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SPECTROSCOPY

BY

E. C. C. BALY, F.R.S.

GRANT PROFESSOR OF INORGANIC CHEMISTRY IN THE UNIVERSITY OF LIVERPOOL
FELLOW OF UNIVERSITY COLLEGE, LONDON

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39 PATERNOSTER ROW, LONDON
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PREFACE

In the following pages I have endeavoured to present the subject of Spectroscopy from the practical side. As full details as possible have been given of the methods of working with the various types of instruments. In the many branches of Applied Spectroscopy, as distinct from the statistical work, it has been quite impossible to deal with the great number of researches of the present time. Typical investigations have, therefore, been selected, both with the view of indicating the lines upon which present work is being carried on, and, further, in the hope, which I trust is not a vain one, that more workers may be encouraged to enter this fascinating and prolific field of research.

I have given no set tables of wave-lengths, because these tables are published in a most convenient form by Dr. Marshall Watts, and their inclusion would have necessitated the sacrifice of a considerable amount of the text.

My thanks are due to the many authors who kindly have allowed me to reproduce drawings and illustrations from their publications. To Professor Ames, of the Johns Hopkins University, am I particularly indebted for placing at my disposal the drawings and description of the Rowland grating ruling engines. I am also indebted to Professor Kayser's *Handbuch der Spectroscopie* for information upon his work

with Professor Runge on Spectral Series, and the work of the latter with Professor Paschen on the Zeeman effect. I have also to record my cordial thanks to my friends who have given me much valued help—Mr. H. J. Harris, Professor F. T. Trouton, Messrs. J. K. H. Inglis and A. W. Porter.

E. C. C. B.

UNIVERSITY COLLEGE, LONDON,
April, 1905.

PREFACE TO THE SECOND EDITION

SINCE the first edition of this book appeared there have been published a very great number of papers describing most important investigations in Spectroscopy. The advance of research in this subject during the last six or seven years has been exceptionally great, and I have found it exceedingly difficult satisfactorily to deal with this work and still to keep the book within reasonable limits. Even with the increase in size I cannot but feel that I have done scant justice to most valuable and striking investigations. I have endeavoured, however, as far as possible to give a *resumé* of the salient points of the more modern work, and I have also ventured to add at the end of the relevant chapters a list of references to the literature which I trust may prove of value to those who wish to read up the various subjects in greater detail than I have been able to include in the text.

I tender my most cordial thanks to those kind friends who took the trouble to send me notes on the inaccuracies and misprints that were present in the first edition. I would especially in this connection thank Mr. H. M. Reese of the Columbia University for his most valuable assistance.

To many friends am I indebted for their direct help in the preparation of this new edition. Amongst these I must

mention two, Mr. P. A. Baldock, B.Sc., who was kind enough to undertake the photographs of spectra which have been included, and also to Miss W. Judson, B.Sc., to whose keen interest and hard work I am more indebted than I can say. My readers may find reason to thank Miss Judson in the extensive index which she has prepared, and which I feel sure will prove a valuable adjunct to the book.

E. C. C. B.

THE UNIVERSITY, LIVERPOOL,
March, 1912.

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SPECTROSCOPY

CHAPTER I

HISTORICAL

THE foundation of spectroscopy may be traced in the discovery by Sir Isaac Newton, in the year 1666, that the amount of refraction suffered by different coloured rays of light is different with the same medium. He proved this in the first place by looking through a glass prism at some pieces of red and blue paper, when he noticed that the relative positions of the different coloured pieces appeared to be altered. In the second place Newton soon afterwards showed that a ray of sunlight is a combination of a number of rays of various colours, each of which suffers a different amount of refraction or bending on being made to pass through a glass prism, and that of these rays the red is least and the blue most refracted. The historical experiment actually carried out by Newton is familiar to every one, in which he caused a pencil of sunlight, which was admitted through a round hole in the shutter of a dark room, to pass through a glass prism and then fall on a screen. He thus obtained what he called a spectrum, that is, an orderly arrangement of a series of coloured images of the hole in the shutter, these coloured images appearing in different positions by virtue of the different amount of refraction suffered by rays of various colours. Before Newton had carried out these experiments, the colours produced by the passage of white light through a prism were supposed to be produced in the prism, for, up till that time, people had

imagined that the white light was actually changed into the different colours.

The phenomenon of the refraction of light and the laws connected therewith were, of course, well known in Newton's time, having been first discovered by Snell in 1621, and further worked out and first published at a later date by the great philosopher Descartes. Although both Snell and Descartes were unaware of the composite nature of white light, they succeeded in proving the existence of a constant relation between the angles when light is refracted; and Newton, as the result of his discovery that white light is a mixture of many different colours, was able to extend the applicability of the Snell and Descartes relation, and show that, while it differs for rays of different colours, it is constant for rays of the same colour.

Now, the paths of light rays through isotropic media always lie along straight lines, that is to say, they travel with a constant velocity; the velocity depends on the nature of the medium. When light passes from one isotropic medium into another, it suffers generally a change in velocity, and this change tends to cause a change in direction, the new path being a straight line at some angle with the first path. This bending of the path of the rays is called refraction, and the angular measure of the amount of bend is called the angle of deviation. This angle of deviation varies with the inclination at which the rays fall on to the boundary surface between the two media. It has a zero value when the rays fall perpendicularly on to this surface, and tends towards a maximum the more obliquely they fall. The amount of deviation suffered by a ray of light in passing from one medium to another depends upon the relative velocities of light in the two media and the angle at which the ray falls on the boundary surface.

The following laws were found by Snell and Descartes to hold good for all cases of simple refraction.

The incident and refracted rays lie upon opposite sides of the normal to the boundary or refracting surface at the point of contact, and the normal and the incident and refracted rays lie in the same plane.

The sines of the angles of incidence and refraction bear a constant relation to one another—a relation which is solely dependent upon the nature of the two media (Snell's law).

These laws will be better understood from a particular case. In Fig. 1 let the straight line AB mark the separation between any two isotropic media, for example, let AB represent a surface of water; and further, let a ray of light, CD, strike this water surface at the point D.

This ray, therefore, at the point D will be divided into two portions, one of which is reflected off in the direction DE, thus continuing its path in the first medium, air, while the other portion enters the water and pursues the path DF. This path DF is not a continuation of the path CD, but is refracted from it to some extent, and if CD be continued to O, the amount of the bending is shown by the angle FDO, which is the angle of deviation.

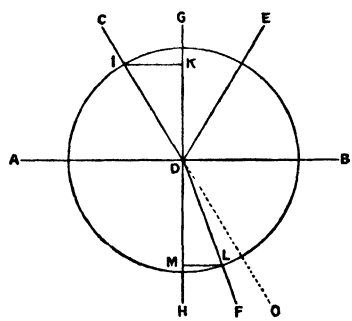


FIG. 1.

Through the point of incidence D the straight line GDH is drawn normal to the refracting surface, and this gives the angle of incidence CDG and the angle of refraction FDH.

Now, the first law of refraction states that the refracted ray DF always lies on the opposite side of the normal GH to the incident ray CD, and, further, that the two rays CD and DF lie in the same plane as the normal GH. To find the relation, stated in the second law, between the angles of incidence and refraction, draw any circle with D as centre, and from the points where this circle cuts the incident and refracted rays, draw the straight lines IK and LM perpendicular to the normal GH.

Now, the sine of the angle CDG is equal to $\frac{IK}{ID}$, and the

sine of the angle FDH is equal to $\frac{LM}{LD}$, and therefore, if the angles CDG and FDH be called i and r respectively—

$$\frac{\sin i}{\sin r} = \frac{\frac{IK}{ID}}{\frac{LM}{LD}} = \frac{IK}{LM}, \text{ since } ID = LD.$$

Snell's law states that the ratio $\frac{\sin i}{\sin r}$, or $\frac{IK}{LM}$, is constant for the same pair of media, whatever the value of i may be. This ratio is called the index of refraction, and is usually denoted by the symbol μ.

If the incident ray is normal to the surface, then the angle i is zero, and therefore, since $\sin 0^\circ = 0$, the angle r is also zero; this means, of course, that no refraction takes place, and the ray passes straight into the new medium.

It is important to notice that the index of refraction is a relative term depending on the two media; for example, in the above case it is a measure of the ratio of the velocities of light in air and in water; in general, by the index of refraction of a substance is always meant, unless specially noted to the contrary, the ratio of velocities of light in air and in the substance. The term "absolute index of refraction" refers to the value obtained with the specified substance in a vacuum.

The direction in which the refraction of the light takes place as a general rule depends upon the densities of the two media, and, although there are exceptions, it generally follows that, when a ray of light enters a dense medium from a rare one, it is refracted towards the normal, and conversely when passing from a dense into a rare medium it is refracted away from the normal. This is the case with the example shown in Fig. 1, where the light enters a denser medium and is refracted towards the normal; exceptions to this are known, as, for example, certain oils, which, though they are less dense than water, have a higher index of refraction than water, and, therefore, the velocity of light in them is less than in water.

It is interesting to consider more fully the simple case of

refraction shown above in Fig. 1, because certain important results can be obtained from it. If the index of refraction for two media be known, the different values of the angle of refraction resulting from different angles of incidence may readily be calculated with the help of a book of mathematical tables. This may be done for air and water, assuming the index in this case to be 1·34, which is sufficiently accurate for the present purpose.

By Snell's law we have—

$$\frac{\sin i}{\sin r} = 1{\cdot}34,$$

$$\text{and } \sin r = \frac{\sin i}{1{\cdot}34}.$$

From this it is possible to calculate the different values of r when i is given different values, and these are set forth in the following table :—

TABLE 1.

Angle of incidence.	Angle of refraction.		
0°	0°	0′	0″
10°	7°	29′	0″
20°	14°	51′	48″
30°	22°	1′	27″
40°	28°	49′	26″
50°	35°	4′	0″
60°	40°	30′	20″
70°	44°	48′	41″
80°	47°	36′	45″
90°	48°	35′	25″

In the column headed angle of incidence are given values of this angle, increasing by 10° from 0°, or normal incidence, to 90°, when the incident ray lies along the surface of the water, while in the second column are given the corresponding values of the angle of refraction. Since the angle of incidence cannot have a greater value than 90°, it follows from the table that, in the case of air and water, the largest possible value of the angle of refraction is 48° 35′ 25″.

Let us now consider the converse case of the light passing from water into air, and let AB in Fig. 2 again represent a boundary surface between air and water. The incident ray CD now strikes this surface from the water, and again, as before, is divided into two portions, one of which is reflected from the surface along the path DE, while the other leaves the water and follows the path DF, and, since the air is less dense than the water, DF is refracted from the normal. The relations given in Table 1 evidently hold good in this case, and by their means it is possible to follow the changes produced in the angle FDG when changes are made in the angle CDH; for example, when the angle CDH has a value of 40° 30′ 20″, the angle FDG measures 60°, and so on. If the angle CDH be increased until it reach the value 48° 35′ 25″, the angle FDG will become equal to 90°, and therefore the emergent ray will lie along the surface of the water. Now, 90° is evidently the largest possible value of the angle GDF, so that, if the angle CDH be increased beyond the value of 48° 35′ 25″, none of the light will be able to leave the water at all, but the whole will be reflected along the path DE. This is true for any two media, and thus we have the result that light cannot pass out from a dense medium into a light medium, but is totally reflected when the angle of incidence exceeds a certain definite value, which, in the case of water and air, has been shown to be 48° 35′ 25″.

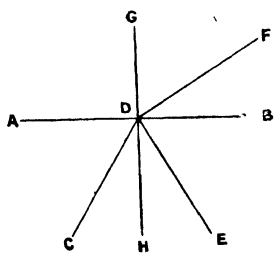


FIG. 2.

This particular value of the incident angle is called the *critical angle*, and can, by Snell's law, very readily be calculated for any two media when the relative value of the index of refraction is known. In the equation $\frac{\sin i}{\sin r} = \frac{1}{\mu}$, it is only necessary to put $r = 90°$, for it has been shown that i reaches the critical value when $r = 90°$.

Therefore, since $\sin 90° = 1$,

$$\frac{1}{\sin i} = \mu, \text{ and } \sin i = \frac{1}{\mu}.$$

For example, the refractive index of a particular class is 1·62, and therefore $\sin i = \frac{1}{1{\cdot}62} = 0{\cdot}6187$, from which i is found to be 38° 13′ 30″, which is the critical angle for the glass in question.

The greater the value of the index the smaller is the critical angle, and it is interesting to note that the brilliance of a diamond in a deep setting is due to the very small value of the critical angle, which is about 19° 30′, so that all the light which reaches the bottom surface at a greater angle than this is totally reflected, with the result that much less light passes out through the bottom than would be the case with glass or similar substances.

The following points must be remembered in connection with the simple refraction of light:—first, that a certain quantity of the light is always reflected, and in no case can total refraction occur; and second, that no refraction from a dense into a rare medium can take place unless the angle of incidence is less than a certain critical angle whose sine is equal to the reciprocal of the index of refraction.

In the cases previously considered the refraction at a single boundary surface only has been dealt with; it is, of course, necessary to deal with two boundary surfaces at least for any practical purpose. The simplest case is that of the passage of a beam of light through a medium with parallel surfaces, such as a plate of glass; this is shown in Fig. 3.

Let AB and CD represent the upper and lower parallel surfaces of a piece of plate-glass, and let the ray EF fall on the surface AB, making an angle of incidence i. Part of the ray enters the glass, being refracted towards the normal, and pursues the path FG, making the angle of refraction r. By Snell's law, therefore—

$$\frac{\sin i}{\sin r} = \mu.$$

Again, the ray FG on reaching the lower surface CD is

divided into two parts; one of which is reflected and the other passes out into the air, being refracted from the normal. By Snell's law, therefore, again—

$$\frac{\sin r'}{\sin i'} = \mu$$

It follows that—

$$\frac{\sin i}{\sin r} = \frac{\sin r'}{\sin i'}.$$

But by construction the angle i' is equal to the angle r, and, therefore, the angle r' must be equal to the angle i.

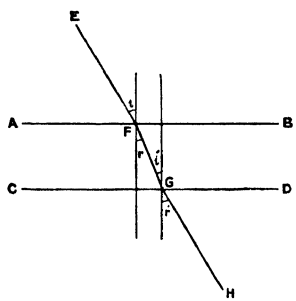


FIG. 3.

The refraction at F and G is, therefore, equal, but in opposite directions, so that the ray of light on emerging into the air from the glass pursues a path parallel to its original path; a plate of glass with parallel sides, therefore, when introduced into the path of a beam of light, in no way alters the direction of the path.

The case is different, however, when the two boundary surfaces are not parallel to one another, but are inclined at some angle to one another. The deviation in the path of

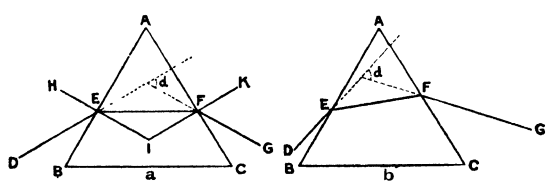


FIG. 4.

a ray of light produced by the refraction at the first surface is not counteracted at the second surface, but is always increased. For example, let us take the case of a prism.

Let AB and AC in Fig. 4 represent the refracting surfaces of the prism ABC, which are inclined together at the angle

BAC. Then, if the ray DE fall on the surface AB, making an angle of incidence DEH, part will enter the prism and follow the path EF, which makes an angle of refraction FEI. The relation between the angles DEH and FEI is defined by the value of the index of refraction. The ray EF on reaching the second surface AC is refracted away from the normal and passes along the path FG, the relation between the angles GFK and EFI being also defined by the index.

It is evident that the deviation in the path of the ray DE, produced by the refraction at the first face, is increased still more by that which occurs at the second face; the total deviation, which is the sum of the deviations at the two surfaces, is shown by the angle d, which is obtained by prolonging the paths of the incident and emergent rays. It will readily be seen on reference to the two cases shown in Fig. 4 that the angle d has the lesser value in case a; indeed, it can be proved that the total deviation is the least possible when the ray passes symmetrically through the prism, that is to say, when the angle DEB is equal to the angle GFC. When, therefore, a ray of light passes symmetrically through a prism, the deviation is a minimum; it is important to notice that, in the case of minimum deviation, the path of the rays inside an isosceles prism is parallel to the prism base (BC in Fig. 4).

In the cases of refraction dealt with in the preceding pages a tacit assumption was made that the rays of light were homogeneous, that they consisted of light of only one colour; but since Newton, by his discovery of the composite nature of white light, showed that rays of different colours suffer different amounts of refraction, it becomes necessary to take a wider view of the phenomena. While Snell's law states that the value of the index of refraction is a constant for rays of one colour, it differs for rays of different colours, and Newton as a result of his experiments found that the value of μ for red light is smaller than the value for blue light, or, in other words, that red light suffers less and blue light more refraction with the same medium. The fact of Newton obtaining a spectrum is simply explained, as shown in Fig. 5.

Let ABC represent a prism and DE an incident pencil of

white light. The refraction at the point E will of necessity be different for every ray of different colour in the pencil, and, therefore, every ray will pursue a different path through the prism; three such rays are shown in the figure EF, EG, and EH. All the rays are again refracted at the second face, and their paths become still more divergent, as shown for the three rays FI, GK, and HL. The different colours are thus all separated by the prism, and if they were received on a screen a band of colours would be produced, in which each colour would be placed according to its index of refraction; for example, the blue would appear at the end nearer the base of the prism, *i.e.* at L, while the red would appear at the other end, I, while the mean position would be occupied by green.

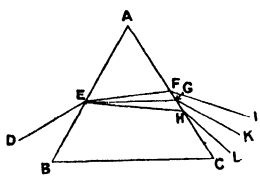


FIG. 5.

The indices of refraction for light of different colours have been measured for many media, and, in so far as they have any practical bearing on spectroscopy, will be discussed more fully in treating of prisms and lenses in Chapter III. A typical example of the indices for a glass with rays of different colours may be given to show the variations in their values—

	μ
Red light	1·612
Yellow light	1·615
Green light	1·619
Blue light	1·623
Violet light	1·631

Now, Newton, in his investigations on the spectrum, did not advance beyond the point indicated, in spite of the fact that he finally came to use a lens between the opening and the prism. It is evident that by this means he obtained better definition than before. On consideration it follows that, if purity of spectrum be desired, the most satisfactory source of illumination will be a narrow slit; for a slit will tend to eliminate all unequal overlapping of its coloured images, and, therefore, to improve

greatly the quality of the spectrum. Newton recognized this, and in his later experiments he replaced the round opening by a slit, but in spite of this he did not advance any further. The reason of this appears to lie in the fact that his prisms were of a very poor quality, with the result that the definition was far from satisfactory. Newton failed to notice that the light from the sun is not perfectly homogeneous, and it was Wollaston who first discovered this by observing the rays of sunlight admitted through a narrow slit in a window blind. Wollaston then noticed a number of black lines, which crossed the spectrum in a direction parallel to the slit. For some reason he did not investigate these lines further, and it was reserved for Fraunhofer, the celebrated optician of Munich, to study them thoroughly, and point out their immense importance—an investigation which laid the foundation-stone of the modern science of spectroscopy.

Fraunhofer first occupied himself in greatly improving the apparatus for studying the spectrum, for, instead of allowing the rays to pass directly through the prism and fall upon a screen, he interposed a convex lens between the slit and the prism, and thus projected the images of the slit on to the screen; he obtained in this way a well-defined spectrum, which showed the black lines very well marked. He also made use of a telescope to examine the spectrum visually, and was able in this way to investigate the phenomena of the black lines more thoroughly. By the use of different prisms and by varying the form of his apparatus, Fraunhofer was able to prove that the black lines have perfectly fixed positions in the solar spectrum, and he therefore concluded that the light which we receive from the sun, although it is to all intents and purposes white, does not give a complete spectrum, but is deficient in certain rays, and that these deficiencies are marked by black spaces in the spectrum. Although the actual meaning of the phenomenon was not known to Fraunhofer, he foresaw the great importances of the lines as landmarks, so to speak, by means of which it would be possible to make accurate measurements of the refrangibility of the different coloured rays. In his investigations, Fraunhofer mapped about

seven hundred of these lines, and labelled the eight chief and most decided of them by the letters of the alphabet, beginning in the red with A, and ending in the violet with H. At the present time these lines are still called the Fraunhofer lines, with the original letters attached, though the lettering has been very considerably extended beyond the limits of the spectrum which Fraunhofer investigated.

This constituted the first part of Fraunhofer's work; the second part was connected with an investigation into the possibilities of measurement of the actual length of the waves of light, in which he succeeded in developing the theory of interference of light so far as to invent and construct for himself the first grating, by means of which he made several measurements of the wave-length of the D line with a wonderful degree of accuracy. The method Fraunhofer used for measuring the wave-length of light by means of a grating is indeed the same as that of the present day; but before entering into a description thereof, it is advisable to consider the work which had been previously carried out on the diffraction and interference of light upon which the method is based.

It was first noticed by Grimaldi in 1665 that a ray of light as it passes by the edge of some opaque object suffers a certain amount of bending, or diffraction as he called it; in other words, the shadow cast by the sharp edge of an opaque body is not necessarily absolutely sharp. For example, when a beam of white light passes through a slit and is allowed to fall upon a screen, the image of the slit formed thereon is seen to be surrounded by coloured bands. Grimaldi also observed that, under certain conditions, when light is received upon a screen from two adjacent sources, darkness is produced, and he stated, though the meaning was not clear to him, that light added to light can produce darkness. Many years afterwards the subject was thoroughly worked out by Thomas Young and by Fresnel, the former of whom in 1801 published the famous principle of interference; these physicists showed that the Grimaldi experiment and many cognate phenomena can be very clearly explained by the wave theory of light. This theory, first developed by Huyghens in 1678, supposes that

light consists of transverse vibrations in an all-pervading medium, called the ether—that is to say, vibrations analogous to those of a stretched string, in contradistinction to sound waves, which are longitudinal. As an illustration, a single ray of light may well be compared to a series of waves passing along a stretched string of very great length, of which let a portion be represented by the curved line in Fig. 6.

The string in a state of rest would lie along the straight line AB, but when in a state of vibration—that is to say, under the influence of a system of waves passing along its length—it assumes some such shape as is shown by the curved line. The limits of the wave motion are evidently given by the line A′B′ on the upper side, and by A″B″ on the lower side. The direction of propagation of the waves is assumed to be in the direction of the arrow, *i.e.* from left to right. If now any one

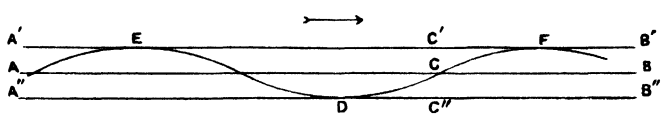


FIG. 6.

particle of the string be considered, it will be seen that, during the passing of the waves, it simply moves to and fro in straight lines between the limits given by A′B′ and A″B″. For instance, let us consider the particle C in the figure; evidently this will move to C″ as the bottom of the wave passes, and then travel to C′ when the top of the wave passes, and finally will return to C—this cycle representing its motions during the passage of a complete wave. Thus, a whole wave-length is represented by the length AC, and in speaking of a whole wave-length of light the complete length from A to C is meant. Every other particle of the string is executing exactly similar motions, though these are not necessarily in the same direction at the same time as those of the particle at C, as, for instance, the particles at D and E. The particle at A, however, performs exactly the same movements simultaneously with C, and in like manner the motions of the two particles at E and F are synchronous. Since both A and C, and E and F are

separated by one whole wave-length, it follows that particles one or more whole wave-lengths apart execute the same movements simultaneously; such particles are said to be in the same phase. Similarly, particles which are separated by one or any odd number of half wave-lengths, such as E and D, are said to be in opposite phase—that is to say, at any moment they are moving with the same velocity, but in opposite directions.

The case of light waves travelling through the ether is similar to the above; the ether particles, if we may so speak, separated by any even number of half wave-lengths, are always in the same phase, while those separated by any odd number of half wave-lengths are always in opposite phase.

We have yet, however, to take account of the undoubted, though small, bending or diffraction that a ray of light suffers as it passes an opaque object such as was first noticed by Grimaldi. Now Huyghens, in considering the means of propagation of light through the ether, laid it down as a general axiom that each ether particle in a state of vibration becomes the source of a new system of vibrations. At any given moment, therefore, every particle in the front surface of a wave acts as the source of a new system of waves, and the combined effect of these disturbances on the adjacent particles after unit time forms the new wave front. It was assumed by Huyghens that these secondary waves, as they may be called, act entirely in the direction of propagation of the main wave; this however is not strictly true, although a maximum effect is produced in the direction of propagation. On these theoretical considerations Grimaldi's diffraction and Young's interference experiments can be explained.

One of the experiments carried out by Young in extension of Grimaldi's original work was to cause the light from two closely adjacent sources to fall upon a screen, and he then found that when white light was used fringes of colour were produced, and alternating light and dark bands in the case of homogeneous light. The explanation of this phenomenon of what are called interference bands follows directly from the wave theory of light, as was shown by Young when the

combined effect of two rays coming from different directions on an ether particle is considered. If the two disturbances be equal in amplitude and reach the ether particle in the same phase, both will tend to move the particle in the same direction, and consequently its motion will be doubled and a quadrupling of the light at that spot will ensue. If, on the other hand, the two disturbances be in opposite phase, one will tend to move the particle in one direction, while the other will tend to move it in the opposite direction with an equal force; the result will be total extinction at that point. Such conditions are obtained in Fig. 7, where A and B are supposed to be two points emitting light of one colour and in the same phase; they must each, therefore, be considered to be a source of a system of waves which are continually expanding in every direction around them. At any given moment waves which started from A and B at the same instant must have travelled the same distance, and a small portion of each wave may be represented by the sets of circles X_1X_2 and Y_1Y_2, X_1X_2 having B and Y_1Y_2 having A as origin, for each set is described with B and A respectively as centres and with equal radii. Each set of circles may be taken to represent one whole wave, that is to say, the two thick circles in each case are one whole wave-length apart, and the two thin circles are a half wave-length distance from the two thick ones in each set. It follows, therefore, that the ether particles lying on all of the four thick circles are always in the same phase of vibration, and that the particles lying on the thin circles are in opposite phase to those on the four thick circles, but are in equal phase amongst themselves. The intersections of these circles mark the points where the ether particles come under the influence of disturbances from both A and B at the same instant; it is the effects produced at these points that must be considered.

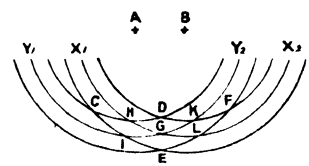


FIG. 7.

At the intersection of the four thick circles at the points C, D, E, and F, the ether particles are simultaneously

subjected to two equal disturbances at the same phase, and therefore a spot of quadruple brightness occurs at these places; the same is to be noticed at G, where the two thin circles intersect. At the points H, I, K, and L, on the other hand, where the thick and thin circles intersect, the ether particles come simultaneously under the influence of two equal disturbances at opposite phase, and therefore spots of total blackness are produced.

It is important to notice in connection with this phenomenon of the interference of light, as it was named by Young, that no loss of energy takes place; the light is distributed in maxima and minima, but the total quantity remains the same, that which is wanting in one place appears in another.

The actual experiment carried out by Young is satisfied by an exactly similar explanation to the above, because he used two sources of light placed very near together, which emitted light at equal phase. He arranged this by allowing a ray of sunlight from a hole in a shutter to illuminate a second screen which was perforated by two small holes very close together; where the images formed by these two holes overlapped upon a third screen, he obtained the interference bands. Now, these two small holes are directly comparable to the sources of light A and B in Fig. 7, for the light which passed through them both was supplied by the single hole in the first shutter, and was, therefore, evidently all of the same phase.

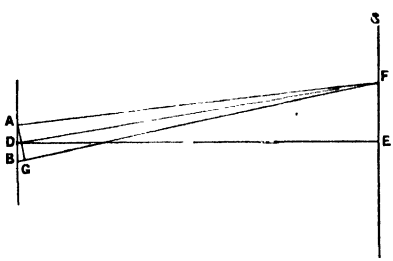


FIG. 8.

It is of importance to calculate the position of the light and dark bands obtained in this experiment of Young's, because it is possible to make rough measurements of the wave-length of light by its means. In Fig. 8 A and B are the two pinholes which are emitting homogeneous light at the same phase, and C is the screen on which the bands are formed. Let us

now consider the illumination of the screen C at any point, F; evidently the straight lines AF and BF will represent the paths of the rays of light arriving at F from A and B respectively. With centre F and radius FA the small arc AG is described from A to the line BF; the length BG, therefore, represents the difference in path travelled by the two rays BF and AF in their journey between the two screens; evidently the waves from the aperture B travel a greater distance than the waves from A, the difference in path being given by the length BG. If now BG is equal to any even number of half wave-lengths, it follows that the waves leaving A and B in the same phase arrive at F in the same phase, and therefore the illumination at F is quadrupled. If, on the other hand, BG be equal to any odd number of half wave-lengths, the waves will arrive at F in opposite phase, and total extinction will occur. The same holds good on the other side of the centre E, and since, of course, E itself marks the position of a bright band, the effect is produced of a central bright band surrounded by alternate minima and maxima of brightness, the minima occurring when BG equals 1, 3, 5, etc., half wave-lengths, and the maxima when BG equals 2, 4, 6, etc., half wave-lengths.

It is possible by means of this experiment to make a rough determination of the wave-length of the light, since we can calculate the value of BG by means of measurements which are quite simply obtained. In Fig. 8 the points F and D are joined by a straight line; then, since the arc AG is very small, it may be considered as a straight line at right angles to DF, and further, since AB is perpendicular to DE, it follows that the angle BAG is equal to the angle FDE—

Therefore $$\frac{BG}{AB} = \frac{FE}{FD}, \text{ and } BG = \frac{FE \times AB}{FD}.$$

Now, in an actual experiment the length FE is very small compared with the distance between the screens, and therefore FD is very little longer than DE, so that we may substitute DE for FD in the above equation without introducing any appreciable error. We have, therefore—

$$BG = \frac{FE \times AB}{DE}.$$

The distances FE, AB, and DE can easily be measured, and thus the length BG can very simply be obtained. It must be remembered that, when F is taken as the centre of a bright band, BG is equal to some even number of half wave-lengths, two if the first bright band be measured, four with the second, and so on; and similarly, when F is taken as the centre of a dark band, BG is equal to some odd number of half wave-lengths, one in the case of the first band, three in the case of the second, and so on.

By an extension of this principle of interference the phenomenon can be explained which was first observed by Grimaldi, and called by him diffraction of light, namely, the appearance of coloured bands round the shadow cast under certain conditions by an opaque object. The true explanation

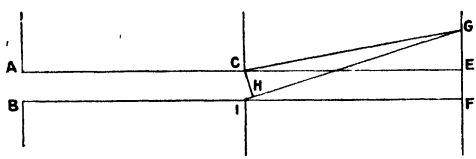


FIG. 9.

of this phenomenon is due to Fresnel, who thoroughly investigated the subject, and showed that all the observations could be accounted for by Huyghens's principle and Young's theory of interference. The most satisfactory results are obtained when a beam of light from a narrow slit is allowed to pass through a second slit parallel to the first and then to fall on to a screen; on each side of the central image and parallel to it well-developed fringes are to be seen, which consist of coloured bands when white light is used, and of alternate bright and dark bands when the light is homogeneous. The explanation of these fringes follows very clearly from what has gone before, as may be seen from Fig. 9, which is a diagrammatic representation of the experiment.

