in the study of iodine it is not at all unlikely that variations from the constant interval law could be detected.[1]

It will be noticed that there is a striking resemblance between the fluorescence spectra of the uranyl salts when these are observed at low temperatures, and the resonance spectra of vapors,—a resemblance which is the more remarkable when we remember the widely different conditions under which emission occurs in the two cases. In neither case, unfortunately, has experiment gone far enough to make sure that the resemblance is more than superficial. In vapors the resonance bands appear to be closely connected in many cases with the ability of the vapor to rotate the plane of polarization in a magnetic field. In the case of the uranyl salts the magnetic rotation has not been tested. On the other hand in the case of vapors the relation between fluorescence and absorption has not yet been definitely determined so that we are not in a position to say either that the vapors show the same remarkable relation between these phenomena that is so characteristic of the uranyl salts, or that the relation is an entirely different one. To my mind it is a matter of considerable importance to determine whether the phenomena of fluorescence really are essentially the same in these two widely different cases. It has already been pointed out that the ordinary cases of fluorescence like that of eosin may be looked upon as being of the same type as the fluorescence of the uranyl salts, apparently the only difference being that the bands are so broad that they fuse together to form a single band of fluorescence and a single band of absorption. If now it should turn out that the fluorescence of vapors is also of the same type we should be justified in concluding that the fundamental processes involved in fluorescence are the same in all cases.

The study of the fluorescence of rarefied vapors and the study of low temperature fluorescence of solids like the salts of uranyl represent to my mind two attempts, along radically different lines, to simplify the conditions under which emission is caused to occur. In the case of vapors collisions occur only rarely, but when they do occur the disturbing effect upon the process of emission must be of considerable importance. In the low temperature fluorescence of solids each radiating molecule is closely surrounded by other molecules all the time and its vibrations are doubtless in consequence greatly modified. But on the other hand the molecular movements due to temperature are relatively sluggish; and collisions between molecules are far less violent than at higher temperatures; possibly at sufficiently low temperatures, especially in crystals, the molecular movements are reduced to vibrations about a position of equilibrium, with no collisions at all. The experimenter has his choice between a molecule which is

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[1] In the measurements of H. and J. Becquerel and H. K. Onnes (Leiden Communications, No. 110, 1909) there is some indication of an increasing interval as we pass toward higher frequencies. In some cases successive intervals differed by as much as 0.1 per cent. In the resonance spectra of sodium each interval is on the average about 2 per cent. greater than the preceding and in iodine 5 per cent.

subjected to large but nearly constant disturbing forces and one which, while ideally free from disturbance most of the time, is obliged to pay for this immunity by occasional periods of extremely great disturbance. I must confess that my preference is for the slow and plodding molecule, in spite of the fact that he is usually found in a crowd. It may be, however, that it will prove possible to combine the advantages of the two methods. If resonance radiation should be discovered in hydrogen or helium for example, or even in oxygen or nitrogen, these gases might be studied in rarefied form at low temperatures, and almost all sources of disturbance would be removed.

It is through the further study of the line spectra of luminescence, of which the resonance spectra of the vapors and the fluorescence spectra of the uranyl salts are typical examples, that I think we may expect the subject of luminescence to contribute most directly to the solution of the problem of atomic structure. Personally I feel that such study offers a more promising line of attack than any other that is now open to us, not excepting even the study of radioactivity or of the X-ray spectra.

Of course I cannot expect this view to be accepted without challenge. In the early days of spectroscopy there was a very general belief that the study of line spectra would enable us to determine the mechanism of emission, and therefore the structure of the radiating atom, in much the same way that we might hope to determine the nature of a sounding body from a study of the relations among its overtones. But the results have been disappointing, and physicists are not nearly so optimistic as they were. Now the subject of luminescence, in so far as it concerns itself with the study of luminescence spectra, is merely a branch of spectroscopy. In fact, if we use the term luminescence in its broadest sense, the greater part of the whole subject of radiation would probably fall under this head. Why should we expect the study of fluorescence spectra to offer more promise than the study of flame or arc spectra? The question becomes more pertinent when we remember that the spectra studied by Wood are as rich in lines and as complicated as arc spectra, while the experimental difficulties are much greater. Again, the resonance spectra and the uranyl spectra resemble closely the band spectra of ordinary spectroscopy; which, with their thousands of closely crowded lines, form a maze of such complexity that only a few spectroscopists have cared to attack them.