AB and CI are the two parallel slits, and EF the central image, formed on the third screen by the beam of light passing directly through the two slits. By the use of the two slits we

are enabled to ensure that all the waves of light leaving CI for the third screen are in the same phase, that is to say, that all the ether particles lying between C and I are in the same phase of vibration; let us now for the present assume that the experiment is made with light consisting entirely of rays of the same wave-length. It follows from Huyghens's theory of the propagation of light that the ether particles lying between C and I become sources of disturbances, which, although their maximum effect is in the direction of propagation of the light, *i.e.* towards EF, yet proceed also in every direction on each side of the central beam. The third screen, therefore, becomes illuminated on either side of the central image; a certain amount of interference, however, takes place amongst these rays, an amount which varies at different points. The central image EF is necessarily very bright for two reasons, the first because the maximum effect of the vibrations of the ether particles between C and I tends directly towards EF, and the second because a minimum of interference occurs at this place. In order to deal with the illumination on each side of the central image let us consider that produced at some point, G, on the screen. The straight lines GC and GI are drawn, and these will evidently include all the rays which arrive at G; it is with the mutual interference of these rays that we are concerned. If with centre G and radius GC the arc CH be drawn, the distance IH will represent the difference in path travelled by the two outside rays IG and CG in their journey to G. When this length IH is equal to any odd number of half wave-lengths, the two outside rays of the pencil arrive at G in opposite phase and neutralise one another; the next pair also interfere with one another, but not entirely, since they do not arrive at G in exactly opposite phase; the next pair again interfere still less, and so on until the ray in the centre is not interfered with at all. Under these circumstances the total amount of interference at G is the least possible, and G therefore marks the position of a bright band. When, however, IH is equal to any even number of half wave-lengths, and the two outside rays arrive at G in equal phase, then there must meet at G an equal number of rays at opposite phase; evidently the

two halves of the pencil will neutralise one another, and in this case G will mark the centre of a dark band. When, therefore, homogeneous light is used there occur on each side of the central image a series of dark and bright bands whose positions depend upon IH being equal to any even and odd number of half wave-lengths respectively. A very rough measurement of the wave-length of the light is also practicable with this experiment in a similar way to that shown before with Young's interference experiment with two adjacent pin-holes.

If white light had been used in the above instead of homogeneous light, coloured bands would have been obtained in place of the alternate bright and dark bands; the explanation of these follows on exactly the same lines as that given for homogeneous light. The point G has already been shown to mark the centre of a bright band when IH equals an odd number of half wave-lengths, and thus, if the light emanating from the ether particles between C and I be a mixture of disturbances of many different wave-lengths, there will be of necessity many positions of G at which the light is brightest—a different one for every ray of different wave-length. Instead of a bright band of one colour, as in the case of homogeneous light, a row of very closely situated maxima of different colours will be obtained, *i.e.* a spectrum, in which the colours are placed according to their wave-lengths. Since violet light has the shortest wave-length this colour will appear on that side of each band which is nearer the central image, and the red, which has the longest wave-length, will appear on the outer side or that which is further from the central image. In place of the bright and dark bands which are obtained with homogeneous light, series of spectra are now observed with their violet ends turned towards the central image; and of these spectra the first satisfies the condition that IH is equal to one half wave-length, the second the condition that IH is equal to three half wave-lengths, and so on. These spectra decrease in brightness the further they are from the central image, owing to the fact that the effect of the disturbances due to the ether particle between C and I is a maximum in the direction of propagation,

and decreases rapidly when the angular distance from this is increased.

In connection with the use of the two terms "diffraction" and "interference," it is important to notice the difference between them; interference is used in reference to those cases in which the mutual action of two or more direct pencils of light is concerned, while the term diffraction is only applied to the case when an actual bending of the rays occurs, and Fresnel's extension of Huyghens's axiom is made use of in the proof of the resulting phenomena.

The application of diffraction methods to the study of spectra was made by Fraunhofer, who so far developed them that he was able by their means to make accurate measurements of the wave-length of light. Fraunhofer conceived the

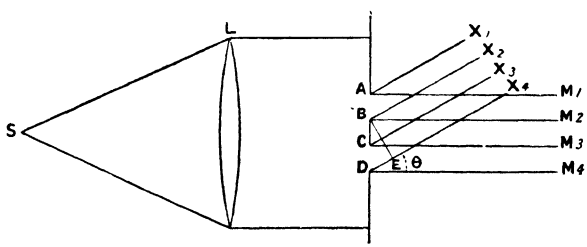


FIG. 10.

idea of using in place of the single slit, as was dealt with in the last case, a number of such apertures placed at an equal distance apart. He collected all the diffracted rays from these apertures with a convex lens, and examined the spectra produced at the focus of this lens. This series of equal and equidistant apertures is called a grating, and it is interesting to note that in devising this apparatus Fraunhofer invented the method of determining wave-lengths by gratings as used at the present time.

A diagram of the apparatus is shown in Fig. 10. Only two of the apertures AB and CD have been drawn, which are sufficient to explain the theory, and L is a convex lens called the collimator, which is used to throw a parallel beam of light from S upon the grating; S is a slit placed parallel to the

grating apertures and illuminated from some outside source. The lens used for collecting and bringing to a focus the rays which pass through the grating apertures is not shown on the diagram, there being no need for it as far as the theory is concerned, because it in no way alters the phase of vibration of the waves.

Now the ether particles lying in the apertures AB and CD become sources of vibrations which proceed chiefly in the line of propagation towards M_1, M_2, M_3, and M_4, but also in other directions, for example, towards X_1, X_2, X_3, and X_4. When these rays are brought to a focus by means of the convex lens, evidently those travelling towards M_1, etc., will produce a bright image of the slit S without any mutual interference taking place, but the case is different with the diffracted rays X_1, etc. In order to investigate the conditions of mutual interference among the latter, the straight line BE is drawn perpendicular to DX_4, when the length DE will represent the difference in path travelled by the two outside rays DX_4 and BX_2, and also by the two outside rays CX_3 and AX_1, and therefore also the difference in path travelled by every pair of corresponding rays in the two pencils. If now DE is equal to any odd number of half wave-lengths, it follows that for every ray in one pencil there is a corresponding ray in the other pencil at opposite phase, and therefore total interference takes place when the rays are combined at the focus of the lens. The same manifestly holds good for every adjacent pair of apertures of the grating.

Again, if DE be equal to any even number of half wave-lengths, then the reverse will be the case, for every corresponding ray in the two pencils will be at equal phase, and therefore the rays from these two apertures and every adjacent pair will combine at the focus of the lens to give a bright image of the slit.

It is, of course, very possible that DE be not equal to either an odd or even number of half wave-lengths; in such a case interference takes place, not between the diffracted rays from adjacent apertures, but between those from apertures which are some way apart. For example, let us suppose DE to be equal to one-hundredth of a wave-length, then the rays from the first

and fifty-first apertures mutually interfere, similarly those from the second and fifty-second, and so on. It can therefore readily be understood from this that, provided there be sufficient apertures, complete interference always takes place except when DE is equal to an even number of half wave-lengths.

In the case of complex light, which consists of waves of many different lengths, there are just as many values of DE, with which a bright image of the slit is produced, and, as each of these has a different colour, a spectrum is produced in which each colour is distributed strictly according to its wave-length. We have, therefore, produced on each side of the central image a first spectrum, which corresponds to the condition that DE is equal to two half wave-lengths; and then, outside of this first

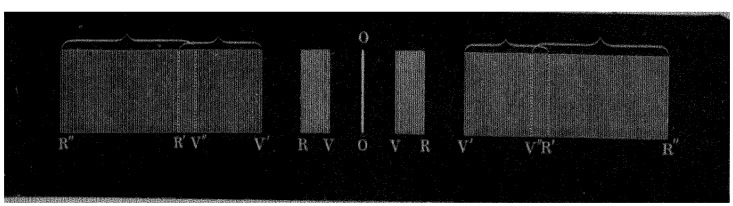


FIG. 11.

spectrum, a second, which corresponds to the condition that DE is equal to four half wave-lengths; and again, outside this, a third, and so on. These spectra are called respectively those of the first, second, third, etc., orders, these being the names which were given by Fraunhofer.

The appearance of the spectra as obtained with a grating is shown in Fig. 11, in which O represents the undiffracted central image.

It often happens that the different orders overlap one another, as is shown in the figure in the case of the second and third orders.

Now, although the length DE in Fig. 10 cannot be measured, it may be very simply arrived at from measurements which are very easily carried out.

In the triangle BDE—

the ratio $\frac{DE}{BD} = \cos BDE = \sin \theta$, where θ is the angle X_4DM_4, or, as it is called, the angle of diffraction.

It follows, therefore, that—

$$DE = \sin \theta \times BD.$$

Now BD is the width of an aperture of the grating *plus* the adjacent dark space; it is called the grating space, and is usually denoted by the letter *b*. We have thus obtained the result that the wave-length of a ray of light is equal to the product of the grating space and the sine of the angle of diffraction; the wave-length of an unknown ray may be found, therefore, by measuring the angle of diffraction obtained with a grating, and by multiplying the sine of this angle by the width of the grating space.

This, however, is only true for the two spectra of the first order, and if it is to hold good for all the orders it must have a more general form. If the wave-length is denoted by λ we may write—

$$n\lambda = b \sin \theta_n,$$

when n stands for the number of the order and θ_n for the angle of diffraction for the nth order.

This development of the theory of diffraction, and its application as a practical means of measuring the wave-length of light, Fraunhofer published in 1821 in a paper he read before the Munich Academy of Sciences. He made his first gratings by winding silver wire round a brass frame, taking great care, of course, to preserve the grating spaces thus produced quite regular for the whole distance. The wires he used in different cases varied in thickness from 0·04 mm. to 0·6 mm., and the grating spaces varied correspondingly from 0·6866 mm. to 0·0528 mm. Fraunhofer made measurements of the black lines in the solar spectrum which he had labelled B, C, D, E, F, G, and H, and the ten values he obtained of the wave-length of the D line with ten different wire gratings were extraordinarily accurate, if we consider that, owing to the large size of his grating spaces, the angles of diffraction were of the

order of one minute of arc. The actual values he obtained were as follows:—

0·0095891 mm.	0·0005888 mm.
0·0005894 „	0·0005885 „
0·0005891 „	0·9005885 „
0·0005897 „	0·0005882 „
0·0005885 „	0·0005882 „

Soon after this Fraunhofer succeeded in making gratings by ruling equidistant and parallel straight lines on flat glass plates; he made two such instruments with grating spaces equal to 0·0033 mm. and 0·016 mm. respectively, and with these found the wave-length of the D line to be 0·0005886 mm. and 0·0005890 mm. The value of this constant as adopted at the present time is 0·0005893 mm.

The importance of Fraunhofer's work cannot be over-estimated; on the one hand, by his investigation of the black lines of the solar spectrum he first showed the possibility of making accurate measurements of the relative dispersive powers of substances, from an ignorance of which Newton failed in making refracting telescopes; on the other hand, by his work on diffraction he founded a method of making absolute measurements of the wave-length of light.

The actual physical significance of the black lines in the spectrum of sunlight was, of course, unknown to Fraunhofer, and it was only by slow steps that any advance was made towards their explanation, which was discovered about thirty-five years later. It had long been known that when certain metallic salts were fed into a flame, such as that of a spirit-lamp, different colours were produced, and in 1822 Sir John Herschel observed that, if such flames were examined through a prism, the light was resolved into single rays, and that bright lines were visible on a dark ground, that is to say, discontinuous spectra were obtained. This fact was also known to Fraunhofer, who further noticed that the yellow spectrum line obtained from the light of the flame of a spirit-lamp fed with common salt was identical in position with the D line of the solar spectrum; he also observed that the line in both these

cases consists of a close pair of lines of equal intensity. It is difficult to decide as to who first made the discovery of the true connection between the bright spectrum lines obtained from metallic salts in a spirit-flame and the Fraunhofer lines, but certainly in 1848 Foucault showed that, if the very powerful light from the electric arc were passed through a flame tinted yellow by a sodium salt, and then examined in a spectroscope, black lines appeared in the spectrum in the identical positions of the D lines. This important result was, however, apparently unnoticed until the whole matter was investigated and completely explained by Kirchhoff in 1859, who, in papers read before the Berlin Academy of Sciences, gave a mathematical deduction and experimental proof of the great law which is known under his name. This law stands as follows:—The relation between the powers of emission and the powers of absorption for rays of the same wave-length is constant for all bodies at the same temperature.

This law of Kirchhoff's thus expresses the following facts. First, a substance when excited by some means or other possesses a certain power of emission; it tends to emit definite rays, whose wave-lengths depend upon the nature of the substance and upon the temperature. Second, the substance exerts a definite absorptive power, which is a maximum for the rays it tends to emit. Third, the ratio between this emissive and absorptive power is constant for all substances at the same temperature. We must imagine, therefore, that the particles of a substance when excited vibrate in certain definite ways which are a function of their chemical nature, and that these vibrations give rise to waves in the ether; the converse of this follows naturally, that the molecules respond readily to these vibrations, and absorb them in the same way as the strings of a piano, for example, respond to and absorb sound waves produced by some other musical instrument in the neighbourhood.

Attention may be drawn to an interesting and important result that follows from Kirchhoff's law. Since the ratio between the powers of absorption and emission is a constant, it is evident that the greater the opacity of a body the more

complete its spectrum, and conversely, the greater the transparency of a body the less complete its spectrum. A lump of metal, for example, when heated to a high temperature must give a continuous spectrum, while, on the other hand, a transparent body cannot be made to incandesce. In order to obtain the true emission spectrum of a substance it must be dealt with in the state of gas.

Kirchhoff was enabled to form a theory of the constitution of the sun based on his knowledge of the origin of the black lines in the solar spectrum. He conceived the idea that the sun is surrounded by a layer of vapours of many substances, which act as filters, so to speak, of the pure white light arising from the incandescence of the interior body of the sun, and abstract therefrom those rays which correspond in their periods of vibration to those of the component molecules of the vapours. This layer is called the reversing layer, because Kirchhoff gave the name reversal to the process of absorption which gives black lines in the spectrum of a substance in place of the bright lines obtained in the emission spectrum. The Fraunhofer lines thus become of extreme importance inasmuch as they form a source of information as to the actual composition of the sun, the existence of an element in the sun being proved by the coincidence of the lines of its emission spectrum with lines in the solar spectrum.

As a natural result of Kirchhoff's discovery a great impetus was given to spectroscopic work, and attention was at once turned to the examination and mapping of the emission spectra of terrestrial substances with the view both of putting these on record and of testing their presence or absence in the solar atmosphere. Bunsen and Kirchhoff stand foremost, with a long investigation into the spectra of many substances; they succeeded also in obtaining reversals of a number of the lines, and in establishing the presence of many elements in the sun. They drew maps of the spectra they observed, which for some time were used as standards of reference, but unfortunately all the results were expressed upon a purely arbitrary scale. The whole spectrum was divided up into a number of equal divisions, which were numbered, and the positions were noted

which the observed lines bore as regards this scale. Kirchhoff also used a similar scale in his work on the spectrum of the sun, and thus the whole of his and Bunsen's individual and joint work was expressed in meaningless units.

Inasmuch as Bunsen and Kirchhoff had proved the existence of many terrestrial elements in the sun, it was a natural consequence that the solar spectrum itself should come to be the standard of reference. The sun possesses a further advantage as a standard, in that the Fraunhofer lines are very fine and sharply defined, so that very accurate determinations of their position are possible.[1] The measurement and mapping of the solar spectrum was carried out by A. J. Ångström, who, following Fraunhofer's lead, measured the wave-lengths of an extremely large number of the lines, and made a map of the spectrum, in which each line was placed according to its wave-length. This map was called by Ångström the Normal Solar Spectrum, and was published in 1868. This great research was carried out with the help of three gratings, which had been ruled on glass by Nobert, every care being taken to render the results as accurate as possible. The measurements covered the region between A and H, that is to say, all the visible spectrum, and the wave-lengths were expressed in ten-millionths of a millimetre, and carried to two places of decimals. This unit of length has been used ever since in wave-length determinations under the name of the Ångström unit.[2]

Now Ångström measured the three gratings by means of a dividing engine, and thus determined for himself the width of the grating space by comparison with the standard metre at Upsala. Unfortunately, however, the length of this standard metre had been wrongly determined by Tresca, who had

[1] There are certain objections to the adoption of the solar spectrum as the standard of reference, which are discussed below, *vide* p. 239.

[2] The unit of length, the ten-millionth of a millimetre, equals 1×10^{-10} metre, and is often called, as suggested by Johnstone Stoney, a tenth-metre. Frequently, also, wave-lengths are expressed in thousandths of a millimetre (μ), or millionths of a millimetre ($\mu\mu$). The wave-length of the D_1 line, for example, may be expressed as follows :—

$\lambda = 0{\cdot}589616\ \mu$, or $589{\cdot}616\ \mu\mu$, or 5896·616 A.U. or t.m., or $5{\cdot}89616 \times 10^{-5}$ c.m.

compared it with the one at Paris on behalf of Ångström, with the result that all the wave-length measurements were a little too small. The actual length of the Upsala metre was afterwards found by Lindhagen to be 999·94 mm. instead of 999·81 mm., which was the value used by Ångström.

Ångström, on discovering the error, deputed his pupil Thalén to correct all the measurements, he himself being too old—indeed, he died before the corrections were finished. In addition to the complete recalculation of Ångström's values, Thalén extended the work by determining the wave-lengths of the spark spectra of all the metals then known (44) by means of a prism spectroscope, directly referring the values to Ångström's normal map.

The publication of Ångström's map marks a definite stage in the development of spectroscopy; for the first time a standard of reference, placed upon a physical basis, was put upon record. The determination of wave-lengths of lines in unknown spectra was now made possible by a direct comparison between the unknown spectrum and that of the sun, and the calculation of the unknown wave-lengths by a simple process of interpolation between those of the lines in Ångström's map. An additional most important consequence was that the results of different experimenters were referred to the same standard and brought into line, so that they could be collated and compared amongst themselves.

CHAPTER II

HISTORICAL—*continued*

In the last chapter none of the work was taken into consideration which has been carried out by various experimenters upon the extreme ends of the spectrum. As is well known at the present time, the visible portion by no means represents the whole spectrum, as it extends in both directions far beyond the regions which can be reached with the eye. Recent discoveries go to prove that there can exist in the ether waves varying in length from several hundred metres down to a limit so small as to be beyond the powers of measurement of our present apparatus. Light is composed of waves of intermediate lengths which form a very small fraction of the whole. The visible spectrum extends from about 7600 to 3900 Ångström units (0·00076 mm.—0·00039 mm.), but by various means emission spectra have been traced between the limits 3,140,000 and 1030 Ångström units. The history of the discovery and early investigation of these invisible regions is extremely interesting.

It is noteworthy that a fact pointed out by the chemist Scheele in 1777 was the origin of the discovery of the invisible portion beyond the violet. He knew that the salt silver chloride possesses the property of changing from white to purple when exposed to sunlight, and on investigating the effect of the different colours of the spectrum he found that the greatest effect was produced when the silver chloride was exposed to the extreme violet end. Scheele found in this way that the activity of the rays of the spectrum increased towards the violet end.

The actual discoverer of an invisible spectrum was Sir William Herschel in 1800, who was making some experiments

upon the different colours of the spectrum with a view of finding which had the least heating power, as he wished to obtain the most suitable colour for sun glasses to use with his telescope. Herschel caused a beam of sunlight to pass through a prism, and then tested the heating power of each colour upon the bulb of a delicate thermometer; he found that the maximum effect was obtained in the region beyond the visible limit of the red.

In 1840 Sir John Herschel continued the investigation of the subject, and succeeded in proving the fact that the spectrum actually extended beyond the visible limit, and that the Fraunhofer lines were continued into this region. His method of proving this was one of great ingenuity. He painted a sheet of paper with gum and lampblack so as to make it readily absorptive of heat; this paper was then dipped into alcohol and exposed to the sun's spectrum. Had the invisible portion been quite continuous, the alcohol, being so volatile a liquid, would have entirely evaporated, leaving a dry strip where the invisible spectrum had been projected on to the paper. This, however, Herschel found not to be the case, for only partial drying took place, and three or four damp patches were left which marked the presence of absorption bands in the invisible region. The investigation was taken up more fully soon afterwards by many experimenters, and the spectrum was proved to extend far beyond the limit of visibility in the red, and to contain many of the Fraunhofer absorption lines. This portion of the invisible spectrum, which is called the infra-red, consists of the rays of longer wave-lengths which evidence themselves as radiant heat, and, therefore may be readily examined by means of a thermopile, and most of the investigations have been carried out with the help of such apparatus. These apparatus improved in delicacy as time went on, and the emission spectra were found to extend a very great distance in this direction. Amongst other important work upon this part of the spectrum may be mentioned that of Langley in America, who made use of an exceedingly delicate electrical resistance thermometer, which he called a bolometer, and made investigations chiefly into the infra-red portion of

the solar spectrum. Very important researches have also been carried out by Paschen and by Rubens, a full account of whose methods will be given in Chapter VIII. It is interesting to note that photographic plates have been made which are sensitive to these heat rays, and Abney and others have succeeded in obtaining photographic records which extend very far into this region.

As was natural after Sir William Herschel's discovery of the infra-red spectrum, it was soon asked whether or no there existed a similar extension beyond the violet, and in 1803 Inglefield drew attention to Scheele's observations on silver chloride, and thought in consequence that such an extension did exist. The first actual demonstration, however, of there being an ultra-violet region was made by Ritter and by Wollaston, who showed that the blackening of the silver chloride took place quite readily in the regions of the spectrum beyond the visible limit in the violet. In 1842 E. Becquerel succeeded in proving the presence of the Fraunhofer absorption lines in this region of the solar spectrum, by projecting it on to strips of paper which were coated with silver chloride; in this way he photographed it, and detected the presence of a long ultra-violet region which contained many Fraunhofer lines. These he labelled, following Fraunhofer's lead, with the letters L to P, which meant the extension of the spectrum to the limit of about $\lambda = 3400$ Ångström units. This ultra-violet region can best be examined by photographic methods, because the rays of shorter wave-length which compose it happen to be active towards silver salts, and, therefore, investigations in this direction are more easily carried out than those into the infra-red. Glass, however, readily absorbs these rays when they are of shorter wave-length than about 3300 Ångström units, and therefore more transparent substances must be made use of for lenses and prisms. Stokes has shown that quartz and Iceland spar are very transparent to these rays of short wave-length; quartz being the better of the two, because Iceland spar absorbs all waves of lengths shorter than 2150 units. With an apparatus fitted with quartz lenses and prisms it is perfectly easy to reach as far as $\lambda = 1900$ A.U., provided that

the rays have not far to travel through the air, as it has been found that moderately thick layers of air exert a powerful absorption upon these rays. In order to investigate the region beyond the limit of $\lambda = 1850$ A.U. it is necessary to substitute fluorite for quartz in the case of the lenses and prisms, to exhaust all air from the apparatus, and to use a specially prepared photographic plate containing no gelatine. This has been done by Schumann, who succeeded in reaching an estimated limit of 1200 tenth-metres. (An account of this work will be found in Chapter VIII.)

In the case of the infra-red spectrum, also, it has been found that glass readily absorbs the rays of longer wave-lengths, and it is necessary to use lenses and prisms of fluorite, rock-salt, or sylvin for work in this region.

The extension of Ångström's Normal Map of the solar spectrum and the mapping of the ultra-violet region was carried out by Cornu, and was published in part in 1874, and the remainder in 1880. Cornu, of course, used photographic methods, and obtained his spectrum with gratings ruled by Nobert, similar to those used by Ångstrom.

The stage in the development of spectroscopy reached at the time of the appearance of Ångstrom's normal solar spectrum marks its birth as an exact physical science. More and more experimenters entered this field of research, and advances were made in every direction. It is, however, only possible in this short introduction to discuss the work directly leading to the establishment of the standards of reference. With the growth of the science during the next quarter of a century we cannot deal; we must leave it here and take up the thread again at the time when Ångström's map was superseded. This was first done by Rowland, who published a complete normal photographic map of the solar spectrum, based upon a new invention he made in connection with the ruling and mounting of gratings. This map was about 20 metres long, and had a scale of wave-lengths attached, the maximum error in any part being estimated to be under 0·01 of an Ångström unit. The measurements were entirely based upon a new determination of the absolute wave-lengths of one of the D lines which had been

carried out previously by Bell and others. This value is rather greater than that determined by Ångström and corrected by Thalén, and therefore the wave-lengths on Rowland's scale were generally greater than on that of Ångström. The difference, however, was not constant, and varied from about 0·5 to about 1·8 A.U. in different parts of the spectrum. By common consent, in view of the accuracy of Rowland's method and work, his scale was universally adopted as the standard of reference.

In the first chapter the theory of gratings was discussed only as far as it had been carried by Fraunhofer; the simplest case was then given, namely, that of a transmission grating receiving light normal to its ruled surface. In this simple case it was shown that if λ stands for wave-length, b for the grating space, and θ_n for the angle of diffraction corresponding to the order of spectrum n, the relation holds good that—

$$n\lambda = b \sin \theta_n.$$

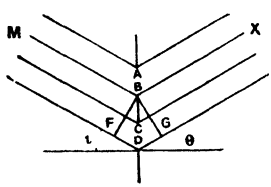


FIG. 12.

Now, a great advance in ruling gratings was made by Rutherfurd of New York, who first ruled glass gratings, and by afterwards silvering them obtained reflection gratings, *i.e.* gratings which give their spectra by reflected light. He finally succeeded in producing very fine reflection gratings by ruling a polished plane metal surface, which in reality presents an easier surface to rule than glass, as it is not so hard, and therefore the ruling diamond is not so much worn. The theory of the production of the spectra with a reflecting grating follows directly from that already given in Chapter I., the source of light acting as if it came from behind the grating and made some finite angle with the normal. The latter case, that of a transmission grating receiving an oblique beam of light, is shown in Fig. 12.

As before, in Fig. 10 (p. 21), only two grating apertures are drawn, AB and CD, these being sufficient for the present purpose. A parallel beam of light falls obliquely on to the grating from M, making the angle of incidence i with the

normal; a great portion of the light passes directly through the apertures, while a portion is diffracted in the direction of X, these rays making an angle of diffraction θ with the normal. If now the perpendiculars BF and BG be drawn, it will be seen that the difference in path travelled by the corresponding rays in each pencil, or the retardation as it is called, is given by the sum of the lengths FD and DG, and therefore when these two lengths together are equal to some number of whole wave-lengths no interference takes place, and a bright image is produced when the diffracted rays are brought to a focus. Now, FD can be shown to be equal to BD sin i, and DG to be equal to BD sin θ,

and therefore $\lambda = \text{BD}(\sin i + \sin \theta)$,
or more generally $n\lambda = b(\sin i + \sin \theta_n)$.

In all cases where the light falls obliquely on the grating a certain amount of retardation is dependent on the angle of incidence as well as on the angle of diffraction.

Exactly parallel is the case of a reflecting grating, as can be seen from Fig. 13.

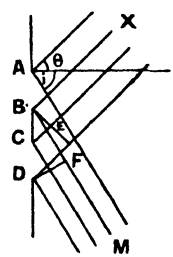


FIG. 13.

A beam of light falls obliquely on the grating, making an angle of incidence i with the normal, and a portion is diffracted towards X, the angle of diffraction being θ. The perpendiculars BE and DF are drawn, and as before the lengths DE and BF represent the retardations. Now, the ray MB is retarded on the corresponding ray MD by an amount equal to the length BF, but, on the other hand, the ray DX is retarded on the ray BX by an amount equal to DE, and therefore the total retardation is equal to BF − DE;

but $\text{BF} = b \sin i$,
and $\text{DE} = b \sin \theta$;
therefore the total retardation $= b(\sin i - \sin \theta)$.

When this value is equal to one or more whole wave-lengths a bright image is seen, and therefore we have the general equation—

$$n\lambda = b(\sin i - \sin \theta_n).$$

If the diffracted rays are on the other side of the normal, that is to say, the same side as the incident rays, then clearly the two retardations are additive, and thus we have the general equation for all the spectra—

$$n\lambda = b(\sin i \pm \sin \theta_n),$$

the positive or negative sign being used when the incident and diffracted rays are on the same or opposite sides of the normal respectively.

Rowland was led to his work on gratings by finding in his search for a source of monochromatic illumination that a good grating was a necessity. He at once recognized that the key to a good grating lies in a perfect screw, and hence he set to work to make one. This he succeeded in doing, and was able thereby to make a dividing engine for ruling gratings far more accurately than had ever been done before.

The screw is first of all cut with the desired pitch and rather longer than is required, a nut several inches long is also cut, with a female screw of the same pitch so as accurately to fit the male screw. This nut is made in four sections, which are clamped together on the male screw. This clamped nut is then worked backwards and forwards along the whole length of the male screw for a very long time, and in this way all the errors are averaged down until they are evenly distributed over the whole length. The nut, of course, requires continually to be tightened during the process to take up the wear, and the temperature must be carefully kept constant. In this way extremely accurate screws can be cut, and indeed all screws for fine micrometers and such apparatus are now made by this method. When he had obtained a screw sufficiently accurate for his purpose, Rowland constructed a grating ruling machine, and succeeded in making gratings far finer than any that had previously been prepared. He has been able to produce gratings with a ruling of 100,000 lines to the inch, though the closeness of the ruling renders such gratings too troublesome to prepare for ordinary purposes.

The principle involved in the ruling of a grating is the drawing of a fine diamond edge across the polished surface of

glass or speculum metal in one direction only. The ruling carriage carrying the diamond point is moved between each stroke a definite amount in a direction at right angles to the stroke. This movement is effected by means of a micrometer screw, and of course it will be evident that the degree of perfection of the grating will depend upon the accuracy of this screw. The machine is driven by clockwork, it being so arranged that when once started a whole grating can be ruled without any attention. This is of great importance, because it will be readily understood that the process of ruling a whole grating, which in the case of the large size takes six days and nights, must be carried out at a constant temperature so as to guard against any expansion or contraction of the surface that is to be ruled. One of the difficulties which frequently occurs in the wearing out of the diamond point, since if any essential change takes place in the shape of the diamond edge the grating will be ruined. It will be readily understood that the successful ruling of a grating is a very delicate operation. It has now been found possible to produce replica gratings either by photography or by making celluloid casts from a ruled grating. For an account of these see p. 208.

In 1881 Rowland conceived the idea of ruling gratings on a spherical mirror of speculum metal. In the previous examples in dealing with the spectra produced by gratings the use of lenses has been assumed for bringing the diffracted rays to a focus, but with a concave grating these are dispensed with, because the grating itself, being ruled on a spherical mirror, focuses the rays and produces the spectra. The mathematical properties of the concave grating Rowland has completely investigated, and the instrument has proved to be one of the greatest inventions ever made in spectroscopy. The methods of mounting the instrument and of working with it will be fully given in Chapter VII., but to a certain degree they must be described at this point in order to explain by what means Rowland arrived at the determinations of his solar standard.

The most important property of this grating, shown by Rowland, is that if the source of light, *i.e.* the slit, and the

grating, be placed on the circumference of the circle which has the radius of curvature of the grating as diameter, the spectra will always be brought to a focus on this circle. For example, let AB in Fig. 14 be the radius of curvature of the grating CD; the circle AFBG is drawn with radius $\frac{AB}{2}$, that is, with E as centre. Then if the slit be placed on the circumference of this circle, for example at F, the spectra will be formed round the circumference, so that if an eyepiece be placed at G the spectra will be seen in perfect focus, and may be examined by moving the eyepiece round the circle.

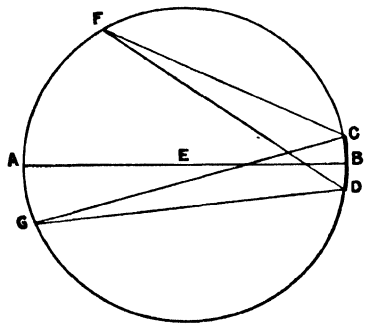


FIG. 14.

Furthermore, Rowland showed that great advantages accrue if observations are made on the spectrum normal to the grating. In the equation deducted on p. 36, we have

$$\lambda = b(\sin i \pm \sin \theta),$$

and therefore when the spectrum is observed directly normal to the grating—

$$\lambda = b \sin i, \text{ because } \theta = 0.$$

If now the eyepiece be moved a very small distance to one side of the normal, then—

$$\lambda + C = b \sin i \pm b \sin \theta,$$

where C is the small change in wave-length observed, and θ is the angular distance through which the eyepiece has been moved. It follows that C is proportional to $b \sin \theta$, and therefore to θ itself, because b is a constant and the sines of small angles are proportional to the angles themselves. But the angle θ is proportional to the linear distance through which the eyepiece

was moved, and therefore it follows that the linear distance through which the eyepiece moves is proportional to the change in wave-length observed, or, in other words, for small distances on each side of the normal the spectrum is itself normal. This fact, which is true, of course, for every grating both flat and concave, is most important, resulting as it does in the observation of truly normal spectra, for in the mounting adopted by Rowland for his concave grating the eyepiece of photographic plate is automatically kept in a position normal to the grating.

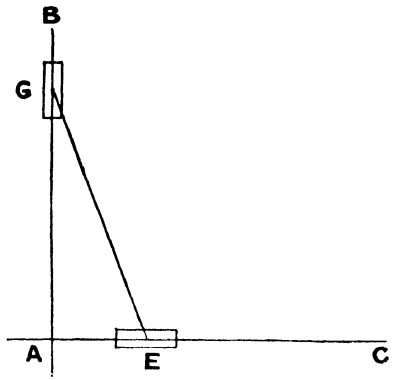


FIG. 15.

AB and AC in Fig. 15 are two girders rigidly fastened to supports, and they carry rails which are accurately adjusted at right angles to one another. On each of these rails runs a carriage, G and E, these two carriages being joined by a beam, GE. This beam is fitted to the carriage in each case by a vertical bearing so as to allow the carriages to move along their rails. The slit is then set up over the intersection of the rails at A, the grating at G, and the eyepiece or photographic plate at E. Under these circumstances it is evident that wherever the grating and eyepiece may be placed, the circle having GE as diameter always passes through the three points G, A, and E.

Furthermore, in order that normal spectra may be always observed, the grating is placed normal to the direction GE, and therefore, by construction, E is made to coincide with the centre of curvature of the grating. When a photographic plate is employed in place of the eyepiece at E, it is necessary that it be bent to fit the circular focal curve, when it becomes possible to photograph a considerable portion of the spectrum normal.

Rowland pointed out that a second very valuable property also results from the above mounting of the grating, and on this can be based the method of relative wave-length determination. In Rowland's special case, as above, the equation of wave-length is simplified to—

$$n\lambda = b \sin i,$$

when observations are made normal to the grating.

It follows, therefore, that for one particular position of the slit—

$\lambda' = b \sin i$ in the first order
$2\lambda'' = b \sin i$,, second order
$3\lambda''' = b \sin i$,, third ,, and so on,

where λ', λ'', λ''', etc., are the wave-lengths in the first, second, and third, etc., orders.

We have therefore—

$$\lambda' = 2\lambda'' = 3\lambda''', \text{ etc.}$$

and thus, at any position of the slit, the various orders of spectra are superposed, and the wave-lengths of each are inversely proportional to the number of the order. For example, on a wave-length of 9000 Ångström units in the first order are superposed exactly 4580 in the second order, and 3000 in the third, and 2250 in the fourth; on a wave-length of 6000 in the third order are superposed 4500 in the fourth order, 3600 in the fifth, 3000 in the sixth, and so on.

These two properties, namely, the normality of the spectrum and the relation of the superposed orders, enabled Rowland to measure the wave-lengths of all the lines in the solar spectrum with great accuracy relatively to the wave-length of one line. This, as before-mentioned, was the D_1 line, whose wave-length was adopted as 5896·156 as a mean of the best measurements. By measuring the lines in the various superposed orders in relation to the D_1 line, Rowland first determined the wave-lengths of fourteen lines in different parts of the spectrum with the greatest possible accuracy, and in a similar way from these lines he determined the wave-lengths

of the principal lines throughout the spectrum. He then photographed the whole normal spectrum from end to end, and from his knowledge of the wave-lengths of all the principal lines he was able to rule the scale of wave-lengths on each plate, and then to enlarge each photograph and its scale together. In this way a very large map of the whole spectrum was obtained, with the scale attached from which the wave-length of any line could be read with great ease. The beauty of the method seemed to lie in the fact that, though the wave-length of the D_1 line is the basis of the scale, yet the relative accuracy of the scale throughout is exceedingly great, far greater than ever possible with separate wave-length determinations.

Rowland was under the impression, owing to the accuracy of these measurements, that if at any time a more correct determination of the wave-length of the D_1 line were made it would only be necessary to multiply his numbers and all determinations referred to them by some small factor. As a matter of fact, as will be seen from the sequel, the accuracy of Rowland's work is not nearly so great as was at first supposed. His measurements contain a periodic error which of course precludes any correction of the whole by multiplying by a constant factor.

Bell's determination of the absolute wave-length of the D_1 line was undertaken with a view of making a standard for Rowland's work; he had access to more accurate and finer gratings than had been obtainable by previous workers, and it was thought that a more accurate value of this constant could be obtained. An account of the methods employed and the results were published in 1887 and 1888,[1] the first paper referring to measurements with two glass gratings, while the second is a much more extended discussion of these and some further measurements with two reflecting gratings, and contains a full account of the errors and methods adopted to eliminate them. These errors arise from the inevitable small imperfections occurring in the ruling of the gratings, errors which are by far the greatest to be met with in the investigations. Bell points out that there are five more or less different

[1] *Phil. Mag.*, **23**. 265 (1887), and **25**. 255 and 360 (1888).

methods of making the measurements, depending on the position of the grating in relation to the collimating and observing telescopes. The wave-length equation may be written in the form—

$$n\lambda = b\{\sin i + \sin(\phi - i)\}$$

if i be the angle of incidence, and ϕ the angle of deviation; then if i be made equal to zero the equation will be simplified to—

$$n\lambda = b \sin \phi,$$

which applies to the first two methods, in which the grating is placed normal to the collimator and observing telescopes respectively.

The third method is the one adopted by Ångström, in which the grating is set nearly perpendicularly to the collimator, and the angle of incidence i formed is measured and kept in the formula.

The fourth method is the one of minimum deviation, which can be shown to take place when the angle of incidence is equal to half the angle of deviation; in this case the wave-length can be found from the equation—

$$n\lambda = 2b \sin \frac{\Phi}{2}$$

The fifth method consists in clamping the collimator and telescope at some known angle with each other, and then rotating the grating. The equation $n\lambda = b\{\sin i + \sin(\phi - i)\}$ can be written in the form—

$$n\lambda = 2b \sin \frac{\Phi}{2} \cos\left(i - \frac{\Phi}{2}\right),$$

and therefore, if δ be the angle through which the grating is turned, and θ the angle between the collimator and telescope, we will have—

$$n\lambda = 2b \sin \delta \cos \frac{\theta}{2}.$$

The method of observation is to adjust the required line upon the cross-wire in the eyepiece, and then rotate the grating until the reflected image is brought upon the cross-wire.

In his own determinations Bell used the second method, with the grating normal to the observing telescope, in the case of two glass transmission gratings, and the fifth with two reflecting gratings ruled on speculum metal. The first two methods are, indeed, the most satisfactory for transmission gratings, because only one angle has to be measured, while the fifth method was adopted for the speculum metal gratings owing to the great weight of the telescopes employed, which were of 16·4 cms. aperture and 2·5 metres focal length. As regards the gratings, they differed very considerably amongst themselves in the matter of size and grating-space; the first was 30 mm. long, with 12,100 lines, and the second was almost the same length, with 8600 lines; these were ruled on different parts of the screw of the dividing engine. The third was 4 inches long, and contained 29,000 lines, and the fourth was the same length, and contained 40,000 lines, being ruled with another dividing engine. The actual readings of the angles were made within one second of arc in every case, and a mean of a very great many was adopted as a final result, the probable error being extremely small. The measurements with the first two gratings were made with the D_1 line in the third and fourth orders respectively, while, with the second apparatus and the third and fourth gratings, other lines had to be observed owing to the limits imposed by the fixed telescopes. With grating No. 3, the line at $\lambda = 5133{\cdot}95$ was measured in the eighth order, and with the fourth grating the line at $\lambda = 5914{\cdot}32$ was measured in the fifth order. From these the wave-length of D_1 could be calculated from Rowland's table of wave-lengths.

By far the most important portion of the work was the determination of the grating-spaces in each grating, and herein lay the most fruitful source of errors. The actual determination of this length was made by comparison with standards of length, which were themselves compared with the international standards with the greatest possible care. It was, however,

not found possible simply to measure the length of the ruled space, and divide this by the number of lines ruled, in order to determine the grating-space, owing to the inevitable inaccuracies which occur to a greater or less extent in every grating. Bell points out in his paper that the grating-space is never regular throughout the whole extent of the ruled surface, and the variations may be classed as regular and irregular. In the first class are put those which are periodic or linear, which produce respectively "ghosts"—that is to say, false images, and differences in focus on opposite sides of the normal. These are not so serious as the variations of the second class, which include the displacement, omission, or exaggeration of a line or lines, and more especially a more or less sudden change in the grating-space, producing a section of the grating having a grating-space peculiar to itself. Bell describes the testing of a grating in the following words:—"Place a rather bad grating on the spectrometer, and, setting the cross-hairs carefully on a prominent line, gradually cover the grating with a bit of paper, slowly moving it along from end to end. In very few cases will the line stay upon the cross-hairs. A typical succession of changes in the spectrum is as follows:—Perhaps no change is observed until two-thirds of the grating has been covered. Then a faint shading appears on one side of the line, grows stronger as more and more of the grating is covered, and finally is terminated by a faint line. Then this line grows stronger till the original line appears double, and finally disappears, leaving the displaced line due to the abnormal grating-space." Although the above is perhaps exceptional, still minute displacements can be seen even with very good gratings. It becomes necessary, therefore, always to examine the grating for the existence and position of any abnormal portion, an investigation which is somewhat simplified by the fact that for the most part abnormal spacing occurs at the end of the ruled surface, generally at the end where the ruling was begun, because the dividing engine after starting requires some time to settle down to a uniform state. Bell recommends the calibration of the entire grating—that is to say, the direct measurement of n grating-spaces taken

successively along the whole of the ruled surface; he carried out this process for all of the four gratings, and found in each some abnormal portion. The values obtained from these observations were combined in each case, and corrections applied to the wave-length as first obtained; evidently these at the best can only be approximate, for on the one hand a minute examination of a grating spectroscopically is impossible, since a small section of ruled surface does not give measurable spectra, and on the other hand, while the calibration values are very accurate, it is impossible to decide exactly how any variations in the grating-space are integrated in the spectrum measured.

A further possible source of error lay in the temperature of the grating, on which of course depends the value of the grating-space. This could easily enough be corrected for when the temperature was known, since the coefficients of expansion have been very accurately determined. The determination of the temperature with the metal gratings was easily made owing to their being such good conductors of heat; in the case of glass gratings, on the other hand, great care had to be exercised in order to keep the temperature constant, because, though glass has such a small coefficient of expansion, yet, being so bad a conductor, it may give rise to serious errors due to straining and bending from unequal heating.

The corrected results which Bell obtained with the four gratings were as follows :—

Grating I.,	wave-length	D_1	5896·18
„ II.	„	„	5896·23
„ III.	„	„	5896·15
„ IV.	„	„	5896·17

of which the mean value is 5896·18 in the air at 20° and 760 mm. pressure, and 5897·90 *in vacuo*. These numbers were, however, subjected to a further correction, and were finally given as 5896·20 in air, and 5897·92 *in vacuo*, while Ångström's value as corrected by Thalén was 5895·81. Important determinations have also been made of this constant by Müller and Kempf, Peirce, and Kurlbaum. Müller and Kempf made use

of four gratings ruled on glass by Wanschaff, and obtained the following somewhat widely differing values at 15° C. :—

	λ
Grating-space, 2151	5896·46
„ „ 5001	5896·14
„ „ 8001	5896·33
„ „ 8001	5895·97

The mean of these is 5896·22, which becomes 5896·25 at 20°. The value Peirce obtained with Rutherfurd's gratings was 5896·27, which, as a result of the calibration of his grating by Bell, was reduced to 5896·20.

Kurlbaum, in his investigation, employed two gratings, one by Rutherfurd and the other by Rowland, the first having 29,521 lines in a space of 43·4 mm., and the other 23,701 in 41·7 mm. The length of the ruled spaces in these gratings rendered the measurement of the grating-space a matter of considerable difficulty, owing to their not being a definite fraction of a metre. The values he obtained were 5895·84 and 5895·96 respectively, and the mean of these is equal to 5895·90 units. These determinations Rowland combined together, weighting them according to the value of the result as follows :—

Weight.	Observer.	D_1
1	Ångström, as corrected by Thalén . .	5895·81
2	Muller and Kempf	5896·25
2	Kurlbaum	5895·90
5	Peirce	5896·20
10	Bell	5896·20
	Mean	5896·156

This final value Rowland adopted as the standard of his wave-length determinations, and hence it is the standard of all the measurements with prism or grating apparatus based on his standard.

Methods of practical wave-length determination in the present day, except in special cases, are always based on the

comparison with a standard spectrum of the spectrum which it is required to measure. By far the most satisfactory method is to photograph the two spectra one against the other on the same plate, and then the unknown wave-lengths are obtained by simple interpolation between the lines of the standard spectrum. The solar spectrum, with Rowland's values, may be used as a standard, or some other spectrum, the wave-lengths of whose lines have been determined with sufficient accuracy in terms of the solar standard. In cases where great accuracy is required, care must be taken only to employ a standard which may be depended upon. The most satisfactory is the spectrum of the electric arc between iron poles, which contains a vast number of lines. It is to be remembered that the solar spectrum only extends to about 3000 Ångström units, owing to the absorption of the ultra-violet rays by the atmosphere, and therefore with prism apparatus it cannot be used for a standard in the far ultra-violet. The methods of work will, however, be more fully discussed in later chapters.

In 1894, Michelson, by a new method, succeeded in determining the absolute wave-lengths of three lines in the spectrum of cadmium in relation to the standard metre at Paris. The method employed was the determination by interference methods of the number of waves of the three spectrum lines contained in 1 metre. The details of the interference apparatus will be found in Chapter IX., and cannot be dealt with here; suffice it to say that the method is free from all the inherent errors of grating measurements, and the values of the three wave-lengths as given by Michelson are generally accepted as being absolutely accurate. The actual values were—

Red line 1 metre = $1553163{\cdot}5 \times \lambda \therefore \lambda = 6438{\cdot}4722$ tenth metres
Green ,, ,, = $1900249{\cdot}7 \times \lambda \therefore \lambda = 5085{\cdot}8240$,, ,,
Blue ,, ,, = $2083372{\cdot}1 \times \lambda \therefore \lambda = 4799{\cdot}9107$,, ,,

Unfortunately these values are considerably below those obtained from Rowland's tables, which are $\lambda = 6438{\cdot}680$, $\lambda = 5086{\cdot}001$, and $\lambda \times 4800{\cdot}097$ respectively. Recently, also Fabry and Perot have measured a number of lines in the

spectra of certain metals and of the sun by interference methods, directly comparing them with Michelson's values for the cadmium lines. It was then found that the difference between the wave-lengths measured by interference methods and those on Rowland's map was not proportional to the wave-length. Clearly, therefore, either Rowland's relative values or the interference values are wrong. The discrepancy has been explained by Kayser,[1] who proves conclusively that the coincidence between the orders of spectra with gratings is not to be depended upon; for this and some other reasons he shows that Rowland's values are by no means good enough for our present needs—the error in them is far greater than the experimental error in accurate work at the present time.

There is no doubt, therefore, that grating measurements must give place to interference measurements, and at the present time the new standard is in process of being set up.

At a meeting of the International Union for Solar Research held at Oxford in 1905 it was decided that—

1. The wave-length of a suitable spectroscopic line shall be taken as the primary standard of wave-length. The number which defines the wave-length of this line shall be fixed permanently, and all wave-lengths shall be measured in the unit thereby defined. This unit shall be called the Ångström.

2. Secondary standards shall be measured by interferometer methods in reference to this primary standard, and these secondary standards shall not be more than 50 units apart.

At Meudon in 1907 the International Union again met and finally chose the cadmium red line as the primary standard, and agreed to designate the wave-length as—

6438·4696 Ångströms.

The Ångström is defined in this way, and it is equal to the tenth metre with an accuracy of about 1 in 10,000,000.

In 1908 Fabry and Buisson published a series of measurements of lines in the arc spectrum of iron to serve as secondary standards. These will be found on p. 351.

In 1910 the International Union met at Mount Wilson,.

[1] *Astrophys. Journ.*, **19**. 157 (1904).

and decided to establish as the secondary standards in the international system the means of the values found by three independent observers, provided of course that no decided discrepancy is to be found in any of the measurements. A few wave-lengths have been published by the Committee, the means being taken of the measurements of Fabry and Buisson[1] at Marseilles, Eversheim[2] at Bonn, and Pfund[3] at Baltimore. The following is a list of the lines[4] all in the spectrum of the iron arc.

6494·993	5658·836	5266·569	4878·225	4466·556
6430·859	5615·661	5232·957	4859·758	4427·314
6393·612	5586·772	5192·363	4789·657	4375·934
6335·341	5569·633	5167·492	4736·786	4352·741
6318·028	5506·784	5110·415	4707·288	4315·089
6265·145	5497·522	5083·344	4601·417	4282·408
6230·734	5455·614	5049·827	4647·439	
6191·568	5434·527	5012·073	4602·947	
6137·701	5405·780	5001·881	4592 658	
6065·492	5371·495	4966·104	4547·853	
6027·059	5324·196	4919·007	4531·155	
5763·013	5302·315	4903·325	4494·572	

It has also been agreed that all wave-lengths measured on this system shall be designated by the symbol "I.A." to indicate the unit used.

A long list of tertiary standards in the arc spectrum of iron has been published by Kayser.[5] By tertiary standards are meant lines the wave-lengths of which have been determined by interpolation between the secondary standards. Kayser's measurements were all made with a full-sized Rowland grating, using the second order of spectrum. Every line was referred to as many of the standards as possible. Kayser expresses himself as convinced by his measurements that there still exist errors of as much as 0·004 to 0·005 Ångström in some of the secondary standards. The list includes about 380 lines between the limits of $\lambda = 6495$ and $\lambda = 4118$.

[1] *Astrophys. Journ.*, **28.** 167 (1908).
[2] *Ibid.*, **31.** 76 (1910).
[3] *Ibid.*, **28.** 197 (1908).
[4] *Ibid.*, **32.** 215 (1910), and **33.** 85 (1911).
[5] *Ibid.*, **32.** 217 (1910).

CHAPTER III

THE SLIT, PRISMS, AND LENSES

The Slit.—As generally used at the present time the slit is formed between two metal jaws, one of which is fixed while the other is moved by a fine-pitched screw, which enables the width of the opening between the jaws to be accurately adjusted. Each of these jaws is fitted into two parallel grooves cut in a metal frame, this plan being adopted in order to ensure the parallelism of the slit opening. Many designs of mounting the jaws have been produced, but perhaps the best and simplest is that shown in Fig. 16 in front and side elevation.

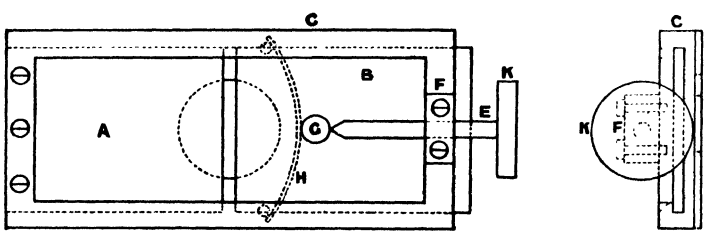


FIG. 16.

The two jaws are shown at A and B, and these are both fitted into two parallel grooves cut along the whole length of the metal frame C. The jaw A is fixed by means of screws into the slit frame, while the jaw B is free and is moved by means of the screw E; this screw works in the block F, which is screwed to the slit frame. The pin G, which is fixed into the jaw B, is kept pressed up against the end of the screw E by means of the curved spring H, so that any movement of E forwards or backwards is at once followed by the jaw B. It is

of great advantage that the screw E be cut with a definite pitch, either a millimetre or half-millimetre, and that the head of the screw K be graduated, in order that the width of the slit opening may be determined. The spring H should be stiff enough to eliminate all tendency to backlash on the part of the micrometer screw E.

Usually a flat metal plate is screwed to the back of the slit frame, and a central hole is cut in this to admit the passage of the light from the slit; this hole is denoted by the dotted circle in the front elevation diagram in Fig. 16. This design of slit with an oblong frame is adapted for large apertures; very often in smaller apparatus the slit frame is made circular instead of oblong, but in other respects the design is the same. The round form of frame is convenient for fitting with a cover, which usually consists of a short piece of brass tubing with an end piece containing a glass window. Such a slit cover is useful when working with flame spectra or any source of light which is inclined to bespatter the slit. It must be noted, however, in connection with this round slit frame that much less bearing surface is available for the slit jaws than in the case of the design in Fig. 16.

An improvement on the above form of slit with one jaw fixed is to have both jaws movable and actuated by the same screw. In this design, when any alteration is made in the size of the opening both sides are made to move equally, and thus the centre of the aperture is not displaced. It therefore becomes possible, for example, in comparing the spectra of a bright and a faint source, to use a wider slit in the case of the latter, because the centres of the lines are not displaced as they would be in the case of a slit having one jaw fixed.

A diagram of a slit with two movable jaws is given in front elevation in Fig. 17. A and B are the two jaws which are fitted into parallel grooves exactly as in Fig. 16, and the motions of both of them are controlled by a micrometer screw. The parts of this screw which pass through the blocks F and G are screwed with a right- and left-handed thread respectively of equal pitch; the block F is fixed to the jaw B, while the block G is fixed to the frame C, which in its turn is screwed to the

jaw A. No thread is cut on the screw where it passes through the block D, but a good sliding fit is made and the collars H, H prevent any forward or backward motion. It follows then that when the micrometer screw is turned both jaws are moved at equal rates and in opposite directions.

The frame C is made of the shape shown in order not to obstruct the passage of the light to the slit.

The edges of the jaws of a slit must always be bevelled, as is shown in Fig. 18, with the bevelled edges inside, away from the source of light. The reasons for this are twofold—first, because it is very much easier in this way to obtain edges which are true, and second, because if the edges were not bevelled but cut square a certain quantity of light would be reflected off these edges tending to produce fuzziness in the spectrum lines.

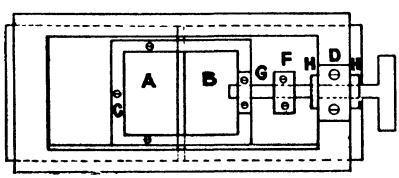


FIG. 17.

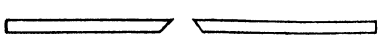


FIG. 18.

It is essential, of course, for any accurate work that the sides of the slit opening be perfectly true and parallel, as otherwise the diameter of the aperture will vary along its length. In addition to the fact that the edges of the jaws must be cut true and square, it is also necessary that the jaws move smoothly in their grooves without any trace of side play, and it is for this reason that the long slit frame shown in Figs. 16 and 17 is to be preferred over any other design; a great length of bearing surface is given to the jaws which minimises the chance of any side play.

A new slit should always be tested for parallelism; this is simply enough carried out by looking through the slit at some source of light, and then slowly closing the aperture by turning the micrometer screw until it just disappears. If properly adjusted the aperture will vanish entirely along its whole length, but, if one end closes first, leaving an evidently wedge-shaped opening, the jaws are out of alignment. The readjusting of a

bad slit is an extremely delicate and difficult operation, and should only be undertaken by an expert. It must be remembered that the bevelled edges of the jaws are extremely tender and very easily damaged. Great care should be taken never to close a slit tightly, or it may be ruined; then again, in cleaning the edges from dust it is best to use a fine splinter of some dry soft wood such as lancewood, and insert it carefully between the jaws, moving it up and down several times.

As regards the best material for the slit, brass is generally used for the framework and often for the jaws, but in this latter case it is not to be recommended, because it so easily corrodes. The best substance for the jaws is the patent white alloy called platinoid, which is very tough, takes a very high polish, and does not corrode. A very ingenious suggestion came from Crookes in the way of quartz jaws.[1] These jaws are cut in the same way as the metal ones (*vide* Fig. 18), and, therefore, the edges form prisms which refract away all the light which falls on them, so that their transparency or semi-transparency offers no objection. They have the advantage of being able to be worked to a finer edge than the metal jaws, and thus are capable of giving better definition. It is preferable that these jaws should be fitted in grooves outside the jaws of an ordinary slit, as described above, and that they should be so adjusted as to press against the metal jaws; in this way the quartz jaws move with the metal ones simply by friction. The reason for this method of mounting them lies in the fact that the fine edges of quartz are so fragile; there is then little danger of the edges being damaged if by any chance the slit is closed too far.

The dimensions of a slit for any spectroscope are, of course, entirely governed by the size and quality of the lenses and prisms with which it is to be associated; generally speaking the following lengths of aperture may be taken as a basis—with 3-inch lenses a 1 to $1\frac{1}{4}$-inch slit may be used, with 2-inch lenses a $\frac{3}{4}$-inch slit, with $1\frac{1}{2}$-inch lenses $\frac{1}{2}$-inch, and with 1-inch about $\frac{3}{8}$-inch, all being clear aperture; the jaws of a slit are generally made rather wider than the actual aperture is intended to be, and then a diaphragm is placed behind to stop down the

[1] *Chem. News*, **71**. 175 (1895).

aperture to that required. For the dimensions of the whole slit mounting the following may be taken as typical of a slit made for accurate work—

The slit frame, 95 × 55 mm.

The slit jaws, 48 × 40 mm.

Clear aperture, 30 mm.

Three draw slides (see Fig. 19), each 10 mm. wide.

Micrometer screw for adjusting movable jaw has a pitch of 0·5 mm.

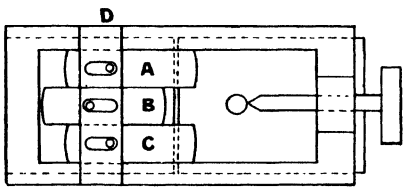


FIG. 19.

A great convenience may be added to a slit for use with prism apparatus in the shape of draw slides fitted on the front of the slit so as to divide it into sections and obtain several apertures. The great advantage of this arrangement, which is due to Lockyer, in work on the comparison of spectra is obvious. Fig. 19 is a diagram of a slit fitted with three such slides—A, B, and C. These

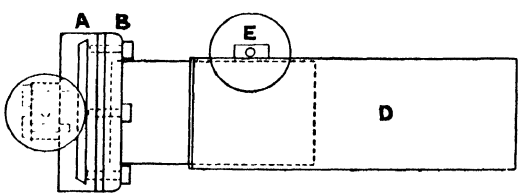


FIG. 20.

are fitted under a band D, which is screwed to the slit frame; each of the slides can move quite independently of the others, so that as many different spectra can be photographed upon one plate as there are slides.

In mounting a slit it is best to fit it to a brass tube having a rack-and-pinion arrangement for focussing, as is shown in Fig. 20. A is the slit frame with its micrometer screw, and B is a flange which is fitted and screwed to the back of A; into

this flange B is screwed a short length of brass tubing which slips into a second piece of tubing D, and is provided with the rack-and-pinion arrangement E.

The Prism.—The simple theory of the refraction of light by a prism has already been given in the introduction for the case of a single ray; the same relations discussed for that case of course hold good when the prism refracts a beam of light, for the beam may be considered as a bundle of rays, each of which is separately refracted. Evidently therefore the simplest and most satisfactory condition is that the beam consist of a number of parallel rays which are all equally refracted. This condition is generally sought after in prism spectroscopes, and was introduced by Fraunhofer, who was the first to make use of the collimating lens; this lens, as the name suggests, collects the rays coming through the slit and throws them as a parallel beam on to the prism face. If the beam of light passing into the prism is very convergent or divergent, considerable disturbances, arising from aberration, tend to appear which militate against good definition in the spectrum obtained.

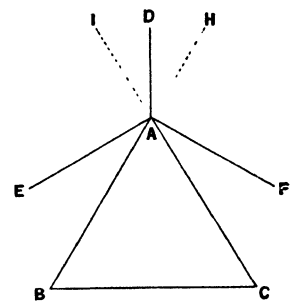


FIG. 21.

The angle contained between the two refracting faces of a prism or the refracting angle, as it is called, which determines to a great extent the amount of deviation produced in the path of a beam of light in its passage through the prism, may be measured as follows. In Fig. 21 ABC represents any prism of which the angle at A is the refracting angle. Let DA mark the direction of a beam of light which falls on the prism; part of this beam will be reflected from the face AB along paths parallel to AE, and part will be reflected from the face AC along paths parallel to AF. Now, if BA and CA be produced to H and I respectively, by the laws of reflection the angles HAD and BAE will be equal to one another, as also will be the angles IAD and CAF; it follows therefore that the angle

IAH is equal to the sum of the angles BAE and CAF. But the angles IAH and BAC are equal to one another, therefore the angle BAC is equal to the sum of the angles BAE and CAF. The whole angle EAF is thus equal to twice the angle BAC.

In order, therefore, to determine the angle BAC it is only necessary to measure the angle between the rays reflected from the two refracting faces of the prism, when a beam of light falls on them as in the diagram, and half the angle found will be the refracting angle BAC. The measurement is carried out quite simply with the help of a spectrometer (*vide* p. 115); the prism is placed on the instrument with the angle which it is required to measure pointing towards the collimator, care being taken that the prism is placed over the centre of the graduated circle. The telescope is then turned until the cross-wires in the eyepiece are exactly adjusted upon the image of the slit as reflected from one face of the prism; the position of the telescope is then read upon the divided circle. The telescope is then turned and adjusted upon the reflected image from the other face of the prism, and if the prism be correctly placed no change of focus of the telescope will be needed. The position is again read, and the difference between the two readings gives the angle through which the telescope has been turned, half of which angle is the angle required.

The method of determining the index of refraction with a prism is due to Fraunhofer, who showed that it can be found for a ray passing through a prism at minimum deviation from the equation—

$$\mu = \frac{\sin\frac{A + D}{2}}{\sin\frac{A}{2}},$$

where A is the refracting angle of the prism and D the angle of deviation. This equation can be readily proved from the diagram given in Fig. 22.

Let ABC represent a prism and OPQR the path of a ray at minimum deviation, and which therefore passes symmetrically through the prism. Let TS and US be drawn normal

to the refracting faces AB and AC, and let OP and RQ be produced, when D will be the angle of deviation.

It therefore follows that the angles a and b and the angles f and g are equal to one another.

In the quadrilateral APSQ the angles APS and AQS are both right angles, and therefore the angles A and c are together equal to two right angles.

Again, in the triangle PQS the three angles a, b, and c are together equal to two right angles,

therefore $$A + c = a + b + c$$

and $$A = a + b;$$

but since $$a = b$$

therefore $$a = b = \frac{A}{2}.$$

Now, in the triangle VPQ the three angles e, f, and g are together equal to two right angles, and therefore, since the two angles e and D are together equal to two right angles,

$$e + f + g = e + D$$

and $$f + g = D;$$

but $$f = g$$

therefore $$f = g = \frac{D}{2}$$

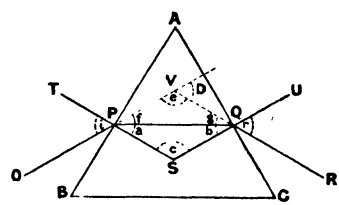


FIG. 22.

Again, the angle i is equal to the angle VPS, that is, the sum of the angles f and a,

therefore $$f = i - a,$$

and since $$f = \frac{D}{2}$$

therefore $$i = a + \frac{D}{2} = \frac{A + D}{2}.$$

Now, by Snell's law, $\mu = \frac{\sin i}{\sin a}$, and therefore, by substituting the values found for i and a—

$$\mu = \frac{\sin \frac{A + D}{2}}{\sin \frac{A}{2}}$$

This equation is of great value, because the index of refraction can be found from the refracting angle and the minimum angle of deviation, both of which can readily be determined. The method of determining the refracting angle of the prism has been given above, and the angle of deviation is equally easily obtained. The slit of the spectrometer is illuminated with the light the index of refraction for which it is required to determine, and the cross-wires of the eyepiece of the telescope are then adjusted on the image of the slit obtained by direct vision without the intervention of the prism. After the position of the telescope has been read the prism is set in place and the cross-wires of the eyepiece set upon the refracted image; care must, of course, be taken that the prism is set at minimum deviation, this being done by turning the prism round first in one direction and then in the other until the position is found at which the deviation is the least possible. The difference between the two readings is the angle of deviation required.

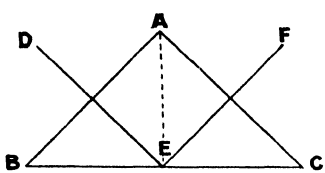


FIG. 23.

The above equation, $\mu = \dfrac{\sin \frac{A+D}{2}}{\sin \frac{A}{2}}$, will be treated more fully under dispersion and resolving power.