The strong argument in favor of luminescence appears to me to lie in the fact that in photoluminescence we have the only case, so far as I know, where the mode of excitation is definite and subject to control. Excitation by kathode rays probably comes next in order of simplicity. In a way it seems absurd to use the word simple in referring to either of these modes of excitation. But if we try to form a picture of the complex conditions that must exist in a flame, or arc, or spark, and compare such cases with the luminescence produced by monochromatic light or by kathode rays of constant and known velocity, it is like comparing the howling of a mob with the sound of a tuning fork. With sufficient patience we might find out how a piano is made by listening to the sounds produced by a crowd of unruly children pounding on the keys. But we would have infinitely better chance of success if we could press one key at a time and observe the result. In the study of photo-luminescence this can be done. In fact it is exactly what Wood *has* done.

In other words, in the case of photoluminescence we can control the excitation. We can determine relations between emission and absorption, and are in a position to tell which of these relations are real and which accidental. It is not merely that we have two methods of attacking the problem of the mechanism of emission and absorption, instead of one; it means a great deal more than that. We can observe the effects produced by the mechanism; or we can determine what agencies cause the mechanism to operate; but, what is more important still, we can correlate these observations and determine what effect is produced by a given stimulus.

The spectra of photoluminescence, complex as they often are, are the simplest spectra that are known. Even Balmer's series loses its appearance of simplicity if we compare it with the constant interval series of the uranyl salts. It may perhaps be urged that the high frequency X-ray spectra possess greater simplicity. Possibly this is true. But the evidence of the most recent work does not support such a view; for as the methods of observation are improved there is every indication that the structure of these spectra is far more complex than was at first suspected. A recent photograph published by Seeman showing a part of the high frequency spectrum of platinum might well be taken for the photograph of an arc spectrum. The history of ordinary spectroscopy seems to be repeating itself. Just as we thought until quite recently that an X-ray spectrum contained only the K and L lines, so there was a time when it was thought that the sodium spectrum consisted of the D line only.

The study of ordinary luminescence cannot, however, take the place of the study of high frequency spectra as a means of determining atomic structure. There is every reason for believing that the X-ray spectra come from the nucleus of the atom; while, as Stark has pointed out, there are strong reasons for thinking that luminescence spectra originate in the vibrations of the valency electrons. In the study of luminescence we attack the outer defenses of the atom; by the aid of the high frequency spectra we attack the citadel. Our problem will not be solved until both are won.

It is interesting to note, however, that in the high frequency spectra themselves we have phenomena that are highly suggestive of luminescence. The characteristic X-rays have sometimes been called "fluorescent X-rays," in recognition of an analogy that is by no means superficial. Characteristic secondary rays are produced only by X-rays of wave-length shorter than that of the secondary rays emitted. Here we have the analogue of Stokes' law. For wave-lengths just a little shorter than that of one of its own characteristic rays a substance shows abnormally great absorption. In other words there is an absorption band immediately adjacent to the emission band on the short wave side. We have here exactly the same relation between absorption and emission that holds in practically all cases of fluorescence. Using data kindly furnished by Dr. Duane I have plotted these absorption bands for several elements and have obtained curves that have the same form as those observed in such substances as eosin and resorufin with ordinary light. Except that the wave-length scale is a thousand times smaller, the phenomena of fluorescence certainly appear to be duplicated in the high frequency spectra in every detail. It would appear, therefore, that the arguments in favor of the study of luminescence spectra will apply equally well to the case of X-ray emission.

In this brief presentation I have not had time to refer to many important phases of my subject. For example, the connection between luminescence and chemical action produced by light; the relation between luminescence and the photo-electric effect; the use of fluorescent dyes as sensitizers for photographic plates; the development of an E.M.F. by the action of light on cells with fluorescent electrolytes; and many other topics whose study is of interest both as an end in itself and as a means of attacking the general problem. My chief object will have been attained if I succeed in arousing interest on the part of some of my hearers in a subject which, in my opinion, has not received the attention that it deserves.

The Law of Fall of a Droplet Through Hydrogen.[1]

By R. A. Millikan, W. H. Barber, and G. Ishida.

THIS paper presents the results of experiments made by the oil drop method on the law of motion of a spherical drop through hydrogen. The constant A in the correction term to Stokes Law as developed by one of the authors is not found to have quite the same value in hydrogen as in air. This means that in different gases the coefficient of slip is not one and the same function of the mean free path as Kundt and Warburg supposed it to be, and this in turn means that Knudsen's conclusion that the molecules of a gas suffer "diffuse reflection" or "re-emission" from a surface upon which they impinge is not in general tenable. Up to $(l/a) = .4$ the law of motion of an oil droplet through hydrogen is found to be given by

$$X = 6\pi\eta a v\left(1 + A\frac{l}{a}\right)^{-1},$$

in which A has the value .820 and l is determined from the Boltzmann formula $\eta = .350\,\rho\bar{c}l$. The same type of formula seems to hold generally up to $l/a =$ about .4, but A for air and oil is now found to be .845 while for air and shellac it is 1.06.

These differences are interpreted as due to differences in the law of rebound of different molecules from different sorts of surfaces.

University of Chicago.

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[1] Abstract of a paper presented at the Chicago Meeting of the Physical Society, November 28, 1914.

Notes on the Atomic Nuclei.[1]

By William Duane.

THE work of Sir Ernest Rutherford and his students on the scattering of α-particles has added great interest to the hypothesis according to which an atom consists of a positively charged nucleus surrounded by negative electrons. The data obtained from experiments on the scattering determine upper limits for the radii of the nuclei (supposed spherical), the limit for gold being 3×10^{-12} cm.

In order to account for the α- and β-rays, which are supposed to come from the nuclei of the radio-active atoms, and also for the relations between the chemical properties of successive radio-active elements, we assume that in general a nucleus consists of positive and negative electrons with an excess of positive charges.

A difficulty arises here. How can a lot of positive electrons remain packed so closely together? They ought to fly apart under their mutual repulsive forces, for the electrostatic forces, varying as the inverse square of the distance, cannot hold them in stable equilibrium.

It is not necessary to go beyond the classical electro-dynamics to find forces of sufficient magnitude to overcome the electrostatic repulsions. A simple calculation will show that, if two nuclei have magnetic moments equal to that attributed to the iron atom, their magnetic attraction will overcome their electrostatic repulsion, provided that the distance between them is of nuclear magnitude.

Let us assume that two iron nuclei, each having the charge E and the magnetic moment M, are placed at the distance r apart, with unlike poles pointing toward each other. The electrostatic repulsion between them is E^2/r^2 and the magnetic attraction, $6M^2/r^4$, if r is large compared with their linear dimensions. The charge E on the iron nucleus equals $26 \times 4.77 \times 10^{-10}$. In calculating the magnetic moment M of the iron atom we may take the maximum value of the magnetization in iron obtained by B. O. Peirce,[2] namely 1796. Dividing this by the number of atoms in a cubic centimeter of iron, 8.612×10^{22}, we get $M = 2.086 \times 10^{-20}$. If r_0 is the value of r for which the electrostatic and magnetic forces are equal to each other,

$$\frac{E^2}{r_0^2} = \frac{6M^2}{r_0^4},$$

and putting in numerical values,

$$r_0 = 4{,}078 \times 10^{-12},$$

a quantity of nuclear magnitude, but somewhat greater than the radius of a gold nucleus.

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[1] Abstract of a paper presented at the New York Meeting of the Physical Society, February 27, 1915.

[2] Proc. of the American Academy of Arts and Sciences, June, 1913.

If the distance between the nuclei is less than r_0 they are held together, and if this distance exceeds r_0, they fly apart.

This suggests an interesting theory of the mechanism of α-radiation. Let us suppose that, owing to internal agitation, a portion of the nucleus of a radioactive atom gets thrown out by chance just beyond the point where the magnetic force can balance the electrostatic. This portion of the nucleus will then fly off just as an α-particle does.