The Total Reflection Prism.—This useful prism is based on the fact, already pointed out (p. 6), that a ray of light cannot pass out from a denser medium into a rarer medium unless the angle of incidence is less than a certain critical angle whose sine is equal to the reciprocal of the relative index of refraction. Such a prism is shown in Fig. 23.

ABC is the prism, and DEF the path of a ray of light through it. The angle of incidence of the light on the surface AB is zero, and therefore no refraction takes place; DEA is the angle of incidence on the surface BC, and if this angle be greater than the critical value for the prism substance the whole

of the light will be totally reflected and pass out through the face AC, where again there will be no refraction owing to normal incidence. This prism is generally made with the angle BAC a right angle, and the two base angles equal to 45°, since in this way the least amount of light is lost in its passage; when the whole of the face AB is illuminated at normal incidence, it is evident that the whole of the light cannot be totally reflected unless the angle BAC is made equal to a right angle. In this case, therefore, the angle DEA is 45°, and therefore 45° must be greater than the critical angle of the substance employed;

we thus have $\sin 45° = \frac{1}{\mu}$,

whence $\mu = 1{\cdot}414$.

It follows from this that a right-angled totally reflecting prism must be made of some substance whose index of refraction is greater than 1·414. All glasses, however, have indices well above this.

This prism is used in spectroscopy for purposes of the visual comparison of spectra in small instruments; for accurate work, however, recourse should be had to photographic methods, using the draw-slides over the slit shown in Fig 19, or some similar device. The prism is made to cover one-half of the slit, and by its means light from a side source is reflected in through the slit, while the light from another source is directed straight in through the other half of the slit. In this way two spectra may readily be compared.

The total reflection prism is also used in the construction of compound prisms, and trains of prisms as are sometimes made use of in modern spectroscopes. A very ingenious example of the former, which has recently been introduced by Hilger, is shown in Fig. 24.

This prism consists of two 30° prisms set against the faces of a right-angled totally reflecting prism, and has the property of always giving the same deviation, 90°, when set at minimum, whatever be the index of refraction. The construction of the prism is as follows:—ABC is the first prism, of which the angles

are, ABC 60°, BAC 30°, and BCA 90°; ACD is an isosceles right-angled prism, so that the angles CDA and CAD are each equal to 45°, while the last prism BDE is similar to the first, having the following angles—DBE 30°, BED 60°, and BDE 90°. It thus follows that the two prisms ABC and BDE are each half an ordinary 60° prism.

When a ray of light enters the prism ABC at minimum deviation, making an angle of incidence i at the surface AB, it travels through the prism parallel to the base BC, and enters the prism ACD at normal incidence, and in consequence suffers no refraction. The ray is then totally reflected at the surface AD, and enters the prism BDE at normal incidence, travelling parallel to the base DE, and finally emerges from the face BE, making an angle e with the normal. Since the light traverses both the 30° prisms at minimum deviation, it follows that the angles i and e must be equal to one another, and also, since the two refracting faces AB and BE are at right angles to one another, that the paths of the incident and emergent rays must be at right angles to one another. Thus, whenever in passing through this prism a ray of light is deviated through an angle of 90°, it follows that it travels through at minimum deviation. In practice, therefore, it is simply necessary to fix the collimator and telescope permanently at right angles to one another, when by rotation of the prism round a vertical axis the different portions of the spectrum can be brought into view, that portion seen at any moment having traversed the system at minimum deviation.[1]

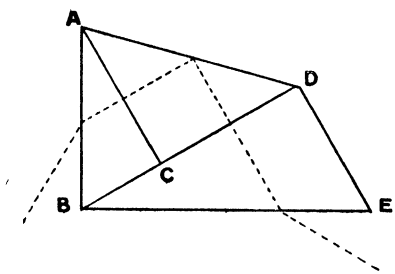


FIG. 24.

There is no need for this prism to be built up actually as described above, and in practice it can be made in one piece

[1] See also p. 122.

in such a way that the four vertical faces enclose four angles equal to 90°, 75°, 135°, and 60° respectively.

A spectroscope such as the one just described, in which the collimator and telescope are fixed and the different portions of the spectrum examined by rotation of the prism, is known as a fixed-arm spectroscope. Very many designs of this type of instrument have been made, some of which will be described in the next chapter; some of these are multiple transmission instruments in which the beam of light from the collimator is caused to traverse the same refracting prism a great number of times, finally escaping into the telescope. One of these instruments, designed by Cassie,[1] may be described as a type. It consists of a 30° prism and a right-angled prism cemented together so that the right-angled edge of the latter is perpendicular to the refracting angle of the 30° prism, as is shown in Fig. 25.

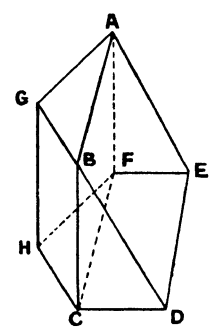


FIG. 25.

ABCDEF is the 30° prism with the right-angled prism AFCBGH cemented against it, though in practice the whole may be cut in one piece. AB is the refracting edge of the 30° prism, and GH is the right-angled edge of the reflecting prism. When the rays pass through this prism at minimum deviation, they fall on the face ABDE, are refracted and travel parallel to the base CD, and on reaching the back are totally reflected and emerge again, parallel to their original path. The prism is used in conjunction with two right-angled prisms, as is shown in elevation and plan in Fig. 26.

The rays from the collimator pass between the two right-angled prisms A and B, as is shown in the elevation, and following the arrows enter the compound prism; they are refracted, and then reflected back and again refracted, as is shown by the arrows in the plan. The rays travel back along a path parallel to the original path and enter the prism A, and thence by reflection into B, and thence back towards the

[1] Cassie, *Phil. Mag.* (6), 3. 449 (1902). See also p. 125.

compound prism C. They thus follow the arrows, going backwards and forwards until finally they pass under the prism C into the telescope. It will be readily seen that this is a fixed-arm spectroscope, with the collimator at a higher level than the telescope. In order to investigate the various portions of the spectrum it is only necessary to turn the prism C round on a vertical axis, whereby the different regions can be brought into view.

The 30° prism used in the above compound prisms is generally called a half prism, because its shape is that of a

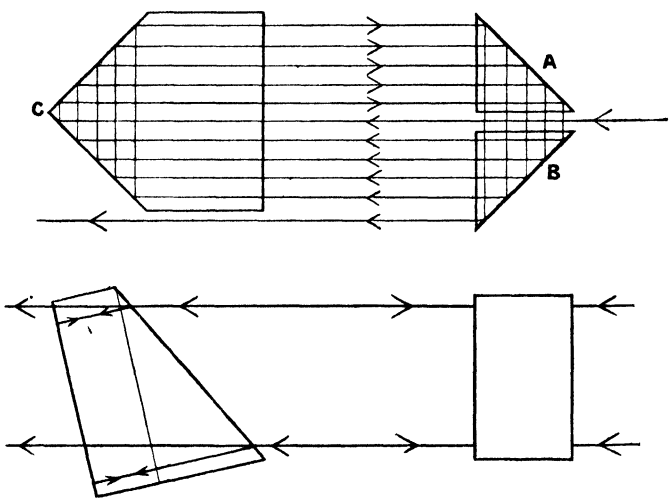


FIG. 26.

60° prism, cut into two equal portions. This half prism is a very useful instrument, and has been employed for various purposes in different spectroscopes. In certain cases, such as multiple transmission instruments of the fixed-arm type, one face of the half prism is silvered, namely, the face AC in Fig. 27. When a ray of light enters such a prism at minimum deviation. it falls at normal incidence upon the silvered surface, and is therefore reflected back upon its own path. By the use of two such half prisms Cassie has designed a multiple transmission

instrument.[1] Thollon[2] made use of a pair of these half prisms in the following way—the two prisms are set with their long faces towards one another, as is shown in Fig. 28, with the path of a ray of light symmetrically through them. One prism, *e.g.* ABC, is fixed so that the face AB is perpendicular to the axis of the collimator, and the other DEF so that the face DF is perpendicular to the axis of the telescope; DEF is fixed to the arm carrying the telescope, so that when the telescope is moved the half prism moves with it. The axis of rotation of the telescope therefore passes through the point G; it can be readily seen from Fig. 28 that as the telescope is moved round the axis G, different parts of the spectrum will come into view, and further, that at all positions of the telescope the ray passing

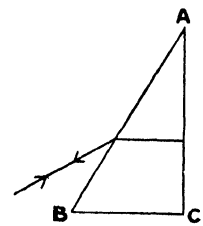


FIG. 27.

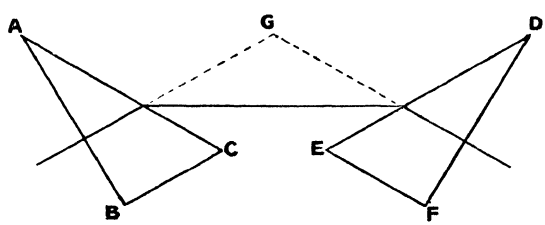


FIG. 28.

along its axis will have passed through the prisms at minimum deviation. This device was used by Mouton in his work on the indices of refraction of quartz for the infra-red rays.[3]

An important property of the half prism can be seen on reference to Fig. 29, which shows a half prism refracting a beam of light. The diameter of the beam *a* is very much less than the diameter of the beam *b*; the half prism, therefore, can be used in a prism train to diminish or increase the diameter of a beam of light. In this way the full aperture may be

[1] *Phil. Mag.*, **3**. 449 (1902).
[2] *Comptes Rendus*, **86**. 595 (1878).
[3] See p 250.

employed of prisms which are larger than the aperture of the collimating and telescope lenses; for example, 60° prisms, with an aperture equal to *b* in Fig. 29, can be used with lenses which have only an aperture equal to *a*. Two half prisms are employed, one at each end of the prism train, and in each case the longest faces are turned outwards; in this way, as Rayleigh has shown, greater resolving power can be obtained than would otherwise be possible with a given aperture.[1]

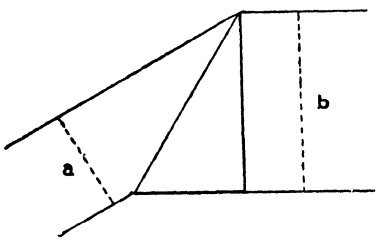


FIG. 29.

Christie has also made use of the half prism in a direct-vision spectroscope.[2]

Dispersion.—If a comparison be made between the values of the indices of refraction for the same rays of light possessed by different substances, it will at once be noticed that the ratios between the indices are by no means the same. For example, in the case of a flint-glass and carbon bisulphide the values for the four rays C, D, F, and H are as follows :—

Line.	Wave-length.	CS_2	Flint glass.
C	6563	1·618	1·624
D	5893	1·628	1·628
F	4861	1·652	1·641
H	3969	1·689	1·674

Thus the ratio between the indices of carbon bisulphide and the glass is for the D line 1·000, for the F line it is 1·007, and for the H line 1·015. It is evident therefore that, if we had two prisms of exactly the same size, one of carbon bisulphide and the other of flint glass, the deviation suffered by the D line would be the same in each case, but that the F line would be more, and the H line still more deviated by the carbon

[1] See p. 78.

[2] *Proc. Roy. Soc.*, **26**. 8 (1877).

bisulphide than by the flint-glass prism. We thus see that a change in the wave-length produces a greater change in the deviation in the one case than in the other, or, as it is usually expressed, the value of $\frac{d\theta}{d\lambda}$ is greater for a carbon bisulphide prism than for the glass prism. The term $\frac{d\theta}{d\lambda}$, or the ratio of the change in the deviation to the change in the wave-length, is called the dispersion. As a result of the fact that the value of $\frac{d\theta}{d\lambda}$ varies with different substances, it is possible to construct compound prisms for direct vision, and also achromatic lenses. In the first case the prism is so constructed that one ray passes through it undeviated, while the others do not, so that a

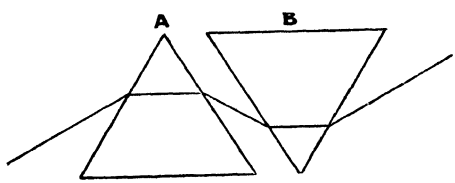


FIG. 30.

spectrum is still produced; in the second case the converse is true, all the rays are brought to the same focus without destroying the deviation. This second case will be treated under the subject of lenses.

It is quite evident that, if two prisms A and B be taken of the same size and material, and be placed in reversed positions, as in Fig. 30, a ray of light on passing through A will be deviated to a certain extent, and on passing through B will be deviated to exactly the same amount in the opposite sense, so that the joint effect of A and B will produce no change in the direction of the ray. If, however, the value of $\frac{d\theta}{d\lambda}$ be different for A and B, then all the rays will not pass through undeviated. For example, let A and B be prisms of carbon bisulphide and flint glass as given above, then clearly a ray of wave-length 5893 will pass through undeviated, but every other ray will

be deviated to a small extent; light of wave-length 3969 will be more deviated in the first prism than in the second, and light of wave-length 6563 will be less deviated in A than in B. The result will be that on looking directly through the combination at a source of light a spectrum will be obtained; such a combination is called a direct-vision prism.

In practice it is not convenient to use a carbon bisulphide prism, on account of the difficulty attendant upon the use of hollow prisms filled with liquid, so that two different glasses must be employed whose dispersive powers are very different. When however this is the case, the indices for one ray are not the same as they are for the D line in the case of carbon bisulphide and glass; this difficulty is readily surmounted by using prisms with different refracting angles. This was first

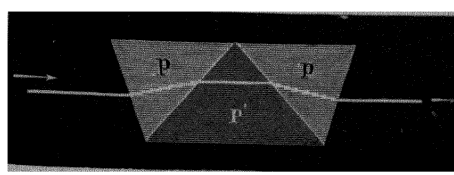


FIG. 31.

done by Amici in 1860, who used flint and crown glass, interposing a flint-glass prism between two crown-glass prisms, as is shown in Fig. 31, with the path of the undeviated ray; five prisms, that is, two of flint and three of crown glass, are also often used. Usually the centre prism (P′ in Fig. 31) of flint glass is now made with a very large refracting angle. This direct-vision combination is especially useful in small pocket spectroscopes; and in these cases a triple combination is usually used, the centre one being made of very dense flint. The prisms are cemented together with Canada balsam; this is both a convenience in construction in order to make them into a single piece of apparatus and also a necessity, as otherwise, in those with wide angles, no light will pass through, owing to the incident angles at the flint prism surfaces being greater than the critical value, so that total reflection would occur.

The Canada balsam, as it has a higher refractive index than air, removes this difficulty.

It will be readily understood that the dispersion $\frac{d\theta}{d\lambda}$ is a function of the dispersing apparatus; that is to say, for example, in prismatic spectroscopes it depends both upon the number and the refracting angles of the prisms employed, and also upon the nature of the medium out of which the prisms are made. In order, therefore, to calculate the value of $\frac{d\theta}{d\lambda}$ for a prism or prisms, it is necessary to take account of both these factors. In all cases of refraction the deviation produced depends upon and varies with the index of refraction, and, further, the index of refraction varies with the wave-length of the light, so we may therefore put—

$$\frac{d\theta}{d\lambda} = \frac{\delta\theta}{\delta\mu} \cdot \frac{\delta\mu}{\delta\lambda} \quad \ldots\ldots\ (1)$$

where $\frac{\delta\theta}{\delta\mu}$ expresses the rate of change in the deviation with change in the index, and $\frac{\delta\mu}{\delta\lambda}$ expresses the rate of change in the index with change in the wave-length. The factor $\frac{\delta\theta}{\delta\mu}$ depends, therefore, only upon the angle of incidence and the refracting angle of the prisms, while $\frac{\delta\mu}{\delta\lambda}$ is solely a function of the medium employed for the prisms. Both these ratios may readily be found.

It has been shown (p. 56) that for a prism at minimum deviation—

$$\mu = \frac{\sin\frac{A+\theta}{2}}{\sin\frac{A}{2}}$$

where A is the refracting angle of the prism and θ the deviation. Now, by differentiation we find that—

$$\frac{\delta\theta}{\delta\mu} = \frac{2 \sin \frac{A}{2}}{\cos \frac{A+\theta}{2}}.$$

But, using the same notation as in Fig. 22, p. 57,

$$\frac{A+\theta}{2} = i = \text{angle of incidence},$$

therefore

$$\frac{\delta\theta}{\delta\mu} = \frac{2 \sin \frac{A}{2}}{\cos i}$$

$$= \frac{2 \sin \frac{A}{2}}{\sqrt{1 - \sin^2 i}};$$

but

$$\sin i = \mu \sin a = \mu \sin \frac{A}{2},$$

therefore

$$\frac{\delta\theta}{\delta\mu} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}}; \quad \ldots \quad (2)$$

which gives us the value of $\frac{\delta\theta}{\delta\mu}$ in terms of the prism angle and the index of refraction.

For a 60° prism this is somewhat simplified, as $\sin 30° = \frac{1}{2}$, and therefore in this particular case—

$$\frac{\delta\theta}{\delta\mu} = \frac{1}{\sqrt{1 - \frac{\mu^2}{4}}}. \quad \ldots \ldots \quad (3)$$

An example may be given to make this clear.

The value of $\frac{\delta\theta}{\delta\mu}$ may be calculated for a 60° prism with an index of refraction of 1·5;

we have here, therefore, $\frac{\delta\theta}{\delta\mu} = \frac{1}{\sqrt{1 - \frac{(1{\cdot}5)^2}{4}}}$

and

$$\frac{\delta\theta}{\delta\mu} = 1{\cdot}512.$$

That is to say, for a very small change in μ upon either side of 1·5 the corresponding change in the deviation is 1·512 times as large, provided the prism be set at minimum deviation. For example, let us suppose that μ were changed from 1·500 to 1·501, then the value of $\delta\theta$ would be equal to 0·001 × 1·512, which = 0·001512. This, however, is in circular measure, and can be found from tables to be 5′ 15″. In other words, if two rays of light passed through the prism, and if the indices of refraction of the prism material were 1·500 and 1·501 respectively, the difference in deviation suffered by the two rays would be 5′ 15″, that is to say, this would be the angle between the two rays after passing through the prism.

It must be remembered that equations (2) and (3) are only strictly true when the prism is set in the position of minimum deviation, and, therefore, perfectly accurate results can only be obtained when the indices of refraction of the rays in question are very little different from that of the ray at minimum.

In practice, however, the equation can be used over large limits without any great error intervening, and it is then useful in designing a spectrograph for the determination of the angular difference between the extreme rays, and hence the length of the spectrum on a photographic plate. In order to obtain the best approximations over such large limits, it is desirable that the index of the ray at minimum deviation be a mean between the indices of the two rays in question. If the two rays have the indices μ_1 and μ_2 respectively, then the mean is $\frac{\mu_1 + \mu_2}{2}$, which let us call μ_3, and we have therefore—

$$\frac{\Delta\theta}{\Delta\mu} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - \mu_3^2 \sin^2 \frac{A}{2}}};$$

but $\Delta\mu$ now equals $\mu_1 - \mu_2$,

therefore

$$\Delta\theta = (\mu_1 - \mu_2)\left(\frac{2 \sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}}\right).$$

This equation is, of course, the more accurate the smaller is $\mu_1 - \mu_2$, but the error only amounts to a few minutes when $\Delta\theta$ is as large as 9°.

Thus far the case of one prism only has been considered; it can, however, be proved that $\frac{\delta\theta}{\delta\mu}$ is simply proportional to the number of prisms, provided they be all of the same size and material. So that if n is the number of prisms we have—

$$\Delta\theta = n(\mu_1 - \mu_2)\left(\frac{2\sin\frac{A}{2}}{\sqrt{1 - \mu_3^2\sin^2\frac{A}{2}}}\right) \quad . \quad . \quad (4)$$

and for 60° prisms $= \dfrac{n(\mu_1 - \mu_2)}{\sqrt{1 - \frac{\mu_3^2}{4}}}$.

For the evaluation of the ratio $\frac{\delta\mu}{\delta\lambda}$ we can make use of Hartmann's simple interpolation formula.[1] The relation between λ and μ can be found from the equations—

$$\left.\begin{aligned} \mu &= \mu_0 + \frac{c}{(\lambda - \lambda_0)^a} \\ \text{and} \quad \lambda &= \lambda_0 + \frac{c}{(\mu - \mu_0)^{\frac{1}{a}}} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where c, μ_0, and λ_0 are constants; a has the value for glass of about 1·2. On putting $a = 1$ we obtain the approximate equations—

$$\left.\begin{aligned} \mu &= \mu_0 + \frac{c}{\lambda - \lambda_0} \\ \text{and} \quad \lambda &= \lambda_0 + \frac{c}{\mu - \mu_0} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In the latter case we may use the deviation in place of μ and write—

[1] *Astrophys. Journal*, **8**. 218 (1898).

$$\lambda = \lambda_0 + \frac{c}{D - D_0}$$

in which case the formula can be used for the interpolation of wave-lengths in a photographed spectrum, if those of certain lines are known. Hartmann has tested this formula and finds that very good results can be obtained.

By differentiation we obtain the ratio—

$$\frac{\delta\mu}{\delta\lambda} = -\frac{c}{(\lambda - \lambda_0)^2} \quad \cdots\cdots \quad (7)$$

the negative sign simply meaning that a small increase in the value of λ produces a decrease in the value of μ. The equation shows that $\frac{\delta\mu}{\delta\lambda}$ can at once be found if we know c and λ_0, which are characteristic constants of the dispersing medium. They can be calculated quite easily if the indices of refraction of three rays are known. As an example, we may take the case of a glass (0·167 of Schott and Genossen, Jena [1]) for which the indices are—

$\mu = 1{\cdot}6076$ for A′ line $\lambda = 7{\cdot}677 \times 10^{-5}$ cm.
$\mu = 1{\cdot}6169$ for D line $\lambda = 5{\cdot}893 \times 10^{-5}$ cm.
$\mu = 1{\cdot}6393$ for G′ line $\lambda = 4{\cdot}341 \times 10^{-5}$ cm.

These values give us three equations, from which the following values of the constants are found—

$\mu_0 = 1{\cdot}58882$, $\lambda_0 = 2{\cdot}2906 \times 10^{-5}$, and $c = 0{\cdot}10113 \times 10^{-5}$

From these constants the values of the indices for other rays may be calculated; for example, for the C and F lines ($\lambda = 6{\cdot}563 \times 10^{-5}$ and $\lambda = 4{\cdot}862 \times 10^{-5}$) the indices are calculated from equation (6) to be 1·6125 and 1·6282. The values given by Schott and Genossen are 1·6121 and 1·6289; the errors are thus + 0·02 and − 0·04 per cent. respectively. This formula does not give such good results if the extreme rays used for calculating the constants are very far removed from one another in the spectrum. This, of course, is only to be expected with a simple interpolation formula, and further, it must be remembered that we have

[1] See footnote, p. 90.

omitted the constant power a from the denominator. It will be found, however, that by calculation of the constants for each particular region of the spectrum required, very excellent approximations can be obtained; in actual practice this is all that will be necessary, because the region of the spectrum photographed at one time can be said rarely to reach from the A line to the extreme ultra-violet.

If the constants are known it is possible to calculate the ratio $\frac{\delta\mu}{\delta\lambda}$ for any substance for light of any wave-length. We have found already that—

$$\frac{\delta\mu}{\delta\lambda} = -\frac{c}{(\lambda - \lambda_0)^2} \quad \ldots\ldots \quad (8)$$

and as an example let us calculate $\frac{\delta\mu}{\delta\lambda}$ in the immediate neighbourhood of the F line for the glass dealt with above. We see, therefore, that—

$$\frac{\delta\mu}{\delta\lambda} = -\frac{0{\cdot}1011 \times 10^{-5}}{(4{\cdot}862 \times 10^{-5} - 2{\cdot}291 \times 10^{-5})^2}$$
$$= -1529{\cdot}5,$$

which means that, in the neighbourhood of the F line, a small change in λ produces a change in μ which is 1529·5 times as great.

Similarly $\frac{\delta\mu}{\delta\lambda}$ may be calculated for any medium with a very close degree of approximation.

We have seen that—

$$\frac{\delta\theta}{\delta\mu} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}},$$

and as the dispersion $\frac{d\theta}{d\lambda} = \frac{\delta\theta}{\delta\mu} \times \frac{\delta\mu}{\delta\lambda}$ we are now in a position to calculate the dispersion for any substance. As an example let us find the angle between the two D lines of sodium after passage through a single 60° prism of the densest Jena flint glass (S 57); for this glass $\mu_0 = 1{\cdot}8824$, $c = 0{\cdot}27148 \times 10^{-5}$,

and $\lambda_0 = 2{\cdot}5095 \times 10^{-5}$. It is first of all necessary to calculate the value of $\frac{d\theta}{d\lambda}$ in the neighbourhood of the D lines; this for the single 60° prism is equal to—

$$\frac{1}{\sqrt{1 - \frac{(1{\cdot}9626)^2}{4}}} \times -\left[\frac{0{\cdot}27148 \times 10^{-5}}{(5{\cdot}893 \times 10^{-5} - 2{\cdot}5095 \times 10^{-5})^2}\right]$$

where 1·9626 is the value of μ_D given for this glass.

We have, therefore $\frac{d\theta}{d\lambda} = 5{\cdot}192 \times [-2371{\cdot}4]$

$$= -12312{\cdot}9.$$

Now, the difference in wave-length ($d\lambda$) between the two D lines within a sufficient approximation for the present purpose is $0{\cdot}006 \times 10^{-5}$ cm.; multiplying this by the dispersion, we find the angle between the two rays to be—

0·0007387 radians, or 2′ 32″ very nearly.

In a similar way we can find the dispersion for any substance with a very close degree of approximation; for convenience, in the tables giving the various materials for prisms on page 91, the values of the constants of Hartmann's interpolation formula are given. Attention may again be drawn to the fact that, when more than one prism is employed of the same material, the dispersion is simply proportional to the number of the prisms.

The value of $\frac{\delta\theta}{\delta\mu}$ for a prism train can be expressed in another way, and one that is more convenient for certain purpposes.

By differentiation of the formula—

$$\mu = \frac{\sin\frac{A+\theta}{2}}{\sin\frac{A}{2}},$$

we see that

$$\frac{\delta\theta}{\delta\mu} = \frac{2\sin\frac{A}{2}}{\cos\frac{A+\theta}{2}};$$

then, by using the same symbols as upon page 57—

$$\frac{\delta\theta}{\delta\mu} = \frac{2 \sin a}{\cos i} = \frac{2\,\frac{\sin i}{\mu}}{\cos i},$$

and therefore $$\frac{\delta\theta}{\delta\mu} = \frac{2}{\mu} \tan i;$$

which gives the ratio $\frac{\delta\theta}{\delta\mu}$ as a function of the angle of incidence on the first prism face.

Another equation which gives μ as a function of λ is the well-known one proposed by Cauchy—

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots$$

where A, B, C, etc., are characteristic constants of the medium. This equation is only, however, approximate, yet the simple expression—

$$\mu = A + \frac{B}{\lambda^2}$$

will give results sufficiently near for many purposes. For example, by differentiation we see that—

$$\frac{\delta\mu}{\delta\lambda} = -\frac{2B}{\lambda^3},$$

and therefore it can be seen that the ratio $\frac{\delta\mu}{\delta\lambda}$ is inversely proportional to the cube of the wave-length.

Although the name dispersion has been given to ratio $\frac{d\theta}{d\lambda}$ in the above, yet the same name is often applied to each of the partial ratios $\frac{\delta\theta}{\delta\mu}$ and $\frac{\delta\mu}{\delta\lambda}$.

Resolving Power.—Lord Rayleigh has shown that, in the case of the image of an infinitely narrow slit produced at the focus of a telescope lens, the linear distance ξ of the first diffraction minimum from the principal maximum is defined by the equation—

$$\frac{a\xi}{m\lambda f} = 1$$

where a is the linear aperture of the lens, and f its focal length, and m is a constant varying from 1·0 for rectangular to 1·2 for circular apertures. From this equation we find that—

$$\frac{\xi}{f} = \frac{m\lambda}{a},$$

$\frac{\xi}{f}$ being the angular distance between the principal maximum and the first minimum of the diffraction rings surrounding the main image. Arguing from this, Rayleigh concludes that, in the case of two rays, if we wish to see them separated or "resolved," the least possible angle that can be allowed between them is equal to $\frac{\xi}{f}$. If, therefore, we express the angle between the two rays by $d\theta$, we then see that the minimum condition for resolution is given by—

$$d\theta = \frac{m\lambda}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where λ is considered as the mean wave-length of the pair. We may now investigate how the necessary condition for resolution of two lines can be obtained by means of prisms. As Rayleigh pointed out, the ratio $\frac{\delta\theta}{\delta\mu}$ for a prism is given by the equation—

$$\frac{\delta\theta}{\delta\mu} = \frac{s_1 - s_2}{a}$$

where s_1 and s_2 are the thicknesses of the prism material which are traversed by the two extreme rays of the beam. In a properly constructed spectroscope in which the beam of light from the collimator just completely fills the prism, s_2 is zero, and s_1 equals the thickness of the prism base t;

therefore

$$\frac{\delta\theta}{\delta\mu} = \frac{t}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

This may readily be seen to be true from Fig. 32, in which EB = a and BC = t.

Now, $$EB = AB \cos i = AB\sqrt{1 - \sin^2 i}$$

$$= AB\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}};$$

again, $$BF = AB \sin \frac{A}{2},$$

and $$t = 2BF = 2AB \sin \frac{A}{2},$$

therefore $$\frac{t}{a} = \frac{2 \sin \frac{A}{2}}{\sqrt{1 - \mu \sin^2 \frac{A}{2}}};$$

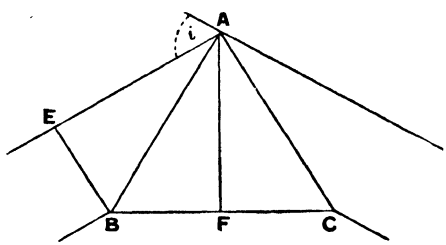


FIG. 32.

this, however, is the value of $\frac{\delta\theta}{\delta\mu}$ from Fraunhofer's equation,[1]

and thus $$\frac{\delta\theta}{\delta\mu} = \frac{a}{t}.$$

Now, by equations (9) and (10) it follows that, for the minimum condition of resolution, omitting the constant m—

$$t = \frac{\lambda}{\delta\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

or in other words—in order that two lines may be seen separated in a prism spectroscope, it is necessary that the total thickness of

[1] See equation (2) above.

the base of the prism or prisms be equal to the quotient of the wave-length by the difference in the indices of the two lines. As an example of the application of this the necessary value of t for a given resolution may be calculated, and the two D lines of sodium may be chosen; further, the glass S 57 dealt with on page 72 may be taken, and the thickness of a prism of this glass calculated which is necessary just to resolve the D lines.

For this glass it was found that $\frac{\delta\mu}{\delta\lambda} = -2371{\cdot}4$,

therefore $\delta\mu = 2371{\cdot}4 \times 0{\cdot}006 \times 10^{-5}$,

assuming the wave-lengths of the two D lines to be 5896 and 5890 Ångström units respectively;

therefore $\delta\mu = 14{\cdot}23 \times 10^{-5}$.

Then, from equation (11) $t = \frac{5{\cdot}893}{14{\cdot}25}$ cms.

$= 0{\cdot}414$ cm.

In order, therefore, to see the D lines resolved it is necessary, in the case of the glass No. S 57 to use a prism whose base is at least 0·414 cm. long. Equation (11) shows very clearly that the amount of resolution obtained with a prism depends entirely upon the size of the base; the angle of refraction has no influence, and it follows that all the possible prisms constructed upon the same base as in Fig. 33 give equal resolution.

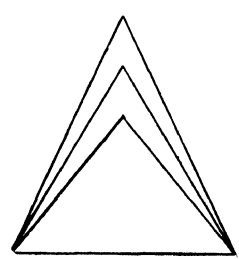


FIG. 33.

When a direct-vision prism system is employed, t in equation (11) must be replaced by $t_1 - t_2$, where t_1 and t_2 are the total thicknesses of the bases of the crown- and flint-glass prisms respectively.