We can estimate its final velocity as follows: Let E and E' be the charges on what is left of the nucleus and on the α-particle respectively, M and M' their magnetic moments and m and m' their masses respectively. If r_0 is the distance between them when the magnetic and electrostatic forces balance, and if the motion is along their common axis, the total work done after the particle passes this limit is

$$W = \int_{r_0}^{\infty} \left(\frac{EE'}{r^2} - \frac{6MM'}{r^4} \right) dr = \frac{EE'}{r_0} - \frac{2MM'}{r_0^3}.$$

For $r = r_0$, $EE'/r_0^2 = 6MM'/r_0^4$, and hence

$$W = \frac{2}{3} \frac{(EE')^{\frac{3}{2}}}{(6MM')^{\frac{1}{2}}}.$$

Since the kinetic energy divides itself between the two moving parts in the inverse ratio of their masses, we have for the final velocity v of the α-particle

$$v^2 = \frac{4}{3} \frac{(EE')^{\frac{3}{2}}}{(6MM')^{\frac{1}{2}}(m + m')m'} \frac{m}{}.$$

The question now arises: what values must be assigned to the magnetic moments? It is natural to suppose that the magnetic moments of the nuclei are due to the magnetic moments of the positive electrons composing them. If so, the maximum value the magnetic moment of a nucleus can have (namely when all the positive poles of the electrons are turned in the same direction), should be approximately proportional to the atomic weight of the atom, and we may calculate from this the minimum value that v can have. The smallest α-ray velocity known is that of the α-particle from Uranium I. The atomic number of this element being 92, we have $E = 90 \times 4.77 \times 10^{-10}$, $E' = 2 \times 4.77 \times 10^{-10}$, $m = 234 \times 1.662 \times 10^{-24}$, $m' = 4 \times 1.662 \times 10^{-24}$, and from the magnetic moment of the iron nucleus

$$M = \frac{2.086 \times 10^{-20} \times 234}{55.47}, \quad \text{and} \quad M' = \frac{2.086 \times 10^{-20} \times 4}{55.47}.$$

Putting these in the formula the minimum value of v becomes

$$v = 1.36 \times 10^9.$$

The most recent measurements of α-ray velocities are those of Sir Ernest Rutherford and Mr. Robinson,[1] who give for the velocity of the α-particle from Uranium I the value 1.37×10^9, in exceeding close agreement with the calculated minimum value.

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[1] Phil. Mag., Oct., 1914.

The other 19 α-ray velocities range up to 2.06×10^9. These can be explained by giving proper values to M supposing that a few of the electrons are reversed and perhaps by assuming that the α-particle is projected in some direction other than along the common magnetic axis, in which case the 6 in the formula becomes smaller.

Doubtless the problem is more complicated than this elementary calculation presupposes. Further a single fact does not prove a theory. On the other hand the fact that we can calculate from magnetic data α-rays velocities which differ from the results of measurement by less than the experimental errors, does appear to have a certain significance, especially when taken in connection with certain other facts, that I hope to present to the Society at some future time.

Harvard University.

X-Rays Produced by Slow-moving Cathode Rays.[1]

By Elizabeth R. Laird.

In these experiments cathode rays from a Wehnelt cathode fall on an anticathode. The Röntgen rays so produced pass through a well shielded window into a measuring vessel, where their presence is indicated either by the charging of a metal plate in high vacuum, or by the ionization produced when the pressure there is a few millimeters. The window is covered with an airtight celluloid film. The variation in the intensity of the radiation as measured by the photo-electric effect is shown in the curve Fig. 1. The sensitiveness of the electrometer was 2.5×10^{-15} ampere per scale division per minute. An effect was not obtained with a primary P.D. less than 200 volts. The same was true when the sensitiveness was increased by the use of the ionization method, although at 550 volts the current was increased more than a hundred times. Experiments were made with other windows. Effects obtained when the window was not quite airtight were shown to be false, in one case light from the Schumann region falsified the results. Some measurements were made on the absorption of these different substances. The celluloid films used transmitted from 40 per cent. to 70 per cent. of the radiation. The absorption in them remained roughly the same when the primary potential was varied from 300 to 1,300 volts.