The necessary conditions for resolution may be differently and rather more conveniently expressed; by equations (9) and (10) above, omitting the constant m—

$$d\theta = \frac{t\delta\mu}{a} = \frac{\lambda}{a},$$

$\frac{\lambda}{a}$ being the minimum allowable value of the two first quantities. Multiplying through by $\frac{a}{d\lambda}$ we obtain—

$$a\frac{d\theta}{d\lambda} = t\frac{\delta\mu}{\delta\lambda} = \frac{\lambda}{d\lambda} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where again $\frac{\lambda}{d\lambda}$ is the minimum allowable value. Now $\frac{\lambda}{d\lambda}$, or the ratio between the mean wave-length of a pair of lines which can just be resolved in a spectroscope, and the difference in wave-length between the two components, is called the *resolving power* of the spectroscope. An instrument which just resolves the D lines is said to have a resolving power of 987. Omitting the constant m, therefore, which is not far from unity, equation (12) shows that the resolving power is equal to the product of the linear (effective) aperture and the dispersion. With a given dispersion, therefore, the resolving power varies directly as the aperture of the apparatus. This is perfectly general, and is true for all dispersing trains, gratings and prisms alike. The resolving power $\frac{\lambda}{d\lambda}$ is usually denoted by the letter r, and, as emphasised before, refers to the condition of an infinitely narrow slit and infinitely narrow spectrum lines, that is to say, lines which are perfectly homogeneous; neither of these conditions can be realised in practice, and therefore the practical resolving power differs by a certain amount from the theoretical value obtained from equation (12). The practical resolving power of spectroscopes will be dealt with in Chapter X.

We have already seen that the ratio $\frac{\delta\mu}{\delta\lambda}$ varies inversely as λ^3, and therefore it follows that in any prism spectroscope the theoretical resolving power also varies inversely as the cube of the wave-length.

Dimensions of Prisms.—In considering the best dimensions for prisms it is necessary, of course, to take account of the dispersion and the losses of light by reflection and absorption

respectively. This has been done by Pickering,[1] who gave tables showing the comparative efficiency of different forms of prisms made from glasses whose indices are 1·5, 1·6 and 1·7 respectively. The dispersion in these cases may be considered as the ratio $\frac{\delta\theta}{\delta\mu}$, which has already been shown to be equal to $\frac{2 \sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}}$ or $\frac{2}{\mu} \tan i$ at the position of minimum deviation.

Loss by Reflection.—It must be remembered that the light refracted by the surface of a medium is partially polarised, and therefore in dealing with the amount which is reflected it is necessary to apply the laws for the reflection of polarised light. Fresnel has shown [2] that in the case of light polarised at right angles to the plane of incidence, if the intensity of the incident ray be put equal to 1, the intensity of the reflected light is equal to $\frac{\sin^2 (i - r)}{\sin^2 (i + r)}$ where i and r are the angles of incidence and refraction; this we may call X. Similarly in the case of light polarised in the plane of incidence the intensity of the reflected light is equal to $\frac{\tan^2 (i - r)}{\tan^2 (i + r)}$, which we may call Y. The amount transmitted, therefore, in each case is equal to 1 − X and 1 − Y. If we regard ordinary light as composed of two beams of equal intensity polarised at right angles to one another, then the amount reflected will be $\frac{X}{2} + \frac{Y}{2}$, and the amount transmitted will be $\frac{1}{2}[(1 - X) + (1 - Y)]$. On meeting a second surface the amount transmitted will be $\frac{1}{2}[(1 - X)^2 + (1 - Y)^2]$, and in general for m surfaces $\frac{1}{2}[(1 - X)^m + (1 - Y)^m]$. This formula Pickering applies to a spectroscope in which the prisms are all set at minimum deviation.

[1] *Phil. Mag.* (4), **36**. 39 (1868).

[2] Fresnel, *Œuvres*, tom. I. pp. 441-479.

These formulæ of Fresnel's, when $i = r = 0°$, that is to say at perpendicular incidence, can both be simplified to the form $\left(\frac{\mu - 1}{\mu + 1}\right)^2$, which is of importance in determining the loss by reflection at the surfaces of lenses.

Absorption.—It is well known that when light passes through a medium a certain amount is absorbed; if I denote the intensity of the incident beam and E that of the emergent or transmitted beam, we then will have—

$$\log\left(\frac{E}{I}\right) = -\beta x$$

where β is a constant depending on the nature of the medium and x is the thickness of the medium. If, then, the intensity of the incident ray be put equal to 1, it follows that the logarithm of the amount absorbed is proportional to the thickness of the medium traversed by the beam.

In the case of prisms x is equal to the average thickness of glass traversed; this is equal to half the base multiplied by the number of prisms which we may put equal to N. Half the base of a prism is, however, equal to $\frac{a \sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}}$ where a is equal to the diameter of the aperture at minimum deviation; hence it follows that with an incident beam of intensity = 1, the logarithm of the amount absorbed will be proportional to—

$$a \,.\, N \,.\, \frac{\sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}} \,.$$

But it has already been shown that the dispersion $\frac{\delta\mu}{\delta\lambda}$ is proportional to $N \frac{\sin \frac{A}{2}}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}}$ and therefore the logarithm

of the amount of light absorbed is proportional to the product of the aperture and the dispersion $\frac{\delta\mu}{\delta\lambda}$. This is an important result, for it means that in spectroscopes of equal dispersion, possessing prisms of the same material, the absorption is the same in all; in other words, it makes no difference to the absorption whether a large number of prisms with small refracting angles or a smaller number with large angles be used, provided both trains have the same $\frac{\delta\mu}{\delta\lambda}$ and be of the same material. The question of absorption, therefore, does not enter into the question of the best dimensions for prisms.

Pickering has calculated the angles of deviation, the dispersion and the amount of light transmitted by prisms of different angles for the three indices 1·5, 1·6, and 1·7. His results are given in the following tables. The deviation is, of course, $= 2i - A$.

TABLE I.—45° PRISMS.

	μ	1 prism.	2 prisms.	3 prisms.	4 prisms.	5 prisms.	10 prisms.
Deviation	1·5	25° 4′	50° 8′	75° 12′	100° 16′	125° 20′	250° 40
	1·6	30° 30′	61° 0′	91° 30′	122° 0′	152° 30′	305° 0′
	1·7	36° 10′	72° 20′	108° 30′	144° 40′	180° 50′	361° 40′
Dispersion	1·5	0·935	1·870	2·804	3·739	4·674	9·348
	1·6	0·968	1·936	2·904	3·872	4·840	9·680
	1·7	1·008	2·016	3·023	4·031	5·039	10·078
Proportion transmitted	1·5	0·916	0·841	0·774	0·724	0·661	0·461
	1·6	0·892	0·799	0·719	0·651	0·592	0·391
	1·7	0·859	0·745	0·653	0·578	0·516	0·324

TABLE II.—60° PRISMS.

	μ	1 prism.	2 prisms.	3 prisms.	4 prisms.	5 prisms.	10 prisms.
Deviation	1·5	37° 10′	74° 20′	111° 30′	148° 40′	185° 50′	371° 40′
	1·6	46° 16′	92° 32′	138° 48′	185° 4′	231° 20′	462° 40′
	1·7	56° 26′	112° 52′	169° 24′	225° 44′	282° 10′	564° 20′
Dispersion	1·5	1·512	3·023	4·535	6·046	7·558	15·116
	1·6	1·667	3·334	5·000	6·667	8·334	16·668
	1·7	1·899	3·797	5·696	7·594	9·493	18·986
Proportion transmitted	1·5	0·895	0·811	0·742	0·686	0·641	0·509
	1·6	0·853	0·748	0·672	0·618	0·578	0·491
	1·7	0·801	0·681	0·608	0·565	0·538	0·505

TABLE III.—ANGLES OF PRISMS 67° 22′, 64°, AND 60° 56′.

	μ	Prism angle.	1 prism.	2 prisms.	3 prisms.	4 prisms.	5 prisms.	10 prisms.
Deviation	1·5	67° 22′	45° 16′	90° 32′	135° 48′	181° 4′	226° 20′	452° 40′
	1·6	64° 0′	52° 0′	104° 0′	156° 0′	208° 0′	260° 0′	520° 0′
	1·7	60° 56′	58° 8′	116° 16′	174° 24′	232° 32′	290° 40′	580° 20′
Dispersion	1·5	67° 22′	2	4	6	8	10	20
	1·6	64° 0′						
	1·7	60° 56′						
Proportion transmitted	1·5	67° 22′	0·863	0·763	0·691	0·639	0·600	0·520
	1·6	64° 0′	0·818	0·702	0·629	0·582	0·552	0·505
	1·7	60° 56′	0·780	0·657	0·588	0·549	0·523	0·501

By means of these tables the comparative values of the different angles can readily be obtained. For example, three trains of 10 prisms, each with angles of 45°, 60°, and 64°, all being with index 1·6, may be chosen.

	Deviation.	Dispersion.	Light transmitted.
10 prisms of 45°	305° 0′	9·680	0·3911
,, ,, 60°	462° 40′	16·668	0·4912
,, ,, 64°	520° 0′	20·000	0·5050

Again comparing trains giving equal deviation—

	Deviation.	Dispersion.	Light transmitted.
12 prisms of 45°	366° 0′	11·616	0·339
8 ,, ,, 60°	370° 8′	13·334	0·532
7 ,, ,, 64°	364° 0′	14·000	0·521

These examples show the superiority of the 60° prism over the 45° prism.

In order to compare the relative values of prisms of different angles, it is preferable to compare together prisms of equal resolving power, as one can then judge more readily their relative merits. If the resolving power be kept constant, but the refracting angle be changed, then the following quantities will vary, the volume of the prism, the length of refracting face, the aperture, the angle of incidence, the loss of light, and the dispersion; the dispersion here being the value of the ratio $\frac{\delta\theta}{\delta\mu}$. Wadsworth[1] has calculated these quantities for different refracting angles, the length of base being kept constant, since all prisms of the same glass, with equal bases, have the same resolving power; this has been done for different values of the index of refraction, namely, 1·8, 1·7, 1·6, and 1·5. He first of all gives the values of the volume and of the length of the refracting face of prisms of unit base, which are as follows:—

[1] *Astrophys. Journ.*, **2**. 264 (1895).

Refracting angle = A.	Length of refracting face.	Volume of prism.	Refracting angle = A.	Length of refracting face.	Volume of prism.
30°	1·932	0·933	64°	0·943	0·400
35°	1·663	0·793	68°	0·894	0·371
40°	1·462	0·687	72°	0·850	0·344
45°	1·307	0·604	75°	0·822	0·326
50°	1·183	0·536	77·5°	0·799	0·312
55°	1·082	0·480	80°	0·788	0·298
60°	1·000	0·433	82·5°	0·758	0·285

In the four following tables are given the values of the angle of incidence, the aperture, loss of light by reflection, and dispersion $\left(\frac{\delta\theta}{\delta\mu}\right)$ for prisms of unit base for the indices 1·5, 1·6, 1·7, and 1·8 :—

$\mu = 1{\cdot}5$.

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	22° 51′	1·780	0·0793	0·5618
35°	26° 49′	1·484	0·0801	0·6738
40°	30° 52′	1·255	0·0815	0·7970
45°	35° 2′	1·070	0·0837	0·9348
50°	39° 20′	0·915	0·0883	1·093
55°	43° 45′	0·782	0·0953	1·278
60°	48° 35′	0·661	0·1047	1·512
64°	52° 39′	0·572	0·1188	1·747
68°	57° 1′	0·487	0·1412	2·054
72°	61° 51′	0·401	0·1795	2·492
75°	65° 57·5′	0·335	0·2280	2·988
77·5°	69° 52′	0·275	0·2938	3·636
80°	74° 37′	0·206	0·4093	4·806
82·5°	81° 30′	0·112	0·6686	8·922

Wadsworth has put these values on to curves, and from an inspection of these or the above tables the best value of the refracting angle to be used in any given case can be determined. If the reduction of the angular dispersion be of primary importance, then it is preferable to use prisms of refracting angles not much exceeding 65° for materials of low refractive

$\mu = 1{\cdot}6$.

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	24° 28′	1·758	0·0993	0·569
35°	28° 45·5′	1·458	0·1060	0·686
40°	33° 11′	1·223	0·1083	0·817
45°	37° 45′	1·033	0·1116	0·968
50°	42° 33′	0·873	0·1151	1·145
55°	47° 33′	0·731	0·1274	1·368
60°	53° 8′	0·600	0·1473	1·667
64°	57° 59′	0·500	0·1735	1·999
68°	63° 28′	0·399	0·2213	2·504
72°	70° 12′	0·288	0·3222	3·470
75°	76° 55′	0·186	0·4976	5·378

$\mu = 1{\cdot}7$.

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	26° 6′	1·735	0·1214	0·5764
35°	30° 44·5′	1·429	0·1292	0·6998
40°	35° 33′	1·189	0·1358	0·8408
45°	40° 35′	0·992	0·1416	1·008
50°	45° 55·5′	0·760	0·1494	1·315
55°	51° 43′	0·671	0·1665	1·491
60°	58° 13′	0·527	0·1991	1·899
64°	64° 16′	0·410	0·2517	2·441
68°	71° 55′	0·277	0·3731	3·608
72°	88° 28′	0·228	0·9772	4·394

$\mu = 1{\cdot}8$.

Angle = A.	Angle of incidence.	Aperture.	Loss of light.	Dispersion.
30°	27° 46′	1·709	0·1585	0·5850
35°	32° 46	1·398	0·1605	0·7152
40°	38° 0′	1·152	0·1643	0·8680
45°	43° 32′	0·900	0·1711	1 111
50°	49° 31·5′	0·768	0·1834	1·302
55°	56° 13′	0·602	0·2100	1·661
60°	64° 10′	0·436	0·2700	2·294
64°	72° 32′	0·283	0·3971	3·532
66°	78° 38′	0·181	0·5675	5·528

index, or 55° for those of high index, since beyond this point any small increase in angle greatly increases the dispersion without decreasing the volume. On the other hand, there is no great gain in reduction of dispersion, and almost none in reduction of loss by reflection, by decreasing the angle below 60°. In the case of a prism for which $\mu = 1{\cdot}5$, the latter loss is only diminished by about 2·5 per cent. by decreasing the angle from 60° to 30°, while the aperture and dimensions of the spectroscope are increased nearly three times.

If the condition of small dispersion is of less consequence, then it is readily seen that the refracting angle may be increased with decided advantage until it reaches the limit imposed by the diminution of the brightness of the image. When there is plenty of light we may even use angles as large as 80°, in which case the telescopes and other parts of the spectroscope are less than one-third as large as for an angle of 60°, and less than one-eighth those required for a 30° prism. It must, however, be remembered that prisms of wide angles are much more difficult to make than those of small, because of the fact that increased distortion is produced in the spectrum by imperfections in the refracting faces. Very much greater care must be taken in the grinding and polishing of the faces, a fact which increases the cost.

In order that a prism should entirely accept the beam of rays from the collimating lens, it is necessary that the length of the refracting faces should be longer than their height. The height of the prism should be equal to the diameter of the lens; this has been shown on p. 76 to be equal to the length of the face $\times \sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}$ when in the position of minimum deviation; for 60° prisms the height equals the length of face $\times \sqrt{1 - \frac{\mu^2}{4}}$.

Thus the length of face $= \frac{h}{\sqrt{1 - \mu^2 \sin^2 \frac{A}{2}}}$ or $\frac{h}{\sqrt{1 - \frac{\mu^2}{4}}}$

for 60° prisms.

We obtain, therefore, the following lengths for prisms of 60°—

$\mu = 1{\cdot}5$ length = height × 1·51
$\mu = 1{\cdot}6$ length = height × 1·67
$\mu = 1{\cdot}7$ length = height × 1·89
$\mu = 1{\cdot}8$ length = height × 2·29.

The Curvature of Spectrum Lines as produced by Prisms.—It will always be found that the spectrum lines as seen in a prism spectroscope are curved, with the convex sides turned towards the red end of the spectrum. This is due to the fact that only the rays from the centre of the slit pass through a principal plane of the prism; by a principal plane is meant a plane perpendicular to the plane of the refracting edge of the prism. All cases of refraction through a prism have hitherto been dealt with on the assumption that the rays pass through a principal plane. It can be proved that in order that the deviation be a minimum, it is necessary that two conditions be satisfied, first, that the rays pass through a principal plane, and second, that the angles of incidence and emergence be equal, as has already been stated. The collimator lens is only able to render parallel the rays it receives from the centre of the slit, and therefore these rays only traverse principal planes of the prism; the rays from the other portions of the slit thus do not traverse a principal plane, and therefore suffer a greater amount of deviation, an amount which increases the further from the centre of the slit the rays start. The lines are, therefore, curved when seen with an eyepiece or received on a photographic plate, their ends being bent towards the violet end of the spectrum.

Materials for Prisms.—The media usually employed for prisms are as follows:—carbon bisulphide, glass, quartz, Iceland spar or calcite, fluorite, sylvin, and rock-salt. Of these, glass is, of course, the most common, owing to its cheapness and also great variety in its dispersive power. Carbon bisulphide has a very high dispersive power, but is very inconvenient, owing to its being a liquid; quartz, Iceland spar, and fluorite are used on account of their great transparency to the ultra-violet rays, though at the

present time fluorite is very rare. Rock-salt and sylvin are useful for their transparency to the infra-red portion of the spectrum.

Carbon bisulphide, when used, must, of course, be enclosed in a hollow prism, which must be kept well closed on account of the great volatility of the liquid. The hollow prism may be made in various ways; usually a glass prism is moulded, approximately with an angle of 60°, and with a hollow core, as is shown in Fig. 34. The faces are then carefully worked to the 60° angle, and plane-parallel plates of glass are cemented on, best with a mixture of glue and treacle. A hole, of course, must be drilled in the top of the prism for the admission of the liquid; this hole has a stopper accurately ground to fit it, which is cemented in after the prism has been filled. The use of a carbon bisulphide prism is not to be recommended, on account of the disturbances which are inclined to be produced in the spectrum as a result of temperature changes. The index of refraction changes rapidly with temperature; the value of $\frac{d\mu}{dt}$ lies between 0·00076 for $\lambda = 7600$ and 0·00091 for $\lambda = 4000$, so that very considerable distortions tend to be produced, owing to convection currents in the liquid.

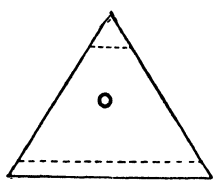


FIG. 34.

The indices of refraction are given in the following table (Ketteler[1]):—

Temperature.	$\lambda = 7605$.	$\lambda = 6563$.	$\lambda = 5893$.	$\lambda = 4861$.	$\lambda = 4341$.	$\lambda = 3969$.
	A	C	D	F	G′	H
− 20°	1·63946	1·64952	1·65950	1·68585	1·70984	1·73617
− 10°	1·63183	1·64174	1·65158	1·67752	1·70114	1·72702
0°	1·62429	1·63405	1·64375	1·66929	1·69252	1·71798
+ 10°	1·61676	1·62638	1·63593	1·66107	1·68393	1·70896
20°	1·60919	1·61865	1·62806	1·65281	1·67528	1·69988
30°	1·60146	1·61078	1·62004	1·64437	1·66646	1·69063
40°	1·59359	1·60277	1·61187	1·63581	1·65752	1·68125

The dispersive power may be estimated by the differences

[1] *Ann. der Phys.*, **35**. 662 (1888).

in the values of μ for the different rays, which are as follows at a temperature of 10° :—

Complete dispersion.	Partial dispersion.				
A to H.	A to C.	C to D.	D to F.	F to G'.	G' to H.
0·09220	0·00962	0·00955	0·02514	0·02286	0·02503

Rubens [1] has measured the indices of carbon bisulphide for the infra-red rays, with the following results :—

λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ
0·777	1·6104	1·164	1·5960
0·823	1·6077	1·270	1·5940
0·873	1·6049	1·396	1·5923
0·931	1·6025	1·552	1·5905
0·999	1·6000	1·745	1·5888
1·073	1·5978	1·998	1·5872

It will be seen, on comparison of these values with those of other substances, that the dispersive power of carbon bisulphide is relatively very high.

A still greater dispersive power is possessed by monobromonaphthalene, which has the advantage over carbon bisulphide in having a smaller value of $\frac{d\mu}{dt}$, that is to say, the change of μ with temperature is less.

The indices of refraction for this liquid are as follows (Simon [2]) :—

	$\lambda = 7680$.	$\lambda = 6563$.	$\lambda = 5893$.	$\lambda = 5350$.	$\lambda = 4861$.	$\lambda = 4341$.	$\lambda = 3610$.
μ	1·62961	1·64366	1·65762	1·66796	1·68142	1·70371	1·76927

Complete dispersion.	Partial dispersion.				
$\lambda = 7680$ to $\lambda = 3610$.	$\lambda = 7680$ to C.	C to D.	D to F.	F to G'.	G' to $\lambda = 3610$.
0·13966	0·01405	0·01396	0·02380	0·02229	0·06556

It will be noticed, from the above, that the total dispersion is, in the case of monobromonaphthalene, 50 per cent. larger than that of carbon bisulphide, but the partial dispersions from

[1] *Ann. der Phys.*, **45**. 238 (1892). [2] *Ibid.*, **53**. 542 (1894).

D to F and F to G′ are less. The value of $\frac{d\mu}{dt} = 0{\cdot}00048$ (Walter[1]), which is considerably less than in the case of carbon bisulphide.

Generally speaking, glass is the best material to use for prisms, unless it be desired to work with the ultra-violet, or extreme infra-red. The advantage of glass lies in its cheapness, and also its toughness; and, further, it is now made in very many varieties, which differ greatly in dispersive power.

The table shown on p. 91 gives a list of different glasses selected from the catalogue of Schott and Genossen, in Jena.[2]

In the first column of this table are given the catalogue numbers, followed by the description of the glasses; in the third column are given the values of the indices of refraction for the D line. The indices for the other rays of the spectrum are not given directly, but in their place the values of the so-called dispersion, which is the difference in the values of the indices of the two rays; for example, the fourth column contains the value of $\mu_F - \mu_C$ for each of the glasses. This is called the medium dispersion, because the brightest rays of the spectrum all lie between C and F. The so-called relative dispersion of a glass is given by the expression $\frac{\Delta\mu}{\mu_D - 1}$, where $\Delta\mu$ is the medium dispersion $(\mu_F - \mu_C)$; the reciprocals of this relative dispersion are given in the fifth column. These values are of importance in the achromatisation of lenses, as will be more fully explained when we deal with these relations. The three following columns contain the values of the partial dispersion, and finally we have the specific gravity; the numbers under each value of the partial dispersion express the ratio between the partial dispersion and the medium dispersion $(\mu_F - \mu_C)$. These ratios and the values of ν define at once the

[1] *Ann. der Phys.*, **42**. 411 (1891).

[2] These glasses were taken from Messrs. Schott and Genossen's list as published in the year 1902. The firm has been kind enough to inform me that they expect to publish a new list of glasses in about a year's time. Although most of the glasses given in the table are no longer made they are kept in the text with a view of showing the relation between the constants of the different types of glass.

Number of glass.	Description.	μ_D	Medium dispersion C to F.	$\nu = \frac{\mu - 1}{\Delta\mu}$	Partial dispersion. A′ to D.	Partial dispersion. D to F.	Partial dispersion. F to G′.	Specific gravity.	Constants of Hartmann's formula. μ_0	Constants of Hartmann's formula. λ_0	Constants of Hartmann's formula. C.
0·225	Light phosphate crown .	1·5159	0·00737	70·0	0·00485 0·658	0·00515 0·698	0·00407 0 552	2·58	1·49919	$1·5286 \times 10^{-5}$	$0·07292 \times 10^{-8}$
S 40	Medium phosphate crown	1·5590	0·00835	66·9	0·00546 0·654	0·00587 0·702	0·00466 0·557	3·07	1·54039	$1·5985 \times 10^{-5}$	$0·07991 \times 10^{-8}$
0·802	Borosilicate crown . . .	1·4967	0·00765	64·9	0·00504 0·659	0·00534 0 698	0 00423 0·553	2·38	1·47930	$1·5188 \times 10^{-5}$	$0·07611 \times 10^{-8}$
0·374	Silicate crown . .	1·5109	0·00844	60·5	0·00547 0 648	0·00593 0·703	0·00479 0·568	2·48	1·49251	$1·6782 \times 10^{-5}$	$0·07752 \times 10^{-8}$
0·1209	Densest baryta crown .	1·6112	0·01068	57·2	0·00680 0·636	0·00753 0·704	0·00610 0 571	3·55	1·58872	$1·7814 \times 10^{-5}$	$0·09241 \times 10^{-8}$
0·608	Crown of high dispersion	1·5149	0·00943	54·6	0·00595 0·631	0·00666 0·706	0·00543 0·576	2·60	1·49544	$1·8432 \times 10^{-5}$	$0·07880 \times 10^{-8}$
0·583	Baryta light flint . . .	1·5688	0·01110	51·2	0·00696 0·627	0·00786 0·708	0·00644 0·580	3·16	1·54623	$1·8906 \times 10^{-5}$	$0·09035 \times 10^{-8}$
0·578	Baryta light flint . . .	1·5825	0·01255	46·4	0·00777 t 0·619	0·00891 0·710	0·00739 0·589	3·29	1·55771	$1·9860 \times 10^{-5}$	$0·09684 \times 10^{-8}$
0·161	Borosilicate flint . . .	1·5676	0·01216	46·7	0·00762 0·627	0·00860 0·707	0·00709 0·583	2·97	1·54298	$1·9010 \times 10^{-5}$	$0·09826 \times 10^{-8}$
0·569	Ordinary light flint . .	1·5738	0·01385	41·4	0·00853 0·615	0·00987 0·713	0·00831 0·600	3·22	1·54685	$2·0406 \times 10^{-5}$	$0·10382 \times 10^{-8}$
0·748	Baryta flint	1·6235	0·01599	39·1	0·00965 0·605	0·01142 0·713	0·00965 0·604	3·67	1·59413	$2·2472 \times 10^{-5}$	$0·10708 \times 10^{-8}$
0·167	Ordinary silicate flint .	1·6169	0·01691	36·5	0·01026 0·606	0·01206 0·713	0·01029 0·608	3·60	1·58882	$2·2906 \times 10^{-5}$	$0·10113 \times 10^{-8}$
0·335	Dense silicate flint . . .	1·6372	0·01831	34·8	0·01099 0·600	0·01308 0·714	0·01124 0·614	3·77	1·60333	$2·1790 \times 10^{-5}$	$0·12579 \times 10^{-8}$
0·165	Dense silicate flint . . .	1·7541	0·02743	27·5	0·01607 0·585	0·01974 0·720	0·01730 0·630	4·78	1·70583	$2·3185 \times 10^{-5}$	$0·17254 \times 10^{-8}$
S 57	Densest silicate flint . .	1·9626	0·04882	19·7	0·02767 0·567	0·03547 0 726	0·03252 0·666	6·33	1·88236	$2·5095 \times 10^{-5}$	$0·27148 \times 10^{-8}$

relative dispersive powers of the various glasses. These glasses were chosen from a great number in Schott and Genossen's list, and show very clearly what great differences can be produced in the optical qualities of glass. The rays referred to by the letters A', C, D, F, and G' are the following :—

A' the potassium red line . . . $\lambda = 7677$ Ångström units
C the hydrogen red line . . . $\lambda = 6563$,, ,,
D the middle of the two sodium lines $\lambda = 5893$,, ,,
F the hydrogen bright blue line . $\lambda = 4862$,, ,,
G' the hydrogen blue line . . . $\lambda = 4341$,, ,,

The three last columns contain the values of the constants μ_0, λ_0, and C in Hartmann's formula (see pp. 70, *et seq.*).

Rubens has measured the refractive indices for certain glasses in the infra-red, of which the following may be quoted :[1]—

Glass No. S 163.		Glass No. 0·451.		Glass No 0·1151.	
λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ
0·740	1·8696	0·778	1·5665	0·798	1·5132
0·790	1·8660	0·830	1·5652	0·851	1·5121
0·846	1·8616	0·890	1·5638	0·912	1·5110
0·912	1·8579	0·958	1·5623	0·982	1·5098
0·978	1·8542	1·038	1·5608	1·063	1·5087
1·085	1·8515	1·132	1·5594	1·160	1·5075
1·185	1·8483	1·246	1·5580	1·275	1·5060
1·316	1·8446	1·382	1·5561	1·415	1·5045
1·481	1·8418	1·556	1·5540	1·593	1·5025
1.692	1·8381	1·780	1·5514	1·820	1·4985
1·975	1·8337	2·076	1·5477	2·120	1·4956
2·368	1·8281	2·490	1·5430		

In the following table are given the values of $\frac{d\mu}{dt}$ for certain glasses measured by Pulfrich,[2] at the various regions specified

[1] *Ann. der Phys.*, **45**. 238 (1892). [2] *Ibid.*, **45**. 609 (1892).

Number of glass.	Mean temperature.	C	D.	F.	G'.	Relative change in dispersion. $= \frac{-dv}{v} \times 100$
S 57	58·8°	1·204	1·447	2·09	2·810	0·0166
0·544	55·1°	0·244	0·281	0·389	0·503	0·0083
0·527	58·3°	− 0·008	+ 0·014	0·080	0·137	0·0079
0·225	58·1°	− 0·202	− 0·190	− 0·168	− 0·142	0·0049

The numbers in the columns headed C, D, F, and G' represent the changes expressed in units in the fifth place of decimals of the indices for 1° C. at the position of the spectrum lines C, D, F, and G'. In the last column the relative change in dispersion is given, which is equal to $\frac{-dv}{v} \times 100$, where $v = \frac{\mu_F - \mu_C}{\mu_D - 1}$.

The firm of Schott and Genossen have succeeded in making glasses which are transparent to a great portion of the ultra-violet. The glass can be made by a new process, which transmits 50 per cent. of the incident light at $\lambda = 2880$ A.U. through 1 mm. thickness. The indices and dispersion of two such glasses are given in the table[1]—

Type.		μ_D	Dispersion C to F.	Partial dispersion.		
				A' to D.	D to F.	F to G'.
U.V. 3199	Crown	1·5035	0·00781	0·00514	0·00546	0·00432
U.V. 3492	Flint	1·5329	0·00696	0·00612	0·00680	0·00552

Fritsch[2] in a preliminary communication gives the following recipe for making a durable glass, which is transparent to the ultra-violet light as far as $\lambda = 1852$. Six grms. of commercial calcium fluoride are mixed with 14 grms. of boron trioxide, both in a powdered form and melted in a platinum crucible. The resulting fluid is then poured out on an unheated sheet of platinum, too rapid cooling being avoided.

[1] E. Zschimmer, *Verh. d. Deutsch. Phys. Gesell.*, **5**. 18-19, 312 (1903).
[2] *Phys. Zeitschr.*, **8**. 518 (1907).

In the following table are given the values of the absorptive powers of certain glasses;[1] the values given are the percentage amounts absorbed by 1 cm. of the glasses at the specified regions of the spectrum.

Wave-length.	640	500	442	415	388	357
Borosilicate crown 0·2281 (144) . .	0·0	0·7	—	1·2	2·5	4·7
Calcium silicate crown 0·3309 (60) .	0·3	0·5	1·4	1·8	2·5	3·4
Densest baryta crown 0·3192 (1209) .	1·6	2·5	3·4	5·2	9 8	35
Telescope flint 0·3053 (2001) . . .	0·7	0·7	3·6	12	30	49
Light barium flint 0·2717 (602) . .	—	1·6	—	2·7	6·0	9
,, ,, 0·3131 (578) . .	0·5	0·9	2·1	2·5	8·6	18
Ordinary silicate flint 0·3234 (103) .	0·0	0·0	—	4·1	9·6	28
Dense silicate flint 0·3096 (102) . .	0·5	0·9	—	6·9	28	41

It is necessary, when work is to be done upon the ultra-violet end of the spectrum, that the prisms should be made of either quartz, calcite, or fluorite. These three substances offer great transparency towards the rays of short wave-length, a transparency which is most marked in the case of fluorite and least in calcite. Fluorite has been found to transmit all the rays as far as the limit $\lambda = 1200$,[2] while quartz is transparent to as far as $\lambda = 1850$, and calcite to $\lambda = 2150$.

The dispersion of fluorite is small, as can be seen from the table given below. It is hardly necessary to mention that the colourless Swiss variety is referred to, the ordinary English fluorspar never being found without considerable colour, and further, rarely transparent. At the present time, however, it appears to be extremely difficult to obtain.

Refractive Indices of Fluorite.—The following values have been obtained by Sarasin,[3] Carvallo,[4] and Paschen:[5]—

[1] Pfluger, *Phys. Zeitschr.*, **4.** 429 (1903).
[2] See p. 303.
[3] *Comptes Rendus*, **97.** 850 (1883).
[4] *Ibid.*, **117.** 306 (1893); and **116.** 1189 (1893).
[5] *Ann. der Phys.*, **53.** 812 (1894).

λ in 10^{-6} metres.	μ		λ in 10^{-6} metres.	μ	
0·1856	1·50940	Sarasin	1·444	1·42676	Carvallo
0·19881	1·49629	,,	1·4733	1·42653	Paschen
0·20243	1·49326	,,	1·5715	1·42607	,,
0·20610	1·49041	,,	1·6206	1·42592	,,
0·20988	1·48765	,,	1·7680	1·42517	,,
0·21441	1·48462	,,	1·9153	1·42438	,,
0·21935	1·48150	,,	1·9644	1·42412	,,
0·22645	1·47762	,,	2·0626	1·42363	,,
0·23125	1·47517	,,	2·1608	1·42317	,,
0·25713	1·46476	,,	2·2100	1·42297	,,
0·27467	1·45958	,,	2·3573	1·42208	,,
0·32525	1·44987	,,	2·5537	1·42092	,,
0·34015	1·44775	,,	2·6519	1·42015	,,
0·34655	1·44697	,,	2·7502	1·41969	,,
0·36009	1·44535	,,	2·9466	1·41823	,,
0·39681	1·44214	,,	3·1430	1·41704	,,
0·41012	1·44121	,,	3·2413	1·41608	,,
0·48607	1·43713	Paschen	3·5359	1·41378	,,
0·58930	1·43393	,,	3·8306	1·41121	,,
0·637	1·43292	Carvallo	4·1250	1·40850	,,
0·65618	1·43257	Sarasin	4·4199	1·40559	,,
0·68671	1·43200	,,	4·7147	1·40244	,,
0·700	1·43192	Carvallo	5·0092	1·39902	,,
0·71836	1·43157	Sarasin	5·3039	1·39532	,,
0·76040	1·43114	,,	5·5985	1·39145	,,
0·777	1·43096	Carvallo	5·8932	1·38721	,,
0·878	1·42996	,,	6·4825	1·37837	,,
0·8840	1·42996	Paschen	7·0718	1·36808	,,
1·009	1·42904	Carvallo	7·6612	1·35672	,,
1·1786	1·42799	Paschen	8·2505	1·34444	,,
1·187	1·42804	Carvallo	8·8398	1·33079	,,
1·3751	1·42696	Paschen	9·4291	1·31612[1]	,,

These values can be expressed extremely well by the formula (Paschen)—

$$\mu^2 = a^2 + \frac{M_2}{\lambda^2 - \lambda_2^2} - k\lambda^2 - h\lambda^4$$

where $a^2 = 2{\cdot}03888$, $M_2 = 0{\cdot}006166$, $\lambda_2^2 = 0{\cdot}0086959$
$k = 0{\cdot}003200$, $h = 0{\cdot}0000029195$.

The following values have recently been obtained by Gifford[2]—

[1] This value is the mean of eight observations, two of which differ somewhat from the rest; the mean of the remaining six is 1·31593.

[2] *Proc. Roy. Soc.*, **70.** 329 (1902); and **84.** 193 (1910).

λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ
0·7950	1·430639	0·361066	1·445339
0·768245	1·430949	0·330285	1·449071
0·706559	1·431711	0·303421	1·453382
0·6708	1·432258	0·274868	1·459661
0·656304	1·432523	0·257312	1·464773
0·6438	1·432717	0·244586	1·469650
0·589317	1·433854	0·231295	1·475162
0·56071	1·434565	0·226513	1·477543
0·5461	1·434990	0·21944	1·481453
0·527011	1·435564	0·214445	1·484569
0·486149	1·437067	0·20988	1·487571
0·4800	1·436910	0·20620	1·490259
0·4359	1·439521	0·20242	1·493182
0·434066	1·439626	0·19881	1·496131
0·4046	1·441530	0·19335	1·501226
0·396168	1·442188	0·18522	1·509889

Quartz and calcite differ from the other materials detailed above in that they are both doubly refracting substances, and further, in the case of quartz account must be taken of the rotation of the plane of polarisation.

In general, when a ray of light enters a crystal of calcite or quartz it is divided into two portions, one of which is refracted according to Snell's law, and in the case of the other the relation between the angles of incidence and refraction depends upon the angle of incidence. This phenomenon, known as double refraction, was first discovered by Erasmus Bartholinus, in 1669, who noticed that objects viewed through a crystal of calcite appeared to be double. It has been since found that all natural crystals, excepting those which belong to the cubic system, exhibit this interesting phenomenon. The ray which obeys Snell's law is called the ordinary ray, and the other the extraordinary ray, and doubly refracting substances can be divided into two classes, namely, those in which the index of refraction of the extraordinary ray is greater than that of the ordinary ray, and those in which it is less. Crystals belonging to the first class are called positive, and those belonging to the second are called negative crystals. The following tables give examples of both positive and negative crystals :—[1]

[1] Preston, *Theory of Light*, p. 310.

POSITIVE CRYSTALS.

	μ_O	μ_E
Quartz	1·544	1·553
Potassium sulphate	1·493	1·502
Dioptase	1·667	1·723
Ice	1·306	1·307
Zircon	1·92–1·96	1·97–2·10

NEGATIVE CRYSTALS.

	μ_O	μ_E
Iceland spar	1·658	1·486
Tourmaline	1·637–1·644	1·619–1·622
Beryl	1·584–1·577	1·578–1·572
Apatite	1·646	1·642
Sodium nitrate	1·5854	1·3369

From these tables it will be seen that quartz crystals are positive, while, on the other hand, calcite is negative. The theory of double refraction was worked out by Huyghens and Fresnel, and cannot, of course, find a place here; suffice it to say, therefore, that since in the case of glass and isotropic substances the form of the wave of light is a sphere, Huyghens assumed that the sphere was also the form of the wave obeying Snell's law in a doubly refracting crystal, *i.e.* the ordinary ray. The form of the extraordinary wave he imagined to be a spheroid, *i.e.* an ellipsoid of revolution, which is the simplest conception next to that of the sphere.

In all doubly refracting crystals there is one, and sometimes two, directions along which double refraction does not take place. These directions are called the optic axes of the crystal; quartz and calcite are both uniaxial, that is to say, there is one direction through these crystals along which there is no double refraction. When prisms, therefore, are made out of quartz or calcite, it is necessary that they be so cut that the rays inside the prism pass along the optic axis of the crystal, because, if not, the double refraction will cause the spectrum lines to be doubled. It has been pointed out (p. 9) that the path of the rays in a prism set at minimum deviation is parallel to the base, and thus it follows that prism of quartz or calcite should be so cut that the optic axis

lies in a principal plane and parallel to the base, in order that the rays at minimum deviation should not undergo double refraction. It so happens that in the case of calcite this is a very wasteful way of cutting the prism, as can be seen by reference to Fig. 35, which represents a calcite crystal. The crystal is a rhombohedron, bounded by six parallelograms, each of which has two angles of 78° 5′, and two of 101° 55′; it will be seen on reference to the diagram that two of the corners of the crystal, and only two, are formed by the intersection of three wide angles. The optic axis lies along the line joining these two angles, and is shown by the dotted diagonal in the figure. The prism must be so cut that the dotted diagonal lies in a principal plane and parallel to the base; this is a difficult operation, because the prism faces are cut at an angle with the lines of cleavage, and, therefore, the crystal is very readily split. The finished prism must also be carefully handled, as it is very easily chipped. In cutting the native crystal it is usual to use a fine copper wire, which has been dipped in a mixture of emery and oil, the wire being drawn backwards and forwards like a saw.

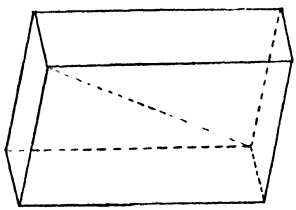


FIG. 35.

Since there is so considerable a difference between the indices of refraction for the ordinary and the extraordinary ray, it follows that double refraction begins to make its appearance when the rays, in passing through a calcite prism, make only a small angle with the optic axis, and, therefore, the spectrum lines will appear sharp only for a very little angular distance on each side of the position of minimum deviation. This entirely militates against the use of prisms of this material for purposes of photographing anything more than very small limits of the spectrum at one time.

The values of the indices of refraction as determined by Gifford are as follows:—

λ in 10^{-6} metres.	μ ordinary rays.	μ extra-ordinary rays.	λ in 10^{-6} metres.	μ ordinary rays.	μ extra-ordinary rays.
0·7950	1·648864	1·482165	0·361066	1·693161	1·502235
0·768245	1·649740	1·482552	0·330285	1·705154	1·507458
0·706559	1·652070	1·483532	0·303421	1·719588	1·513646
0·6708	1·653669	1·484271	0·274868	1·741504	1·522662
0·656304	1·654399	1·484569	0·257312	1·760500	1·530121
0·6438	1·655028	1·484680	0·244586	1·779665	1·537310
0·589317	1·658355	1·486392	0·231295	1·802394	1·545500
0·56071	1·660455	1·487345	0·226513	1·813035	1·549144
0·5461	1·661647	1·487890	0·21944	1·830798	1·555122
0·527011	1·663415	1·488706	0·214445	1·845824	1·559923
0·486149	1·667831	1·490741	0·20988	1·860811	
0·4800	1·668613	1·491102			
0·4359	1·675176	1·494104			
0·434066	1·675517	1·494242			
0·4046	1 681343	1·496906			
0·396168	1·683296	1·497774			

In the case of quartz the double refraction is not by any means so pronounced as with calcite ; the extraordinary ray is very much weaker than the ordinary ray, and, indeed, is difficult to see. The objection to calcite, therefore, does not apply to quartz, and this substance finds great use in apparatus for photographing the ultra-violet end of the spectrum.

There is, however, a further property appertaining to quartz which must be taken into account, namely, the rotation of the plane of polarisation by a quartz crystal. All doubly refracting substances plane-polarise the light which they refract, the plane of polarisation of the extraordinary ray being perpendicular to that of the ordinary ray. Quartz, however, in common with certain other substances, has also the power of rotating the plane of polarised light which passes through it, and Biot has shown that the amount of rotation varies directly with the length of path in the crystal.

When light enters a quartz crystal parallel to the optic axis, it is resolved into two rays which are circularly polarised to the right and left respectively. These two rays possess different velocities, and so will be separated and a doubling of the image will ensue. In the case of a 60° prism of quartz cut so that the optic axis lies in a principal plane and parallel to the

base the angular distance between the two rays is about 27″ in the neighbourhood of the D lines. Now it has been found that there are two kinds of quartz crystals—right- and left-handed as they are called—in the right-handed variety the dextro polarised ray, and in the left-handed variety the lævo polarised ray, being less deviated.

It is thus possible, since the two varieties are absolutely similar in their powers, to eliminate entirely the doubling effect by joining together two equal portions of right- and left-handed crystals; the doubling effect produced in the first half is then entirely destroyed in the second. In the case of quartz prisms, therefore, each whole prism is made of two 30° half prisms, one of which is cut from a right-handed and the other from a left-handed crystal, care, of course, being taken that the optic axis is parallel to the base in each half. This method of cutting the prism is due to Cornu, and is shown in plan in Fig. 36.

The indices of refraction of quartz for the ordinary ray are as follows (Rubens[1]):—

λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ
0·19881	1·65070	2·327	1·5156
0·23125	1·61402	2·59	1·5101
0·27467	1·58750	2·84	1·5039
0·31798	1·57290	3·03	1·4987
0·35818	1·56407	3·18	1·4944
0·40458	1·557059	3·40	1·4879
0·43409	1·553869	3·63	1·4799
0·48616	1·549606	3·80	1·4740
0·53496	1·546633	3·96	1·4679
0·58932	1·544147	4·09	1·4620
0·65633	1·541807	4·20	1·4569
0·76824	1·538930	5·0	1·417
1·160	1·5329	5·8	1·368
1·617	1·5272	6·45	1·274
1·969	1·5216	7·0	1·167

These values, excepting the last four, can be expressed by the following equation:—

$$\mu^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2}$$

[1] *Ann. der Phys.*, **54**. 476 (1895).

where $a^2 = 3{\cdot}4629$, $M_1 = 0{\cdot}010654$, $M_2 = 111{\cdot}47$,
$\lambda_1^2 = 0{\cdot}010627$, $\lambda_2^2 = 100{\cdot}77$.

Better results are obtained by the following (Rubens[1]):—

$$\mu^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2} - \frac{M_3}{\lambda_3^2 - \lambda^2}$$

where $a^2 = 4{\cdot}57877$, $M_1 = 0{\cdot}010654$, $\lambda_1^2 = 0{\cdot}010627$,
$M_2 = 44{\cdot}224$, $\lambda_2^2 = 78{\cdot}22$, $M_3 = 713{\cdot}55$, $\lambda_3^2 = 430{\cdot}55$.

More recently Gifford[2] has obtained the following values for both the ordinary and the extraordinary rays. To these are added the indices for fused silica:—

λ in 10^{-6} metres.	μ ordinary ray.	μ extraordinary ray.	μ fused silica.
0·7950	1·538513	1·547421	1·453398
0·768245	1·539060	1·547997	1·453892
0·706559	1·540500	1·549487	1·455180
0·6708	1·541459	1·550472	1·456072
0·656304	1·541931	1·550948	1·456415
0·6438	1·542309	1·551353	1·456771
0·589317	1·544256	1·553366	1·458477
0·56071	1·545475	1·554619	1·459507
0·5461	1·546168	1·555339	1·460155
0·527011	1·547177	1·556388	1·460995
0·486149	1·549700	1·558988	1·463165
0·4800	1·550132	1·559449	1·463571
0·4359	1·553797	1·563227	1·466741
0·434066	1·553976	1·563406	1·466850
0·4046	1·557151	1·566711	1·469675
0·396168	1·558235	1·567836	1·470542
0·361066	1·563473	1·573243	1·475112
0·330285	1·569742	1·579729	1·480610
0·303421	1·576992	1·587231	1·486881
0·274868	1·587529	1·598132	1·496131
0·257312	1·596246	1·607164	1·503707
0·244586	1·604619	1·615860	1·51096
0·231295	1·614034	1·625647	1·519373
0·226513	1·618198	1·629965	1·523053
0·21944	1·624991	1·637022	1·529103
0·214445	1·630466	1·642704	1·533898
0·20988	1·635698	1·648144	1·538547
0·20620	1·640398	1·653037	1·54271
0·20242	1·645584	1·658443	1·54721
0·19881	1·650917	1·663987	1·551990
0·19335	1·660027	1·673488	1·55998
0·18522	1·675895	1·690069	1·5743

[1] *Ann der Phys.*, **60**. 418 (1897).

[2] *Proc. Roy. Soc.*, **70**. 329 (1902), and **84**. 193 (1910).

Rock-salt and sylvin are used for prisms in cases when the extreme infra-red end of the spectrum is to be examined. Both these substances being soluble in water are very readily affected

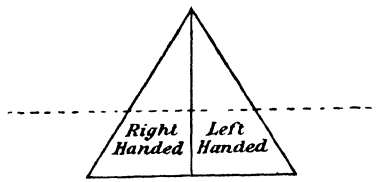


FIG. 36.

by adverse atmospheric conditions, and therefore great care must be taken in their use. The indices of refraction of rock-salt are given in the following tables (Rubens [1]):—

ROCK-SALT.

λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ
0·434	1·5607	6·78	1·5121
0·485	1·5531	7·22	1·5102
0·589	1·5441	7·59	1·5085
0·656	1·5404	8·04	1·5064
0·840	1·5345	8·67	1·5030
1·281	1·5291	9·95	1·4561
1·761	1·5271	11·88	1·4476
2·35	1·5255	13·96	1·4373
3·34	1·5233	15·89	1·4251
4·01	1·5216	17·87	1·4106
4·65	1·5197	20·57	1·3735
5·22	1·5180	22·3	1·3403
5·79	1·5159		

The following equation expresses these results:—

$$\mu^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2}$$

where $a^2 = 5{\cdot}1790$, $M_1 = 0{\cdot}018496$, $\lambda_1^2 = 0{\cdot}01621$, $M_2 = 8977{\cdot}0$, $\lambda_2^2 = 3149{\cdot}3$.

Paschen [2] has obtained the following values for the refractive indices of rock-salt:—

[1] *Ann. der Phys.*, **54.** 476 (1895), and **60.** 724 (1897).
[2] *Ibid.*, **26.** 120 (1908).

λ in 10^{-6} metres.	μ	λ in 10^{-6} metres.	μ
0·58932	1·544313	6·4825	1·513628
0·78576	1·536138	7·0718	1·511062
0·88398	1·534011	7·6611	1·508318
0·98220	1·532435	7·9558	1·506804
1·1786	1·530372	8·8398	1·502035
1·7680	1·527440	10·0184	1·494722
2·3573	1·525863	11·7864	1·481816
2·9466	1·524534	12·9650	1·471720
3·5359	1·523173	14·1436	1·460547
4·12524	1·521648	14·7330	1·454404
5·0092	1·518978	15·3223	1·447494
5·8932	1·516014	15·9116	1·441032

Rubens[1] found the following values for sylvin :—

SYLVIN.

λ in 10^{-6} metres.	μ	λ in 10^{-6} metres	μ
0·434	1·5048	4·81	1·4705
0·486	1·4981	5·31	1·4695
0·589	1·4900	5·95	1·4882
0·656	1·4868	7·08	1·4653
0·940	1·4805	10·01	1·4561
1·584	1·4761	14·14	1·4362
2·23	1·4745	18·10	1·4162
3·20	1·4727	20·60	1·3882
4·05	1·4716	22·5	1·2692

These values are expressed by the equation—

$$\mu^2 = a^2 + \frac{M_1}{\lambda^2 - \lambda_1^2} - \frac{M_2}{\lambda_2^2 - \lambda^2}$$

where $a^2 = 4{\cdot}5531$, $M_1 = 0{\cdot}0150$, $\lambda_1^2 = 0{\cdot}0234$,
$M_2 = 10747$, $\lambda_2^2 = 4517{\cdot}1$.

Paschen[2] has obtained the following values for the refractive indices of sylvin :—

[1] *Ann. der Phys.*, **54**. 476 (1895) ; **60**. 724 (1897).
[2] *Ibid.*, **26**. 120 (1908).

λ in 10^{-6} metres	μ	λ in 10^{-6} metres.	μ
0·58932	1·490443	5·3039	1·470013
0·78576	1·483282	5·8932	1·468804
0·88398	1·481422	8·2505	1·462726
0·98220	1·480084	8·8398	1·460858
1·1786	1·478311	10·0184	1·45672
1·7680	1·475890	11·786	1·44919
2·3573	1·474751	12·965	1·44346
2·9466	1·473834	14·144	1·43722
3·5359	1·473049	15·912	1·42617
4·7146	1·471122	17·680	1·41403

The values of the temperature coefficient $\left(\frac{d\mu}{dt}\right)$ of the five last substances are given in the following table (Pulfrich [1]):—

Substance.	Mean temperature.	C.	D.	F.	G′.	Relative change in dispersion $= \frac{-d\nu}{\nu} \times 100$.
Rock-salt	58·8°	−3·749	−3·739	−3·648	−3·585	0·0148
Sylvin	59·5°	−3·681	−3·641	−3·605	−3·557	0·0143
Quartz ordinary ray .	59·6°	−0·649	−0·638	−0·599	−0·577	0·0076
,, extraordinary ray	59·6°	−0·761	−0·754	−0·715	−0·694	0·0071
Fluorspar	60·5°	−1·220	−1·206	−1·170	−1·142	0·0137
Calcite ordinary ray .	103°	0·071	0·081	0·091	0·100	0·0137
,, extraordinary ray	103°	1·012	1·020	1·073	1·090	0·0078

In the columns headed C, D, F, and G′ the changes in μ for 1° rise in temperature for these rays are given in units in the fifth place of decimals. For example, the value of μ for the ordinary ray with quartz is 1·541807 for the C line at a temperature of 15°; at 16° the value of μ will be 1·541807 − 0·0000065, or 1·5418005.

Lenses.—In the prism spectroscope two lenses are made use of, one the collimator lens, and the other the telescope lens, the

[1] *Ann. der Phys.*, **45**. 609 (1892).

function of the first-named being to collect the rays which come from the slit, and to transmit them as a parallel beam on to the first face of the prism train, while the function of the latter is to collect the rays leaving the last prism face, and to bring them to a focus. Then, further, there is the eyepiece, wherewith to examine visually the rays at the focus of the telescope lens. The focal length of a single lens may be found from the well-known equation—

$$\frac{1}{f} = (\mu - 1)\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

where f is the focal length of the lens, μ the index of refraction of the given material, and r_1 and r_2 the radii of curvature of the first and second surfaces.

As is evident from this equation, the focal length differs for every ray of different colour, and thus a single lens must give with white light a series of coloured images of different sizes distributed along the axis, or, in other words, a spectrum is produced. The change in the focal length of a lens thus depends upon the dispersion of the material. By differentiation of the above equation we have—

$$d\left(\frac{1}{f}\right) = d\mu\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

and thus

$$d\left(\frac{1}{f}\right) = \frac{d\mu}{\mu - 1} \cdot \frac{1}{f}$$

$$= \frac{1}{\nu f}$$

if we put

$$\nu = \frac{\mu - 1}{d\mu}.$$

The ratio $\frac{d\mu}{\mu - 1}$ is known as the relative dispersion of the medium, and may be arrived at in the following way. In the equation for a prism at minimum deviation—

$$\mu = \frac{\sin\frac{A + \theta}{2}}{\sin\frac{A}{2}}.$$

If the angles A and θ are very small, we may substitute their circular measures for their sines, since the sines of very small angles are proportional to the angles themselves; therefore—

$$\mu = \frac{A + \theta}{A},$$

whence $\theta = A(\mu - 1)$.

By differentiation $d\theta = A d\mu$.

Dividing by the previous equation—

$$\frac{d\theta}{\theta} = \frac{d\mu}{\mu - 1}.$$

By the relative dispersion, therefore, is meant the ratio of the difference in the deviation for two rays in the spectrum to the deviation of one ray taken as standard.

The defect of a single lens, called chromatic aberration, was well known to Newton, who was unable to devise a means of overcoming it in the case of telescopic object glasses, and furthermore said it was impossible to do so; this was because he was ignorant of the difference between the relative dispersions of different materials. For this reason Newton turned his attention to reflecting telescopes.

It is possible, however, to correct the defect by using a double convex lens of crown-glass and a double concave of flint, the two lenses being placed in contact to form the complete lens. By the use in this way of two different kinds of glass, it is possible to bring two different coloured rays to the same focus, but this does not necessarily mean complete achromatism, because the dispersions of the two glasses are not geometrically similar, and therefore the remaining rays are not absolutely proportional to one another throughout the spectrum; that is to say, the spectra produced by the two glasses are not brought to exactly the same focus as the two chosen rays. There results in this way a small residuary spectrum, which is called the secondary spectrum. Again, by the use of three different kinds of glasses, three chosen rays may be brought to the same focus, leaving a still smaller tertiary spectrum. Usually, however, lenses for spectroscopes are only made of pairs of glasses, because the Jena firm of Schott and Genossen

have succeeded in producing such pairs so perfectly adjusted that their dispersions are almost absolutely proportional; the secondary spectra from lenses of these selected pairs are extremely small, the lenses being perfectly achromatic over a very large portion of the spectrum.

In dealing with the theory of the corrections, it must be noted that there are two errors in an uncorrected lens, which are as follows:—

First, that a series of different coloured images is formed along the axis of the lens.

Second, that these images are all of different size.

Now, as has already been stated, it is possible, by means of two lenses in contact formed of two glasses with different relative dispersions, to bring two different coloured images to the same focus; therefore, in this case, the second defect will vanish. On the other hand, when the two lenses are not in contact, both the above defects cannot be simultaneously corrected, and it becomes necessary to choose which one shall be corrected.

The condition of achromatism for two lenses in contact, as in the case of the telescopic lens and the collimating lens, may first be considered.

If f_1 and f_2 are the focal lengths of the two lenses respectively, then the relation between the focal length of the pair F is given by the well-known equation—

$$\frac{1}{F} = \frac{1}{f_1} + \frac{1}{f_2}$$

when the rays of light are considered as homogeneous.

In order that the combination be achromatic, it is necessary that the change in the focal length of one lens caused by using light of another wave-length be exactly counteracted by the change in the focal length of the other lens; under these conditions, the focal length of the combination will be the same for the two rays. The necessary condition is evidently given by the equation—

$$d\left(\frac{1}{f_1}\right) + d\left(\frac{1}{f_2}\right) = 0,$$

or

$$\frac{1}{\nu_1 f_1} + \frac{1}{\nu_2 f_2} = 0 \text{ (see p. 105)}$$

when this equation is satisfied, the combination will be achromatic for two rays.

The brightest portion of the spectrum to the eye is included between the C and F rays, and usually, therefore, in apparatus employed for visual work, the lenses are achromatised for these two rays. In the list of glasses made by the firm of Schott and Genossen, the values of ν for these two rays are given, as may be seen on reference to the table of selected glasses given on p. 91. In choosing a pair of glasses for an achromatic lens, it is necessary to select two which differ considerably in values of ν, and then if the above equation of condition be satisfied, a lens can be made which is perfectly achromatic for the two rays of the spectrum known as C and F.

Strictly speaking, such a lens will not be achromatic for the other rays of the spectrum unless the dispersions of the two glasses are geometrically similar throughout the spectrum. In actual fact, however, it has been found possible to make pairs of glasses which, although they differ considerably in their values of ν, still possess very similar partial dipersions. Such a pair of glasses are the following:—

No.	Description.	μ_D	$\mu_F - \mu_C$	ν	$\mu_D - \mu_{A'}$	$\mu_F - \mu_D$	$\mu_G - \mu$
S 30	Dense barium phosphate crown	1·5760	0·00884	65·2	0·00570 0·644	0·00622 0·703	0·00500 0·565
S 8	Borate flint . .	1·5736	0·01129	50·8	0·00728 0·645	0·00795 0·704	0·00644 0·571

These two glasses differ considerably in the values of ν, and their partial dispersions are very similar; for example—

$$\frac{\mu_D - \mu_{A'}}{\mu_F - \mu_C} = 0{\cdot}644 \text{ and } 0{\cdot}645 \text{ respectfully.}$$

$$\frac{\mu_F - \mu_D}{\mu_F - \mu_C} = 0{\cdot}703 \text{ and } 0{\cdot}704 \quad ,,$$

$$\frac{\mu_G - \mu_F}{\mu_F - \mu_C} = 0{\cdot}565 \text{ and } 0{\cdot}571 \quad ,,$$

If a compound lens be made of these two glasses, and the equation—

$$\frac{1}{\nu_1 f_1} + \frac{1}{\nu_2 f_2} = 0$$

be satisfied, so that the lens be perfectly achromatic for the C and F rays, then it will also be quite achromatic for the A′ and D rays, and very nearly so for the G′ ray.

A similar pair of glasses, suitable for the object glasses of ordinary telescopes when achromatism for the three rays C, D, and F is sufficient, is the following :—

No.	Type.	μ_D	Medium dispersion C − F.	ν	Partial dispersion.	
					C − D.	D − F.
0·2388	Telescope crown .	1·5261	0·00852	61·7	0·00250	0·00602
0·2001	Telescope flint .	1·5211	0·01007	51·7	0·00296	0·00710

The partial dispersions in each case are almost absolutely proportional, as may be seen by dividing that for D to F by that for C to D, when the first glass gives 2·4008 and the second 2·3960. As may be readily understood from the above two instances, the achromats produced by the best makers leave very little to be desired. Very often in the case of a telescope lens used for photographing the spectrum, it will be found that the achromatism is perfect from C to F or G, and that for the regions beyond G the lens is a little uncorrected, that is to say, the focal lengths for rays of shorter wave-length than G are rather too small. This may be met in practice by setting the photographic plate at a slight angle, the part intended to receive the blue end of the spectrum being brought a little nearer to the lens. This does not appreciably disturb the focus of the rays at any other part of the spectrum. For example, the telescope lens of one of the spectrographs at the University, Liverpool, has a focal length of 5 feet; the whole spectrum can be photographed in perfectly good focus from C to L by giving a very slight tilt to the plate.

Gifford has recently found it possible to correct the chromatic aberration of a quartz lens by means of a second lens made of calcite or of fluorite, and exceptionally fine achromatic lenses can be made from these two combinations. These lenses, especially the quartz-fluorite achromat, give an almost perfectly flat field for the whole spectrum to $\lambda = 1850$.

It has also been found possible to produce exceedingly fine achromatic lenses from a combination of quartz and rock-salt. Owing to the danger of atmospheric action on the rock-salt this type of lens is made by enclosing the rock-salt lens between two quartz lenses so that it is entirely protected from the atmosphere. These lenses are now used in many apparatus in place of the quartz-fluorite combination.

The correction for chromatic aberration of a system of lenses separated by an interval cannot be entirely carried out unless each component is separately achromatised. It is only possible, without this, to correct one of the two defects, and it is necessary to choose whether the different coloured images are to be made the same size, or whether they are to be brought to a focus in the same plane. Such a system occurs in eye-pieces, and as the eye is a much better judge of size than of distance, the first defect is usually corrected, and the lenses so adjusted that the images are formed all of the same apparent size.

The equation of condition may be found in a similar way to that deduced for two lenses in contact. This equation is as follows:[1]—

$$\frac{x\omega}{f} + \frac{(x+a)\omega}{f^1} = \frac{ax(\omega+\omega^1)}{ff^1}$$

where x is the distance of the object in front of the first lens, a is the distance between the lenses, f and f^1 the focal lengths of the two lenses for one ray, and ω and ω^1 the relative dispersions of the two glasses $\left(=\frac{1}{\nu}\right)$.

This equation, however, may be much simplified in the case of an eyepiece, when x is very much larger than a, since the centre of the object glass is very distant compared with the distance between the lenses of an eyepiece. Hence—

$$\frac{\omega}{f} + \frac{\omega^1}{f^1} = \frac{a(\omega+\omega^1)}{ff^1},$$

and

$$a = \frac{\omega f^1 + \omega^1 f}{\omega + \omega^1}.$$

[1] *Geometrical Optics*, 2nd ed., p. 228. By R. S. Heath. University Press, Cambridge. 1895.

A great advantage is to be gained by making the two lenses of the same glass, because when corrected for two rays the eyepiece will be perfectly achromatic, therefore we have—

$$\omega = \omega^1,$$

and

$$a = \frac{f^1 + f}{2}.$$

The distance between the lenses must be half the sum of their focal lengths, when the eyepiece, as far as the first defect is concerned, will be perfectly achromatic.

The special form of eyepiece used with a spectroscope is nearly always that known as the Ramsden, which consists of two plano-convex lenses placed with the convex sides towards one another, as is shown in Fig. 37. Both lenses are made of the same focal length, and therefore, in order to secure the best correction for achromatism, the distance between them should be equal to the focal length of either. As in this way the second lens is placed in the focus of the first, the eye sees magnified images of all the defects, such as bubbles in the second lens; the distance between the lenses, therefore, in practice is generally reduced to two-thirds of the focal length, which makes no serious difference to the achromatism, and at the same time throws out of focus to the eye the faults of the second lens.

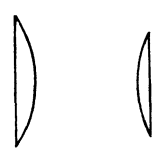


FIG. 37.

The great advantage of the Ramsden form of eyepiece for spectroscopic work lies in the fact that it is used outside the focus of the telescope object glass, so that the eye is enabled to focus a wire or similar object placed in the focal plane of the objective at the same time as the image formed by the objective. The eyepiece fits into an outer tube, which carries a fixed wire or pointer, this pointer being used as an index in measuring the position of a spectral line; in this way the index can be focussed independently of the lines themselves. Usually, two spider webs are used, which are set at an angle to one another, and cross one another in the centre of the field of view; the webs, though excellent when bright lines are being observed, are very difficult

to see in the case of faint lines, and it is, therefore, preferable to use a bright pointer. This is best made by grinding the end of a needle flat on one side, which is then fixed with the flat side turned towards the eye; a beam of light is thrown on to this pointer from a small mirror, as is shown in Fig. 38.