Aluminium, copper, platinum, and quartz used as anticathodes gave practically the same intensity of radiation, a smaller amount was obtained from the gas alone, *i. e.*, with the anticathode displaced.

Experiments were made to measure the velocity of the secondary electrons. The results would show that with a primary voltage of 550 some electrons are present with velocities corresponding to 100 volts or more. The difficulty of avoiding secondary effects from the walls or window of the chamber has not been entirely overcome, the correction for this would be expected to make the velocities higher.

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[1] Abstract of a paper presented at the Philadelphia meeting of the Physical Society, December 28–31, 1914.

Experiments were also made with another form of apparatus to test the polarization of the radiation. Only a slight amount of polarization was found.

The results with cathode ray velocities less than 200 volts do not agree with those of Dember and of Whiddington. The properties of the radiation as far as observed with the primary potential in the neighborhood of 550 volts are those of the Entladungsstrahlen from the spark at atmospheric pressure.

These experiments and the following ones were made while the writer was holder of the Sarah Berliner Research fellowship for women.

MT. HOLYOKE COLLEGE.

X-RAYS FROM THE ELECTRICAL DISCHARGE.[1]

BY ELIZABETH R. LAIRD.

IT has been found that the rays from the discharge in air at a pressure of 6 mm., previously known as Entladungsstrahlen at diminished pressure, cause a secondary radiation of electrons when falling on a metal plate in a high vacuum, and that the velocity of at least a portion of these electrons measured by an retarding field corresponds to 3,500 volts. The variation with pressure of the ionization produced between parallel plates leads also to the inference of a secondary radiation which is inappreciable after travelling a distance 0.017 cm. in air. The corresponding mass coefficient of absorption in aluminium was found to be approximately 590. These data are of the order of those obtained with X-rays of K type from calcium or L type from silver. These magnitudes show that one should not expect these more penetrating Entladungsstrahlen from a steady discharge at this pressure.

MT. HOLYOKE COLLEGE.

AN AGGLOMERATION THEORY OF THE VARIATION OF THE SPECIFIC HEAT OF SOLIDS WITH TEMPERATURE.[1]

BY ARTHUR H. COMPTON.

THIS work is based on the assumption that a degree of freedom of an atom in a solid cannot possess less than a certain critical amount of thermal energy. If its total energy falls below this value, the degree of freedom becomes "agglomerated," and remains in this condition until it again receives energy greater than the critical value.

The probability that a degree on freedom shall remain "unagglomerated" is found to be,

$$P = e^{-\epsilon/2RT} = e^{-\tau/T} \qquad (\tau = \epsilon/2R),$$

where ϵ is the assumed critical energy. The ratio of the specific heat at the relative temperature T/τ to its value at infinite temperature is then found to be,

$$C_v/C_\infty = e^{-\tau/T}(\tau/T + 1).$$

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, February 27, 1915.

This expression for the variation of the specific heat with temperature agrees very well with the experimental data, apparently better than the formulæ of Einstein and Debye which are based on the quantum hypothesis.

Princeton University.

A New Device for Rectifying High Tension Alternating Currents.[1]

By Saul Dushman.

The action of the rectifier (kenotron) depends upon the emission of pure electron currents in extremely high vacua from an incandescent metal, when the latter is made cathode. Different types of kenotrons have been devised, such as a "headlight" tungsten filament placed inside a molybdenum cap, or a molybdenum cylinder with the tungsten filament placed along its axis. The current carrying capacity of the kenotron depends only upon the area and temperature of the filament (Richardson equation for electron emission), while the minimum voltage drop (V) depends upon the area, shape, and distance apart of the electrodes, and increases with the current actually rectified (i) according to an equation of the form

$$i = k \cdot V^{\frac{3}{2}}$$

(Langmuir's "space charge" equation). When i is measured in milliamperes, the magnitude of k varies in usual cases from 5×10^{-3}, for kenotrons suitable for 100,000 volts D.C. to 250×10^{-3} for kenotrons designed for 10,000 volts D.C.