The pointer is shown at A, and is illuminated by a beam of light directed by the mirror D down the tube C. Care must

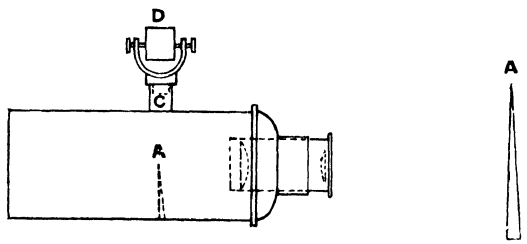


FIG. 38.

be taken that the end of the pointer is very fine, and that it can be clearly seen against a black background.

In its most complete form the eyepiece is provided with two dark shutters, one on each side, which slide in and out; these are useful to cut off the illumination from any bright lines which may be present on either side of a faint line under observation.

The micrometer eyepiece is a modified form of the above; in this apparatus the index is made movable, being actuated by a micrometer screw carrying a divided drumhead, by means of which the travel of the index can be measured. These instruments usually have one movable spider web, and also stationary webs fixed across the field parallel to the movable web and distant from one another exactly five or ten threads of the micrometer screw. They can be used for measuring the distance between the lines in the spectrum visually or on a photographic plate; the readings obtained are, of course, only empirical, and their value must be previously determined, as will be more fully discussed later.

CHAPTER IV

THE COMPLETE PRISM SPECTROSCOPE

In the last chapter the optical parts of the prism spectroscope—that is, the slit, prism, and lenses—were described in detail; it remains now to treat of their mounting to form the complete instrument. It will be readily understood that, originating with the simple instrument used by Fraunhofer and modified by Bunsen and Kirchhoff, many methods have been adopted and corresponding designs made depending upon the particular nature of the work to which the instruments were applied. Very little use would be served, even if space permitted, by following out the varied forms of spectroscopes that are in

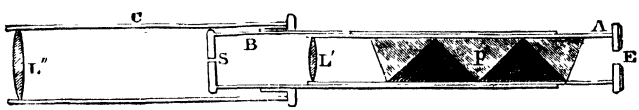


FIG. 39.

use; it is preferable rather to discuss fully the useful types which embody the best notions, and to point out the lines to be recommended to any one who wishes to make or design his own instrument.

The simplest form of spectroscope is the direct-vision instrument, a diagram of which is shown in Fig. 39.

This instrument consists of two tubes, A and B, which slide one into the other; the larger of these carries the slit S at one end, and the smaller the prism train P and the lens L'. The slit S in the cheaper instruments is made with fixed jaws, but in those of better quality both jaws are movable, the slit being opened or closed by turning a collar which is fitted round the

tube. The lens L′ is an achromat of short focus, and the prism train P in the most recent instruments consists of three prisms, the centre one being of very dense flint-glass. This train is packed into the tube with strips of cork to prevent its slipping. At E a diaphragm is fitted as shown. When in use the instrument is focussed by sliding the smaller tube in or out until the best definition is obtained; in order to prevent the tube carrying the lens and prism train from turning round and getting out of alignment with the slit, a small stud is fixed to the outside of the prism tube A, which works in a slot cut lengthwise in the outer tube B. An accessory is shown in Fig. 39 in the shape of a collimating lens, L″, which is mounted in the

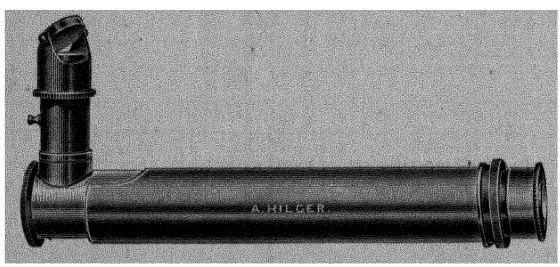


FIG. 40.

tube C. This tube, C, is made to slide over the tube B in order to allow the rays to be focussed upon the slit.

Sometimes a photographic scale is added to this instrument, the image of which is projected in through a side tube and viewed by reflection from the last prism face. This, however, is only useful for the roughest possible measurements. Such an instrument is shown in Fig. 40.

This instrument, which costs from one to three pounds, is very useful for qualitative examination of spectra, especially in work with vacuum tubes or flames. In the former case, when the vacuum tubes are provided with a capillary portion, as they usually are, there is no need to use a slit, since the narrow column of light can take its place. It is only necessary to look directly at the vacuum tube through the prism train without

any lens; this is a very convenient method of working on the spectra of gases, as much greater illumination is obtained.

In spectroscopic work, when it is required to determine the wave-lengths of the lines recourse must be had to some method of measuring their positions in the spectrum. This is always carried out, in the case of prism apparatus and generally with gratings, by measuring the angular deviations of the lines and comparing them with the deviation of lines whose wave-lengths have already been determined. For very accurate work this is done by means of photography; the two spectra, the standard and unknown, are photographed contiguously one above the other on the same plate, and the wave-lengths of the unknown lines found by measuring their position relatively to the lines in the standard spectrum. This comparison may be made visually, but it is in this case preferable to calibrate the spectroscope beforehand. This latter method is usually adopted for ordinary work, where great accuracy is not required, and where only the visible spectrum is involved. The instrument generally employed is the spectrometer, by means of which the angular deviations of the lines are read directly; it is possible, of course, to use any kind of scale in place of the deviations, because both must be reduced to wave-lengths, but this is not advisable on account of the liability of the arbitrary scale to get out of adjustment.

A diagram of a simple spectrometer is shown in elevation and plan in Fig. 41, but, as will be seen, the stand is omitted; the whole apparatus is in reality firmly screwed to a pillar with a tripod base, each leg of which has a levelling screw.

In this type of apparatus the telescope is fixed to an arm which is pivoted at the centre of the table of the instrument, and its angular movement can be measured on the graduated circle. In the diagram the telescope is shown at A, and the collimator at B, and both fit tightly into the carriers C, C; these carriers are fastened by two screws into the blocks D, D, their bottom surfaces being rounded, as shown, to enable the levels of the collimator and telescope to be adjusted. The blocks D, D are fixed by the screws E, E and F, F to the two arms G and H; the holes cut in these arms, where the screws

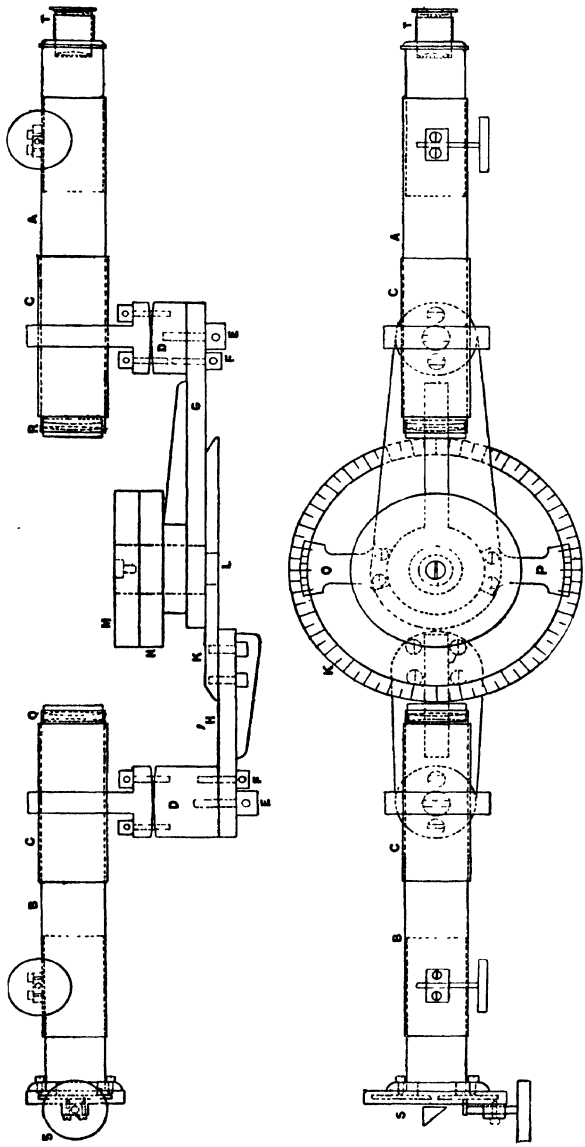


FIG. 41.

F, F pass, are elongated to admit of small adjustments to the telescope and collimator in a horizontal plane. Both the arms are strengthened by ribs, as shown, and H, carrying the collimator, is firmly screwed to the central table K, while G, carrying the telescope, is accurately fitted to the central steel pin L, and is free to rotate round it. The prism table M is also made to rotate round the pin L, this motion being useful for bringing the prism into the position of minimum deviation; the lower table N is fixed, and is graduated so that the angular movements of M may be measured if required. The central table K is also divided, and the movements of the telescope are read from the verniers O and P, the accuracy of reading being usually about 30″ of arc. The lenses of the collimator and telescope are shown at Q and R, the slit at S, and the eyepiece at T; both collimator and

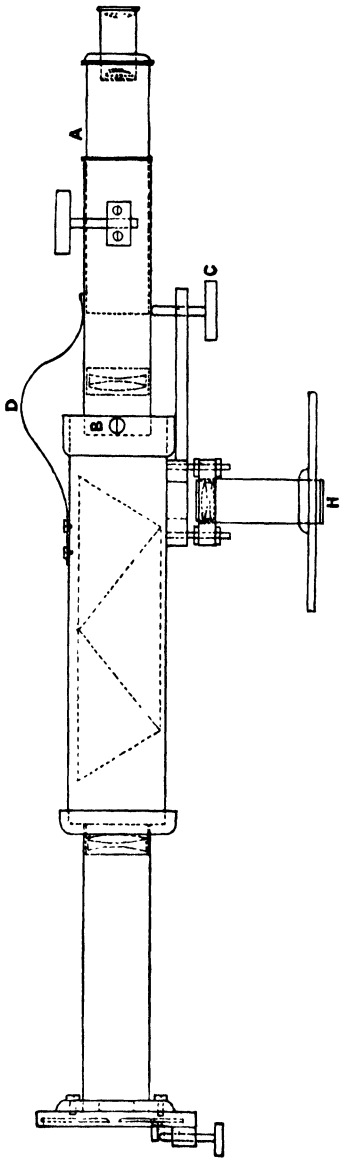


FIG. 42.

telescope are provided with rack-and-pinion adjustments for focussing.

A simple measuring instrument has also been made in which a direct-vision prism train is employed, and has been used for ordinary work by Ramsay. A diagram of such an instrument is shown in Fig. 42; the distinguishing feature consists in pivoting the telescope A at the point B so that it is free to move only in a horizontal plane, which is also a principal plane of the prism system. The motion of the telescope is controlled by the micrometer screw C, a spring D being fixed to keep the telescope pressed up against the end of C. Readings of the positions of the spectrum lines may be read in two ways, either by the graduations on the drumhead of the micrometer screw, using some form of index or pointer in the eyepiece, or their positions may be read upon a photographed scale H, seen by reflection from the last prism face.

The complete instrument is shown in Fig. 43.

In the spectrometer shown in Fig. 41 certain faults of construction are evident, and these must be eliminated if an accurate instrument is required. The chief of these is the want of rigidity. For example, the arms G and H are too slender, as also are the two carriers C and C; a slight pressure of the hand upon the telescope eyepiece during a reading causes a shifting of the spectrum lines, which naturally prevents any accuracy of reading. Though perhaps this instrument is sufficiently rigid for ordinary work, some such design as shown in Figs. 44 and 45 must be employed if any good work is to be done in which the direct measurement of angular deviation is involved.

In the instrument shown in Fig. 44 it will be seen that the telescope is rigidly fastened to the heavy arm A, which is accurately ground on to the central vertical axis, and carries a counterpoise B. The divided circle is 12 inches in diameter, and is read by means of two travelling wire micrometer eyepieces C and D, by means of which the circle divisions can be subdivided to 1″ of arc. Two tangent screw motions E and F are fitted, one for slow adjustment of the arm carrying the telescope and the other for moving the graduated circle round

the axis in order to enable readings to be made upon different portions of the graduations; this latter adjustment is used to

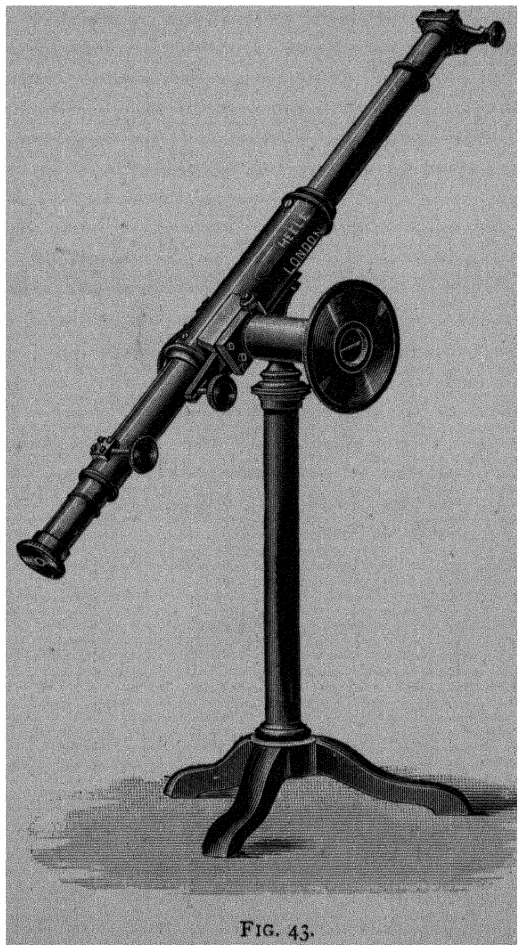


FIG. 43.

eliminate any errors of graduation. The collimator is carried by a separate standard G, which forms part of the tripod stand of the instrument. The prism table I can be rotated upon

its vertical axis by the rod H, the two being connected by bevel gearing.

Fig. 45 shows a spectrometer made by Hilger for Mr. J. W. Gifford, who has very kindly allowed me to reproduce it. The main features of this instrument are clearly enough shown in the illustration; there are, however, certain details to which it is necessary to draw special attention. It will be at once noticed that the brass tubes as usually used for the telescope and collimator have been replaced by leather bellows; this is owing

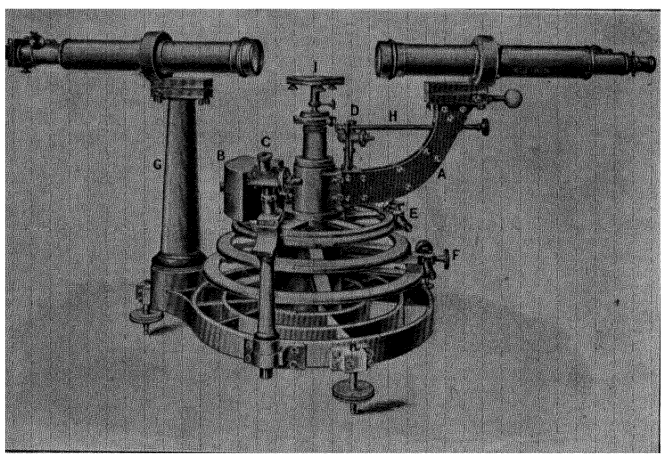


FIG. 44.

to the fact that there is always a slight amount of side-play in the focussing arrangements when brass tubes sliding into one another are used. The adjustments for focussing in this instrument can be seen underneath the leather bellows, and consist of tongued and grooved metal slides, as long as possible, so as to give plenty of bearing surface. At the eyepiece end of the telescope there is a photographic attachment, as shown in the illustration, and the eyepiece is visible outside the camera box; when used for visual work the dark slide is removed. The main graduated circle of the instrument is

18 inches in diameter, and can be read by means of micrometer eyepieces to within 1″ of arc. The prism table is also graduated, and can be read by means of a short telescope. Both the prism table and the fine adjustment of the telescope can be manipulated from the eyepiece end of the instrument, the former by the handle to be seen just under the telescope bellows, and the latter by the handle under the telescope arm. The key shown at the lower end of the telescope bearing, just above the tripod stand, is for the purpose of throwing the fine adjustment in or out of gear.

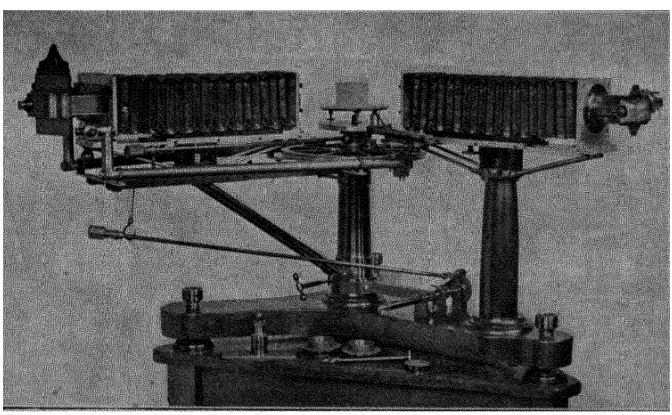


FIG. 45.

There is also another type of instrument which may be described here, namely, the fixed-arm spectroscope, although perhaps some of these instruments are not adapted for quantitative work. By a fixed-arm spectroscope is meant an instrument in which the telescope and collimator are immovable, and the spectrum is made to pass along in front of the observer by rotating the prism train. In this type may be included the Littrow instrument, in which the principle of auto-collimation is adopted, that is to say, the same tube serves for both collimator and telescope. The simplest form of fixed-arm spectroscope is one in which the constant deviation prism

shown on p. 60 is employed; in this instrument the telescope and collimator are fixed in the same horizontal plane, and at

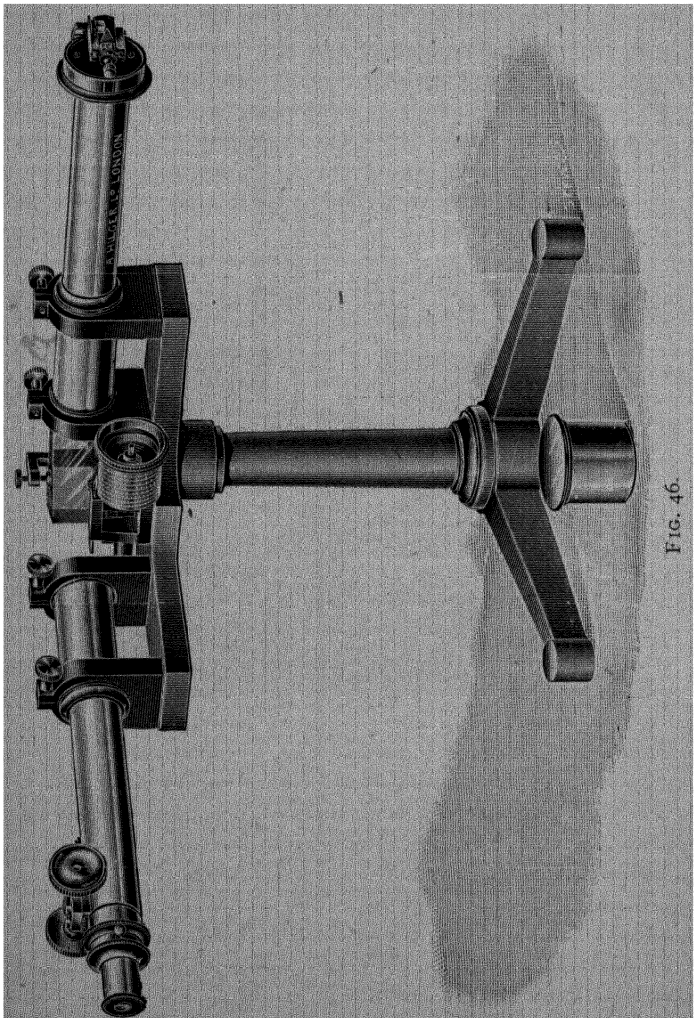


FIG. 46.

right angles to one another. The constant deviation prism is mounted upon a table which can be rotated by a tangent screw,

and in this way, as follows from the construction of the prism, the rays seen through the telescope are always those which traverse the prism at minimum deviation. This instrument is particularly suited for the preliminary analysis of the light before it enters an interferometer, or echelon grating (see Chapter IX).

Recently this instrument has been improved by Hilger, who has converted it into a direct reading wave-length spectrometer. The prism table is rotated by means of a tangent screw carrying a drum-head, upon which is a scroll graduated

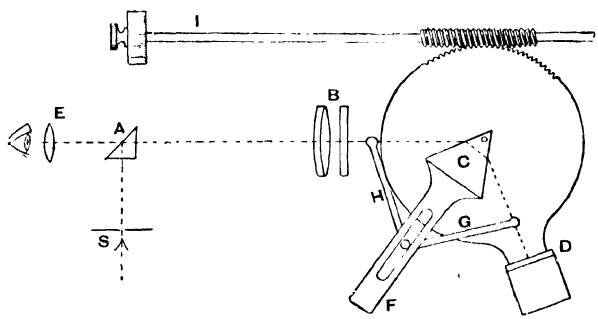


FIG. 47.

in wave-lengths. The eyepiece carries a spider web, which is adjusted on the spectrum line, and then the wave-length can be read directly off on the drum-head. The spider web itself may be moved a little to either side by means of a small screw projecting from the eyepiece, so that if at any time the instrument requires adjustment this may readily be carried out. This instrument, although the accuracy is not very great (about two Ångströms), proves exceedingly useful in ordinary spectroscopic work. The instrument is shown in Fig. 46.

Another instrument of this type is the one in which the multiple transmission prism system devised by Cassic is used. This prism system was shown on p. 62, and, it will be seen, requires the telescope and collimator to be fixed with their axes parallel to one another, but not coincident; the latter must

be a little higher than and a little to one side of the former, the amount of displacement being determined by the size of the prisms. The spectrum is made to traverse the field of view in the telescope by rotating the prism C (Fig. 26) round a vertical axis. Several other instruments of this type have been devised.

A diagrammatic plan of a Littrow type of spectroscope is shown in Fig. 47. The light enters the slit S, and then is totally reflected by the prism A; the lens B directs it as a parallel beam upon the prism C. This transmits the rays at minimum deviation, and they then fall normally upon the plane mirror D which reflects them back through the prisms to the lens B, whence they pass to the eyepiece E. The instrument is so adjusted that the rays on the return journey pass above or below the right angle prism A. At F is shown an arrangement for automatically keeping the prism in the position of minimum deviation; the tie G is pivoted upon the arm carrying the mirror D, which is free to rotate round a vertical axis directly under the centre of the prism C. The tie H is pivoted upon the stand of the apparatus; both the ties G and H are pivoted together to a pin working in the slot in the arm F, which carries the prism C. In order to cause the spectrum to move across the field of view it is only necessary to rotate the arm carrying the mirror D through a certain angle; it is clear that the prism C will move through half that angle, and therefore will be automatically kept in the position of minimum deviation.

A similar instrument, in which a concave mirror is used in place of the lens B in the last case, has been devised by Wadsworth,[1] and is shown in Fig. 48.

In this instrument the light enters the slit at *s*, and is then directed by the right-angle prism *a* on to the concave mirror at *b*; from here the light passes through the prism *c* to the plane mirror *d*. By this mirror it is reflected back along its path, and passing under the prism at *a* it reaches the eyepiece at *f*. As will be seen, the prism at *c* is provided with the same arrangement as in the last apparatus for automatic adjustment in the position of minimum deviation.

[1] *Phil. Mag.*, **38**. 137 (1894).

Wadsworth [1] has also designed a multiple transmission spectroscope, which partakes of the Littrow type. A diagram

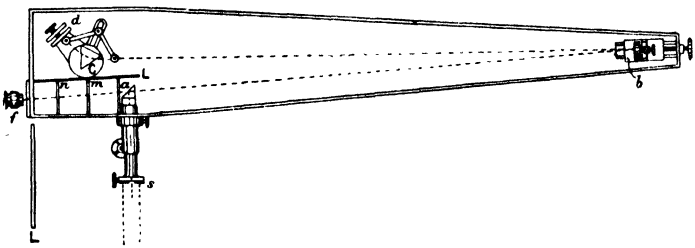


FIG. 48.

is shown in Fig. 49; the light coming through the slit at S is totally reflected by the right-angle prism on to the concave mirror A, by which it is directed as a parallel beam on to the refracting prism. The rays traverse the prism at minimum deviation, and are reflected by the plane mirrors B, C, and D, and then again enter the prism. On emerging they are again reflected by the plane mirrors E, F, and G, and enter the prism

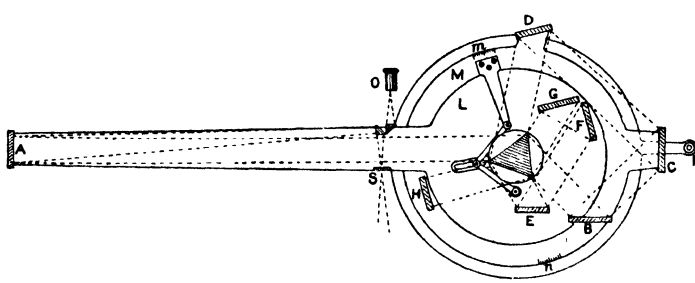


FIG. 49.

a third time. They then fall upon the plane mirror H, which is placed perpendicularly to their path; they are thus reflected back along their path till they reach the concave mirror A, by which they are focussed through the reflecting prism into the eyepiece at O. The light thus traverses the prism six times,

[1] *Astrophys. Journ.*, **2**. 264 (1895).

each time at minimum deviation. The method of adjusting the mirrors and refracting prism is automatic, and is obtained as follows. The first set of reflectors, B, C, D, and the final reflector H, are all fixed on the vernier circle M of the spectroscope, and rotate together with it; and the second set of reflectors, E, F, and G, are mounted together on an inner table, fixed to the arm which carries the concave mirror A, slit S, and observing eyepiece or plate-holder O. The prism itself is mounted on a third table, connected with the outer movable table M by means of the usual minimum deviation attachment. The outer divided circle *n* also rotates, and has attached to it an arm R for a small observing telescope, which is used only in the preliminary adjustment.

On account of the great number of reflections that the light has to undergo, this instrument is only suitable where very bright sources can be employed. At the same time it has the advantage of giving very high resolving power with only one prism, a consideration of some importance if a costly material is employed for the refracting prism.

It must be remembered that the accuracy of wave-length determination by visual reading cannot be compared with that obtained by photographic methods; in the latter cases photographs of the unknown spectrum and a standard spectrum are taken upon the same plate, superposed upon one another, or in juxtaposition, and the wave-lengths of the unknown lines are determined by measuring their positions on the photograph relatively to the known lines. A further disadvantage of the visual method lies in the fact that the ultra-violet region is not visible to the eye. In an apparatus for the photography of the spectrum a photographic plate is placed in lieu of the eyepiece in the focal plane of the telescope objective. It is obvious that the necessary apparatus may be very much simpler than in the case of a visual instrument, because there need be no moving parts. The name usually given to the apparatus designed for spectrum photography alone is a spectrograph.

It is, of course, possible to fit a photographic attachment to any of the spectroscopes described above; such an accessory is shown in Fig. 50. It consists of an oblong box A, to which

is screwed the brass tube B; this tube B fits into the telescope tube in place of the eyepiece. The frame C is supported by two metal strips, which are shown at D; this frame C is pivoted so that it can be moved a little one way or the other around a vertical axis, this adjustment being necessary to correct for the possible want of achromatism of the telescope lens. The frame A is cut away, as shown, to allow for this movement, and leather bellows are fixed to A and C to keep out all extraneous light. The frame C is provided with grooves, just as in

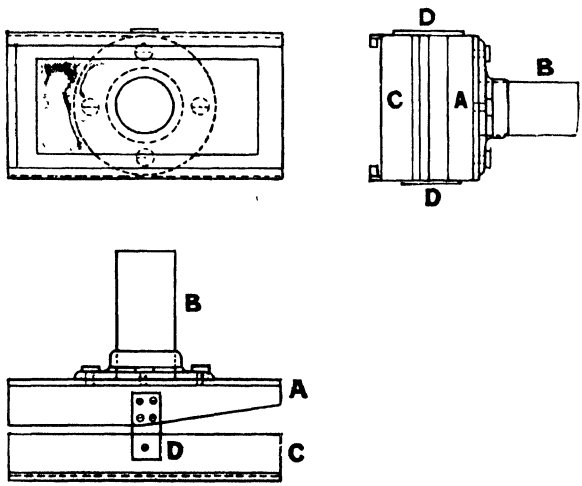


FIG. 50.

an ordinary camera, into which the dark slide fits. This little apparatus may be used to obtain photographs of small regions of the spectrum, small because the tube B has a small angular aperture, so that only a very short section of the spectrum can pass through at one time. It is very convenient to have vertical slides fixed upon the frame C to carry the dark slide. In this way if the latter is sufficiently broad several photographs can be taken upon each plate; it is then preferable that the frame C have a horizontal rectangular aperture just sufficiently large to allow the free passage of the light to the plate. By altering the height of the plate-carrier in the vertical slides on

C different portions of the plate can be exposed in turn, and in this way photographs of many spectra can be obtained on the same negative.

It is far better, however, if a spectrometer mounting be employed to remove the telescope tube altogether, and set in its place a wooden box, as shown in Fig. 51 in plan; the box is made to fit the spectrometer mounting in the same way as the original telescope. The telescope lens is at A, and is provided with a focussing arrangement B; the rest explains itself. In this way none of the spectrum received by the telescope lens is cut off by any part of the apparatus.

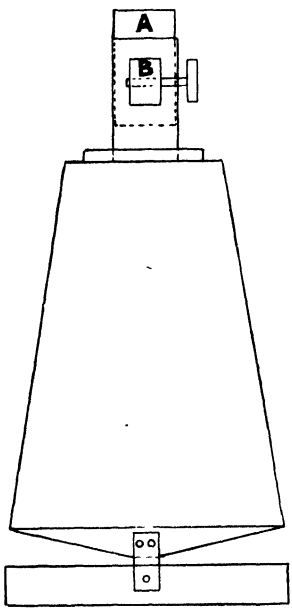


FIG. 51.

In Fig. 52 is shown a diagram of a mounting for a spectrograph as has been set up at the The University, Liverpool, which, perhaps, may be described on account of its extreme simplicity. The lenses are 2 inches in diameter, and of 5 feet focus, and there are two 60° prisms of glass, 0·167 (see list on p. 91). Both lenses are mounted in heavy brass cells screwed into brass tubes 2·5 inches in diameter and 6 inches long. The whole of the mounting of this apparatus is of wood, and is as simple as possible. It consists of two frames—one for the slit and collimator, and the other for the telescope lens and camera fittings. Each frame is composed of two pieces of 2-inch quartering, 6 feet long, bolted together with three iron bolts, one at each end and one in the middle. The pieces of quartering are separated by three small distance pieces, 1 inch thick, one at each bolt. The two pieces of quartering are shown at A, and the bolts at B, with the

distance pieces C. It will be seen from the figure that a 1-inch slot is formed along the frames, and the tables carrying the lenses, etc., are provided with lugs, which fit into these slots. Underneath each frame is screwed the 1-inch board D, which serves to strengthen the whole, and guard against warping. Both frames are exactly similar, and form a very convenient basis for the mounting.

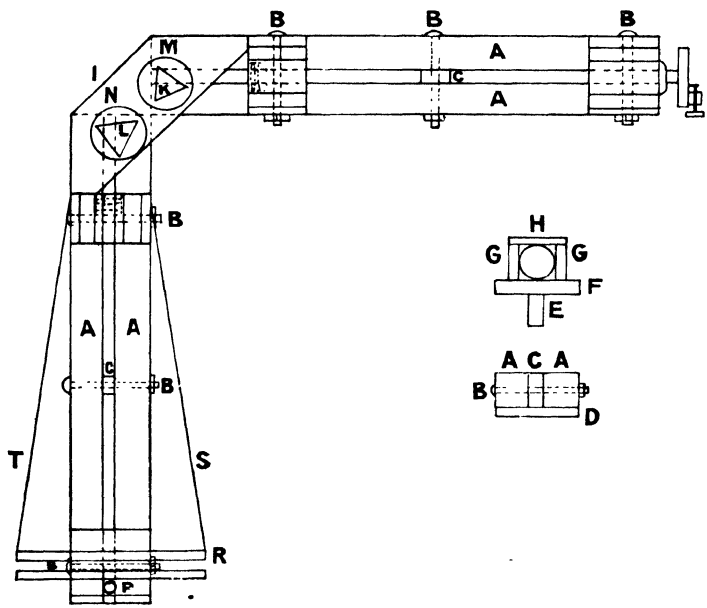


FIG. 52.