Owing, however, to the fact that the filament temperature limits the maximum current which the kenotron can rectify, it is possible for the voltage over the latter to exceed the value given by the above equation, as the rectifier takes the difference between the maximum voltage available and that consumed in the load. Care should therefore be taken in using the kenotron to avoid short-circuits of the load, or some form of protective device should be used.

The actual energy losses in the kenotron may be reduced to less than two per cent. of the energy rectified.

Currents as high as 1,500 milliamperes may be rectified, but it is much more convenient to design the kenotrons so that each unit controls about 10 kw. As two or more kenotrons can be operated in parallel, this presents no limitation to their use. An arrangement of two or four kenotrons with a transformer and condensers will give direct current which can be made as free from pulsation as desired.

A detailed article dealing with this subject will be found in the General Electric Review for March, 1915.

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[1] Abstract of a paper presented at the New York meeting of the Physical Society, February 27, 1915.

THERMAL CAPACITY OF TUNGSTEN AT INCANDESCENT TEMPERATURES, AND AN APPARENT LAG OF RADIATION INTENSITY WITH RESPECT TO TEMPERATURE.[1]

BY A. G. WORTHING.

THE characteristic equation for a uniform filament mounted in an evacuated bulb, heating or cooling from one temperature to another due to a change in the heating current is

$$IV = f(T) + cm\frac{dT}{dt}$$

on the supposition that it passes through a succession of steady states. I, V and T represent the instantaneous values of current, potential drop, and temperature, m the mass of the filament, c the thermal capacity of the substance of the filament and t time. The three terms represent respectively the rate of heat production in the filament, the rate of radiation of energy from the filament, and the rate of change in the heat energy of the filament. The instantaneous values of I and V were measured on a potentiometer with the aid of a pendulum device. The values assumed for $f(T)$ were the wattages under steady current conditions corresponding to the resistances given by V and I. In some cases the cooling effects of the junctions were eliminated by taking the differences obtained using two filaments differing only in length when heated by the same current. In all cases it was found that the $c-T$ relation obtained when the filament was heated from some low temperature to some higher temperature, was different from that obtained when it was cooled from the higher temperature to the initial low temperature. The difference was always consistent with the assumption that while the temperature is changing, the radiation intensity lags with respect to the temperature as determined by resistance measurements. Assuming the mean of such $c-T$ relations to be the desired relation, and the temperature scale that determined by Mendenhall and Forsythe the following values have been obtained.

T in °K	c in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$
1,600	.042
1,800	.044
2,000	.047
2,200	.050

Results thus obtained are in good agreement with results obtained by a slight modification of Corbino's method in which the same filaments were used.

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CLEVELAND.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 27–28, 1914.

On the Reflecting Power of a Certain Selenium Crystal.[1]

By L. P. Sieg and F, C. Brown.

THE reflecting power, and other optical constants of metallic and amorphous selenium mirrors have been determined several times. The latest work has been done by Foersterling and Fréedericksz.[2] While working with large selenium crystals the question arose as to whether or not the optical properties of these crystals were the same as for the metallic modification or the amorphous varieties, or differed with the different types of crystals. Only a preliminary study was made, but work is being done in this laboratory toward obtaining a complete study of the optical properties. The reflecting power of the selenium as used by Foersterling and Fréedericksz was practically constant from wave-length 0.289 μ to 0.740 μ, varying from 0.36 to 0.25 at the longer wave-length. The present work indicated with certainty that the reflecting power for a lamellar crystal, from 0.37 μ to 0.80 μ was practically constant. Exactly what the coefficient is, has not been determined with any great accuracy, as the principal concern was to discover any variations, if any, in the reflecting power. This information was of great importance in connection with work on the light-sensibility curves.

State University of Iowa.

The Arc in a Longitudinal Magnetic Field.[1]

By R. F. Earhart.

SOME experiments were made with a carbon arc, using both cored and solid carbons, when the arc was placed in a uniform magnetic field. The lines of magnetic force were parallel to the axis of the carbon electrodes. The effect of establishing fields varying up to 2,000 c.g.s. units was to reduce the current and to increase the P.D. between the terminals. The behavior was studied by determining the characteristic curves for the arcs with fields of different strength. The characteristic curve produced when the field is established is similar to one which would be obtained by lengthening the arc. It was noticed that the heat developed at the positive carbon was increased when the field was established. In such case an increased length of carbon became red hot. This indicated that the anode fall in potential had been increased. Such was found to be the case when an exploring electrode was introduced. The cathode drop was increased but the anode drop had a greater relative increase than the cathode drop. The instability of the arc is increased with the application of the magnetic field. Unequal consumption of the carbon tips causes considerable difficulty.

Ohio State University.

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 27–28, 1914.

[2] Ann. d. Phys., 43, p. 1227, 1914.

TRANSMISSION OF SOUND THROUGH FABRICS.[1]

BY F. R. WATSON.

THE transmitting power for sound of different materials was determined by allowing sound to pass through the material in question and noting how much the intensity was diminished as compared with the unhindered sound when the material was removed. A whistle blown by a constant air pressure and backed by a parabolic reflector directed the sound through an open doorway into an adjacent room where its intensity was measured by the deflection of a Rayleigh resonator. One, two and three layers of material were then placed successively over the doorway and the intensities measured each time. The preliminary results indicate that the intensity falls off in a decreasing geometrical progression as the thickness of material increases in an arithmetical progression.

UNIVERSITY OF ILLINOIS.

A DIFFERENTIAL DYNAMIC METHOD FOR THE ACCURATE DETERMINATION OF THE VAPOR PRESSURE LOWERING OF SOLUTIONS.[1]

BY E. W. WASHBURN.

THE chief sources of error in the determination of vapor pressure lowering of solutions by the gas-saturation method as heretofore carried out are (1) the difficulty in measuring with sufficient accuracy the large volume of gas aspirated; and (2) the error due to temperature variation in successive experiments. Both of these sources of error can be practically entirely eliminated by placing the saturation trains, containing the pure solvent and the solution respectively, close beside each other in a well stirred constant temperature bath and aspirating the gas through both saturation trains in succession, the solvent vapor being removed from the gas stream by suitable absorbers placed immediately after the last saturator in each train. Under these conditions it is not necessary to know the volume of the gas aspirated, which can, therefore, be made as large as desired. Moreover, temperature variations even as large as 0.1 degree in a well stirred bath will not produce an appreciable error since both solution and solvent are affected nearly alike.

With this method and with solution in the first saturator and pure solvent in the second the relative vapor pressure lowering is given by the following expression:

$$\frac{p_0 - p}{p_0} = \frac{D_m(B - P_1 - p_0) - m_0 D_p}{m_0(B - P_2) - D_m p_0}.$$

D_m is the difference in the amounts of solvent vapor taken up by the two absorbers respectively and this difference is directly determined by placing the

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[1] Abstract of a paper presented at the Chicago meeting of the Physical Society, November 27–28, 1914.

absorbers (which are identical in form) on opposite pans of a balance. m_0 is the mass of solvent evaporated from the saturator containing the solvent, as determined by the increase in mass of the second absorber. B is the barometric pressure. p_0 is the (approximate) value of the vapor pressure of the pure solvent. P_2 is the difference between the barometric pressure and the pressure at which the aspirated gas leaves the second saturator while $D_p (= P_2 - P_1)$ is the difference in the pressures at which the aspirated gas leaves the two saturators respectively. Both P_2 and D_p which are very small are directly and accurately measured by means of two small inclined differential water manometers which are connected at the proper points in the system.

The precision of the result is wholly determined by the precision with which D_m is measured since all of the other quantities can be easily measured with 10 or 100 times the precision necessary. D_m increases with the concentration of the solution employed and with the quantity of air aspirated.

This method has been tested in this laboratory by Mr. H. B. Gordon and by Mr. E. O. Heuse. With molal aqueous solutions at 25° they find that an accuracy of about 0.25 per cent. is attainable in the value of $\frac{p_0 - p}{p_0}$ by this method.

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