A diagram of the tables carrying the lenses and slit is shown at F; these are all of 1-inch wood, 5 inches square, and, as mentioned above, are firmly screwed to 1-inch lugs E, which fit into the slots. They can thus be put in any position, and, when all adjustments have been made, are securely fastened by screws into the pieces of quartering. The method of mounting the carrier tubes of the slit and two lenses, which is the same in each case, is as follows:—

The two side pieces G, G, which are screwed to the table running the whole length, are set at just sufficient distance apart to allow the carrier tubes to pass between them. The top H, slightly arched on its under side, can then be fastened down by screws into the side pieces, and serves to hold the carrier tubes firmly in their position.

The main prism table I, which is a board of 6 inches wide and $\frac{7}{8}$ inch thick, is screwed to the projecting end of the collimator frame at an angle of about 45°. The two prisms shown at K and L are mounted by a little Chatterton cement at each corner on two tables, $3\frac{1}{2}$ inches square and $\frac{3}{16}$ inch, which are shown at M and N. These two tables are held by a single screw through their centres into the main table underneath, and are thus free to revolve. By this device, each prism can be rotated for the minimum deviation adjustment, and can be finally fixed in the required position by a small screw through the corner of its small table.

A small astronomical telescope is mounted to examine the spectrum reflected from the first surface of the second prism. The advantages of this are obvious for purposes of visual comparison, and for observing whether the slit is correctly illuminated.

The camera frame is fixed entirely separately from the collimator frame. It is held by a single bolt about 1 inch from the end, not shown in the plan, which, passing through the supporting table, is clamped by a nut underneath. This bolt is placed vertically under the second prism, and thus the camera frame can be rotated, if necessary, for examination of different parts of the spectrum. The camera has, however, been made wide enough to take as much of the spectrum as is usually required for practical purposes; and, therefore, unless it be desired to examine the extreme blue part of the spectrum, this adjustment is not required.

The table which carries the dark slide differs slightly from the others; the chief difference lies in the fact that it is not fastened to its lug, but is held by a bolt, P, passing through its centre and the lug underneath. An angular adjustment is thus rendered possible, in addition to the motion parallel to the

axis of the telescope lens. This adjustment, of course, is necessary in order to bring the photographic plate at the required angle to the axis of the lens, which is necessary for good focus. The position of the table can be fixed by a butterfly nut and large washer underneath the frame. A frame is erected vertically on the table, against which the dark slide is held by strong steel springs.

The length of the camera table and its frame is 12½ inches over all, with a centre aperture in the frame of 11 inches by 3½ inches.

The dark slide needs no special description. It carries a plate 11 inches by 3 inches, this length of plate being sufficient to photograph as much of the spectrum as can be focussed at the same time, with sufficient accuracy for good measurement.

As at present fixed, the spectrum photograph extends from wave-length 7000 to about 3800 Ångström units. The focus with this range is perfectly good, and though the prisms and lenses will give a spectrum extending to 3100 Ångström units, the focus has not been found to be sufficiently good for the whole range, and, therefore, the ultra-violet portion is excluded, but can be obtained by swinging the camera frame round its bolt, as described above.

With regard to the method of covering the apparatus in order to protect it from daylight, this is done by means of two thicknesses of satteen, supported by light wooden laths, which are fastened to the upright side supports on the lens and slit tables. The satteen is nailed down on each side of the quartering, after being stretched tightly over the laths. A special arrangement, of course, is necessary in the case of the covering of the camera frame. The method adopted is as follows: a light frame, R, about 15 inches long by 6 inches high, is erected vertically on the camera frame about 4 inches in front of the camera table. Four laths, S and T, pass from the corners of this to the uprights on the table carrying the telescope lens. A double thickness of satteen is stretched over these and nailed underneath, along each side of the quartering. The space between this frame and the dark slide frame is covered loosely with satteen. The satteen is nailed all round the two frames,

but is not stretched tightly between them, and a considerable latitude in the position of the dark slide table is thus obtained.

Any open spaces such as occur at the corners of the mounting of the carrier tubes for the slit and two lenses are filled in with dark tailor's wool.

The prism part of the apparatus is covered with a loose velvet cloth, which is supported by a light wooden rail, carried by supports erected from the large prism table.

This arrangement has been found perfectly to exclude all light, for, though the room is often brilliantly lighted with sunshine, the most rapid plates are not fogged, even with long exposures.

This apparatus has been thus described in detail in order to show how a perfectly serviceable mounting can be set up with the help of a carpenter at the cost of only a few shillings. In making a spectrograph, the essential point is that the slit, lenses, and prisms be of good quality; the mounting may very well be left to the ingenuity of the experimenter. A great number of designs have been brought forward, and any one of these may be adopted; but for ordinary laboratory work in photographing spectra it would appear that some such simple apparatus described above is as good as could be wished; in æsthetic appearance, perhaps, it may fail to please, but this is of small consequence in an apparatus destined for much use.

It is very evident that owing to the inability of the eye to detect light vibrations of shorter wave-length than about $\lambda = 4000$, it is necessary to employ photographic methods when dealing with the ultra-violet regions of the spectrum. Although Schott and Genossen have introduced a glass which is transparent to the ultra-violet rays as far down as $\lambda = 2800$, still an apparatus suitable for the photography of the whole ultra-violet must have its optical parts made of some material more transparent to these rays than glass. Quartz is by far the best substance, for calcite is not transparent to the extreme ultra-violet, and, moreover, the double refraction exhibited by it is a great drawback. In a prism spectrograph, therefore, intended for use in the ultra-violet, it is desirable that the

prism at all events should be made of quartz. As regards the lenses, if fluorite only were obtainable at a reasonable price,

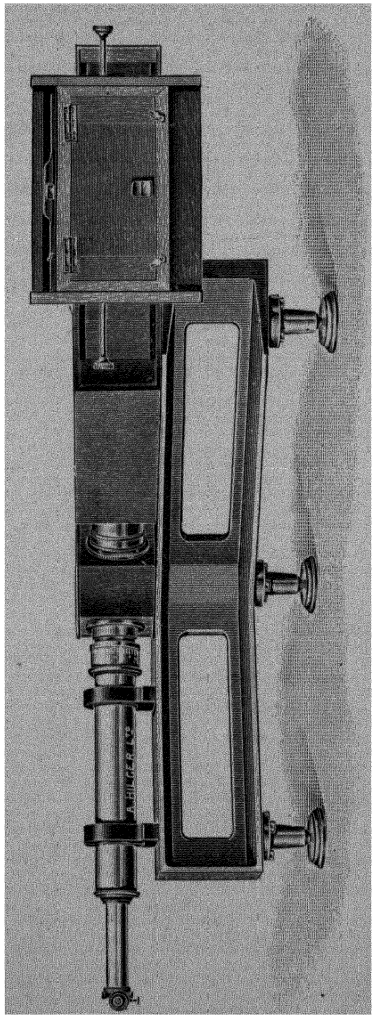


FIG. 53.

the quartz-fluorite achromatic combination would be of great

service. On the other hand, the quartz calcite combination suffers from the want of transparency to the extreme ultra-violet already mentioned. Generally speaking, if quartz lenses be used alone it will be found that the foci lie on a curve. Films must on this account be used so that they can be bent to the focal curve of the instrument. It is quite possible to construct a spectrograph with quartz optical parts and to cut a template which fits the focal curve. This template is mounted in the dark slide, and the photographic film is pressed up against the template by some suitable means.

It has recently been found possible, however, to cut the quartz prism and lenses in such a way that the focal curve is almost flat, although it lies at an acute angle (27°) with the axis of the telescope lens.

Instruments of this type are now to be obtained, and they rank amongst the most convenient forms for work in the ultra-violet region of the spectrum. They have the advantage of being absolutely transparent to all the ultra-violet rays, and at the same time giving excellent definition. Such an instrument is shown in Fig. 53.

A novel form of quartz spectrograph has recently been devised by Féry,[1] who makes use of a prism with curved faces and thereby eliminates all lenses. The theory of the instrument is exceedingly simple, as may be seen on reference to Fig. 54, where R is the radius of curvature of the front face of the prism MPQN. Then the lines CP, CQ make equal angles i with the normals AP, AQ. The slit is placed at C, and for any bundle of monochromatic rays from C falling on the front prism face they will be refracted, making the angles r with the normals. If the paths of these rays be prolonged they will meet at B, which is the centre of curvature of the second curved face of the prism, MN. This second surface is silvered or nickeled, and therefore the rays will be returned to an exact focus on the slit. It is easy to see that the points ABCQP all lie on a circle, so that the two centres of curvature, the slit and the spectrum, lie upon the same circle. In actual practice

[1] *Journ. de Physique*, **9**. 762 (1910); and *Astrophys. Journ.*, **34**. 79 (1911).

the slit is moved round the circle a little so as to increase the incidence angle *i*, with the result that the spectrum will be brought to a focus on the circle a short distance from the slit. The complete instrument is shown in Figs. 55 and 56. In Fig. 56 P is the prism, F the slit, E the curved photographic plate, and A a condensing lens. A further point in connection with this apparatus is that a certain amount of astigmatism occurs, as in the case of Rowland's concave grating (see p. 188). A comparison of two spectra by draw slides over the slit is therefore not possible, but is carried out by means of a movable screen, with a rectangular opening, which is placed immediately in front of the photographic plate.

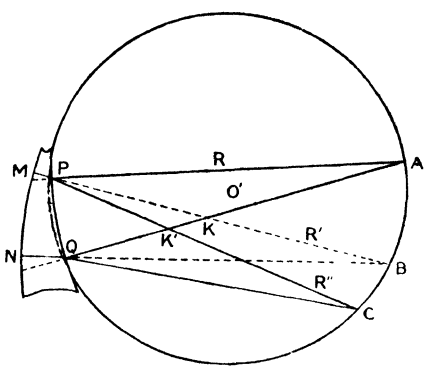


FIG. 54.

A very useful addition to any spectrograph is to have the dark slide which carries the photographic plate working in vertical grooves. In this way by moving the plate up or down in its grooves a number of photographs may be taken upon the same plate. A rack and pinion arrangement should be attached so as to allow the dark slide to be brought to any desired position, and it is also well to have a scale marked on the frame carrying the dark slide, so that the position of the plate may at any time be read. It is necessary, if a great number of spectra are to be photographed upon one plate, to limit the width of each spectrum sufficiently to allow of this

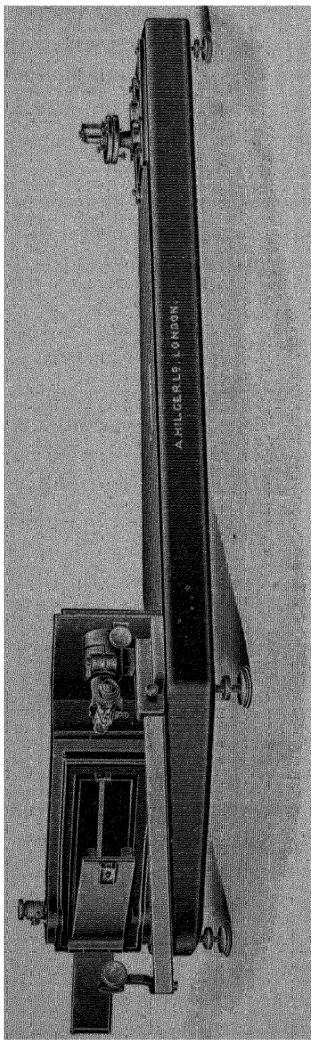


FIG. 55.

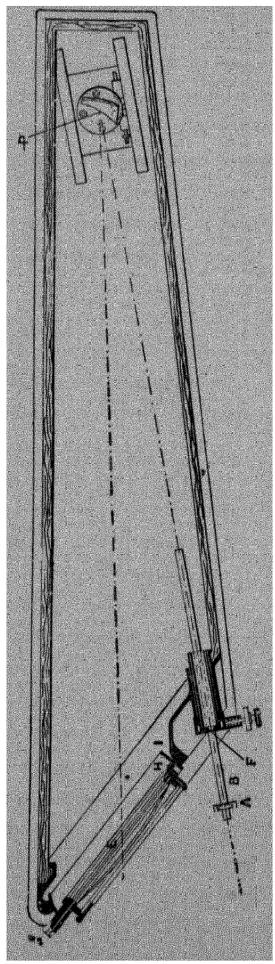


FIG. 56.

without the successive photographs over-lapping. This may be done either by using only a very short slit or by having a screen with a narrow rectangular opening placed just in front of the photographic plate. The above arrangement is shown in Fig. 53.

CHAPTER V

THE PRISM SPECTROSCOPE IN PRACTICE

The Adjustment of the Prism Spectroscope.—For the complete adjustment of a prism spectroscope it is necessary that the following conditions be satisfied :—

(1) That the collimating lens direct a beam of parallel light upon the first prism face.

(2) That the optic axes of the collimator and telescope pass through the same principal plane of the prism whatever may be the position of the telescope.

(3) That the opening of the slit be parallel to the refracting edge of the prism.

The methods of adjustment of the apparatus, so that these three conditions may be satisfied, may be described in detail for the case of an ordinary spectrometer with one prism, such as the instrument shown in Fig. 41. Similar methods are applicable to the more complex instruments. First of all, the telescope of the instrument should be focussed for parallel rays; the eyepiece is first adjusted so that the cross-threads are in good focus, and then the telescope is directed towards some very distant object, such as a church spire or flagstaff, and the whole eyepiece moved in or out until the object is seen to be well defined. This focus will be found to be sufficiently near to that actually necessary for objects at an infinite distance, that is to say, for parallel rays. The slit of the instrument is then illuminated by some convenient source of light, such as an ordinary gas-flame, and the telescope and collimator brought into line with one another so that the image of the slit can be seen direct without the interposition of the prism. The collimator

is then focussed until a perfectly sharp image of the slit is seen; the collimator will then be approximately in correct adjustment. The centre of the image of the slit should be seen in the centre of the field of view in the telescopic eyepiece, and then the axes of the telescope and collimator will form portions of the same straight line.

A convenient way to test this adjustment is to cover the slit with a piece of cardboard having a small hole cut in it a millimetre or so in diameter.[1] In this way only the central portion of the slit is exposed to the illumination, and this should be seen in the centre of the field of view in the telescope; if it appears above or below the centre the collimator and telescope are carefully adjusted until they are properly level. Care must also be taken to see that the slit opening is truly vertical. The prism is then put in place and levelled so that the refracting edge is vertical and parallel to the slit.

One of the following methods may be used for the more accurate adjustment of the collimator focus for parallel rays. First, Schuster's method[2]—the prism is set in the position of minimum deviation, and the telescope turned so that the image of the D line or some other convenient ray is seen. The telescope is then turned a little to one side of the image; it is evident that there are now two positions of the prism, one on each side of that of minimum deviation, which will bring the image of the line again into view in the centre of the field of the telescope. The prism is turned to these two positions in succession, and the line observed in each case; if the line appears in perfectly good focus at each time, then the telescope and collimator are both accurately adjusted for parallel rays. If, however, as is more probable, the focus of the line appears better at one time than at the other, the following procedure is adopted. The prism is first turned to the one position, and then the collimator is focussed until the line is seen perfectly sharp; after turning the prism to the other position the telescope

[1] Very often the slit is provided with a wedge-shaped diaphragm which works in grooves outside the jaws. This is very convenient in the above adjustment.

[2] *Phil. Mag.*, 7. 95 (1879).

is focussed to produce the best definition. After one or two repetitions it will be found that the condition will be obtained that the line remains in perfect focus whichever way the prism is turned. This corresponds to perfect adjustment of both the collimator and telescope for parallel rays.

The second method is that devised by Lippmann,[1] who employs two strips of plane-parallel glass plate, which are set one above the other and at right angles to one another. This apparatus is set in the path of the rays from the collimator; if these rays be truly parallel no effect will be produced, but if they

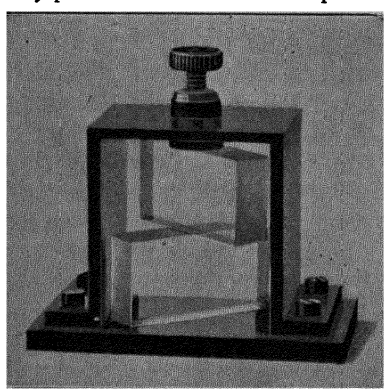


FIG. 57.

be convergent or divergent, the upper and lower halves of the image of the slit will appear relatively displaced. The apparatus is shown in Fig. 57.

In an ordinary spectrometer with achromatic glass lenses, when the collimator has been adjusted for giving parallel rays of one wave-length, this adjustment will be suitable for all the rays of the spectrum. It must be remembered, however, that the eyepiece is not achromatic in every sense of the word; as was explained in Chapter III., the eyepiece is so adjusted that the different coloured images all have the same apparent size. As these are still distributed along the axis, a different focus of the telescope is required for rays of different wave-lengths. When non-achromatised lenses are employed, such as simple

[1] *Comptes Rendus*, **129**. 569 (1899).

lenses of quartz, if the focus of the collimator be found for rays of known wave-length, the focus for any other ray may be found by simple calculation from the ordinary formulæ of lenses, and the relative position of slit and collimating lens altered accordingly. It is very convenient for this purpose to have the focussing tube of the collimator graduated in millimetres in order to allow of a definite change in the focus being made, such as will be required in moving from one part of the spectrum to another.

In the adjustment of prism apparatus for the photography of the spectrum, we have, in addition to the previous adjustments, the focussing of the photographic plate in order to obtain the best definition. Generally speaking, in apparatus in which considerable portions of the spectrum are photographed upon one plate, the collimator is adjusted for parallelism and the prisms set at minimum deviation for the mean rays of the region photographed. Better definition of the photographed lines is more likely to be obtained in this way. There are two separate adjustments to be attended to with respect to the photographic plate, viz. the distance of the plate from the camera lens, and its angle to the axis of the lens; these adjustments resolve themselves into a series of trials by error. In the photographic apparatus described in the last chapter the camera back was shown to be mounted in such a way that it can be rotated round a central vertical axis; this is necessary in order to obtain the required tilt of the plate. A preliminary focussing of the plate may readily be obtained by the use of a ground-glass screen as is customary in ordinary photography; a photograph of the spectrum is then taken, and if the definition is not satisfactory the camera back is moved to or from the lens and a second photograph taken. This is repeated until the lines in the central portion of the plate are in perfect focus. It only remains now to alter the tilt of the plate until the whole spectrum, or as much of it as possible, is in focus.

While in the case of glass, quartz-fluorite, or quartz-calcite achromats it is possible to obtain a flat field, and therefore to use glass photographic plates, this is generally impossible with uncorrected lenses, especially if large portions of the spectrum

are to be photographed upon the same plate. Under these circumstances the focus of the objective lies upon a curve, and it becomes necessary to use films. A frame cut to agree with the focal curve is fixed in the plate-holder, and the film is held up against this frame during an exposure.[1]

In the final adjustments for the focus it is advisable to use a source of light the spectrum of which is known to consist of fine, sharply defined lines. Metallic spectra very often contain lines which are diffused on one or both sides; such lines are of little use in the adjustment of the apparatus for the best definition. One of the most satisfactory sources of illumination for this purpose is a vacuum tube containing carbon dioxide or air, as the spectrum given by such a tube when the electric current passes through it is one of bands of extremely fine lines.

For the purpose of improving the illumination it is customary to focus an image of the source upon the slit by means of a condensing lens; in this way, unless the source is very large or very near the slit, considerably more light is obtained. An advantage is also gained in the case of flame spectra, in that the slit is not subjected to any possible spluttering or splashing of the salt in the flame.

The Methods of Wave-length Determination with the Prism Spectroscope.—In the case of the prism spectroscope, almost all methods of determination of the wave-lengths of spectrum lines are carried out by processes of comparison between them and the lines of other spectra, the wave-lengths of which have already been accurately determined; that is to say, the position of the unknown lines in the spectrum are measured relatively to the positions of certain well-known lines, and the wave-lengths are obtained by interpolation. In the case of the visible portion of the spectrum this may be done by means of eye observations if great accuracy be not required, but, generally speaking, photographic methods are to be recommended from their greater reliability.

For visual work some sort of scale must be employed, on which the positions of the lines are read; this may be a scale photographed upon glass, which, by reflection from the last

[1] See, however, the quartz spectrograph described on p. 134.

prism face, is viewed at the same time as the spectrum, and is so adjusted as to appear above or below it, and adjacent to its edge. This was used by Bunsen and Kirchhoff, and the position of the lines may be readily read upon it, but only quite roughly, so that the method can hardly be recommended at the present time. It is important to note that such a photographed scale very easily shifts its position relatively to the spectrum; it is necessary, therefore, that the scale be provided with some form of adjustment, by means of which its position can be altered; when using the instrument at any time, care should be taken that the scale is correctly placed, which may quite readily be realized by arranging that some line, such as the D line, be brought to the same reading; this must always be carried out before any series of measurements are made.

Far better than the method of the photographed scale is the method of measuring the deviations of the line, which may be carried to a greater pitch of accuracy. The apparatus used for this purpose, known as the spectrometer, has already been sufficiently described, and it only remains to show how the method is put into practice. If possible, it is better always to work with the prism in the position of minimum deviation for every ray examined; this is a necessity in the case of calcite prisms, and is to be preferred with those of other media. In actual observations the fixed pointer in the eyepiece is first of all focussed, and then, after focussing the image of the slit directly without the intervention of the prism, the position of the telescope is read upon the divided circle; the telescope is then moved until the pointer is adjusted exactly upon a spectrum line, when the position is again read upon the divided circle. Consecutive readings should show the smallest possible or no difference amongst themselves.

In order to find the wave-length of an unknown line from such visual methods one may use the method of graphical interpolation or an interpolation formula such as Hartmann's which was mentioned on p. 74. The use of this formula is very simple, but will be understood more easily when applied to a photographed spectrum, and therefore it will be exemplified below (see p. 158). The method of graphical interpolation

consists in drawing the dispersion curve of the spectroscope; that is to say, the curve expressing the relation between wave-length and the deviation produced. In order to obtain this curve, a number of well-known lines in different parts of the spectrum are chosen, and their deviations measured as accurately as possible. These numbers, with the wave-lengths or oscillation frequencies of the lines, are then plotted on squared paper, and a curve drawn through the points obtained; this curve must, of course, be perfectly smooth, without any sudden changes of direction, and it is the more accurate the greater the number of lines measured for the purpose. When this curve has once been drawn for an instrument, the determination of the wave-length of an unknown line becomes very simple; it is only necessary to measure its deviation, when the wave-length can be read directly off from the curve.

The choice of lines must be left to the discretion of the experimenter, but it must be remembered that only sharp and well-defined lines should be taken. The most satisfactory in this respect are the lines given by gases under reduced pressure, and those given by hydrogen and helium will probably be found to be sufficient for ordinary purposes. Collie[1] has pointed out that if the helium and hydrogen be mixed with mercury vapour, certain lines in the mercury spectrum will appear very strongly accentuated. He recommends the use of such a vacuum tube for the calibration of a spectrometer. The wave-lengths of the lines in this spectrum are as follows:—

Helium,	red,	7065·48	Ångström units.
Helium,	red,	6678·37	,, ,,
Hydrogen,	red,	6563·04	,, ,,
Mercury,	orange,	6152·3	,, ,,
Helium,	yellow,	5875·87	,, ,,
Mercury,	yellow,	5790·5	,, ,,
Mercury,	yellow,	5769·5	,, ,,
Mercury,	green,	5461·0	,, ,,
Helium,	green,	5015·73	,, ,,
Helium,	green,	4922·10	,, ,,
Hydrogen,	blue,	4861·49	,, ,,
Helium,	blue,	4713·25	,, ,,
Helium,	violet,	4471·65	,, ,,
Mercury,	violet,	4358·6	,, ,,
Hydrogen,	violet,	4340·66	,, ,,

[1] *Proc. Roy. Soc.*, **71**. 25 (1902).

There are in this list fifteen lines which are fairly equally distributed over the spectrum, and should prove sufficiently numerous for the purposes of the calibration curve of an ordinary laboratory instrument. If, however, more lines are required in order to render the curve more accurate, these may readily be found in the spark spectra of cadmium and of copper, and some other metals. From the helium, hydrogen, and mercury lines, it is quite possible to draw a calibration curve which is almost correct throughout its whole length; when once this curve has been drawn it is a simple matter to read the deviations of more lines which may afterwards be put upon the curve. When the spectra of metals are employed it is often difficult to recognise any lines amongst the great number which are visible; but by means of the approximate calibration curve, the wave-lengths may be found with sufficient approximation to recognise them in a list of the lines of the element. The true wave-lengths may then be used to correct the curve. The **principal** lines in the visible regions of the spark spectra of copper and cadmium may be given here—

Cadmium.	Copper.	Cadmium.	Copper.
6439·3	5782·3	4217·1	4932·5
5379·3	5700·39	4127·1	4911·0
5338·6	5292·75	4095·0	4704·77
5086·1	5218·45[1]	4057·7	4651·31
4800·1	5153·33[1]	3988·4	4275·32
4678·4	5105·75	3984·7	
4415·9	4955·8		

It will be found that if, instead of the wave-lengths, the oscillation frequencies of the lines be used, the shape of the curve will be flatter, and thus it becomes rather easier to draw. By the oscillation frequency is meant the number of waves contained in one centimetre in vacuo, that is to say, the reciprocal of the wave-length reduced to vacuum. In order to reduce the wave-length of any line measured in air to its real value in vacuo, it is necessary to multiply by the refractive index of air for light of the particular wave-length. The

[1] These are inclined to be diffused.

refractive indices of air have been determined with great accuracy by Kayser and Runge;[1] the values they found at 0° C. and 760 mm. pressure are expressed by the following equation :—

$$10^7 (\mu - 1) = 2878{\cdot}7 + 13{\cdot}16\lambda^{-2} + 0{\cdot}316\lambda^{-4},$$

when λ is expressed in 10^{-6} metrès or thousandths of a millimetre. This formula shows that the index of air lies between 1·00029 for $\lambda = 0{\cdot}8000 \times 10^{-6}$ metres, and 1·00035 at $\lambda = 0{\cdot}2000 \times 10^{-6}$ metres.

Recently the indices of refraction of air have been determined by Rentschler[2] using an interference method. The values found extend from $\lambda = 5770$ to $\lambda = 3341$ and are expressed by the following formula :—

$$10^7 (\mu - 1) = 2903{\cdot}1 + 3{\cdot}80\lambda^{-2} + 1{\cdot}23\lambda^{-4}.$$

In making the corrections in actual practice it is simplest to add a small number to the wave-lengths. A table of these corrections can be readily constructed; as can be seen, they lie between 2·52 Ångström units at $\lambda = 8000$, and 0·70 at $\lambda = 2000$. Such a table is given complete in Watts' *Index of Spectra*, Appendix E, p. 51.

In Fig. 58 are shown two calibration curves of a spectrometer, one, A, being drawn with the wave-lengths of the spectrum lines, and the other, B, with the oscillation frequencies; the same lines are used in each case. As can be seen from the curves, the angular deviations of the lines are expressed on the abscissæ; on the ordinates are expressed the wave-lengths in one case, and the oscillation frequencies in the other case.

The determination of wave-lengths in this way by visual observation can be quickly carried out, and serves excellently well for the identification of lines in a qualitative way; it is possible, of course, to use an instrument of high dispersion and resolving power, and by its means draw a dispersion curve on a large scale, from which the wave-lengths of unknown lines may be determined with considerable accuracy. For the drawing of such an extended curve a great number of points must be read so as to obtain the required accuracy, and it is

[1] *Ann. der Phys.*, **50**. 293 (1893). [2] *Astrophys. Journ.*, **28**. 345 (1908).

doubtful whether it is worth the extra trouble and expense involved. It is far preferable to have recourse to photographic methods of comparison, which are able to give much more accurate results with very much less costly apparatus. The

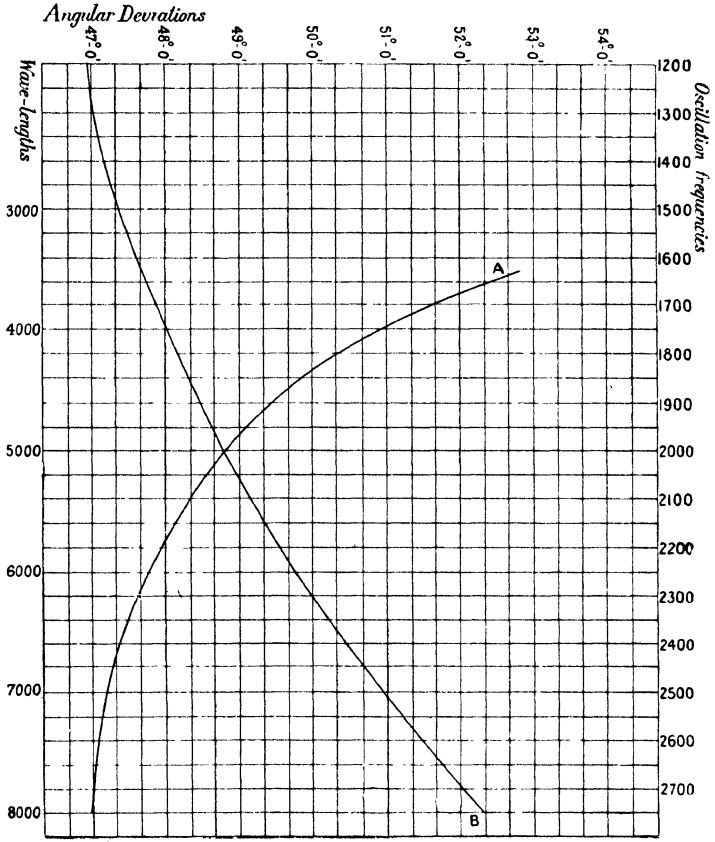


FIG. 58.

method consists in obtaining, with the same instrument, photographs of the unknown spectrum, and a standard spectrum upon the same plate, when the unknown wave-lengths are obtained by interpolation from the wave-lengths of the lines in

the standard spectrum. The method is quite similar to the graphical interpolation described above, because the photograph gives a permanent record of the deviations suffered by the various lines, and since the standard spectrum is so chosen as to contain a great number of lines, there is no need to draw the dispersion curve. In this photographic comparison of spectra care should be taken that the two spectra be quite contiguous to one another, still better, that they should overlap one another a little, in order to render the relative measurement of the two photographs more accurate.

It will be found on comparing two spectra that unless the rays from the two sources of light fall upon the slit at the same angle, the two spectra will be slightly displaced relatively to one another upon the photographic plate, owing to the fact that different parts of the collimating lens are used in each case.[1] In accurate work, therefore, it is necessary to guard against this by ensuring that the two sources of light are placed in identical positions. This may be readily arranged for by the use of a lens for focussing an image of the source upon the slit. An image of the light source chosen as the standard, *e.g.* the arc between iron poles, is focussed upon a portion of the slit, care being taken that the arc, the slit, and the centre of the collimating lens lie on the same straight line. When the spectrum of this source has been photographed, the arc is removed and the second light source placed in its place, so that, without moving the condensing lens, the image of the source is focussed upon the slit a little above or below the place upon which the image of the arc was previously thrown. The spectrum of this light is now photographed, and it will then be found that the two spectra upon the plate are quite correctly placed in relation to one another. It is hardly necessary to point out that the slide of the camera plate-carrier

[1] For this reason the right-angled comparison prism is useless for the accurate comparison of spectra; this accessory is to be recommended only for rough visual comparisons. For more accurate work, when two spectra are photographically compared, it is necessary to photograph the two sources in succession through adjacent portions of the slit as described in the text.

should not be shut after it has once been opened until the two photographs have been obtained, as otherwise the plate is certain to be moved; it is necessary to cover the slit with a piece of black paper, which is removed during the exposing of the plate; or, better, the draw slides described upon p. 54 may be used, and will be found to be extremely useful for the purpose. When a photograph of the standard and the unknown spectrum has been obtained in this way, it only remains to measure the relative positions of the known and unknown lines from which the wave-lengths of the latter may be computed.

A word may be said here regarding the choice of the standards of comparison. The most satisfactory of these is the spectrum of the iron arc, although it entails perhaps more trouble owing to its being of so complex a nature. This spectrum, however, is not always available, owing to the want of the necessary appliances, and, further, its complexity renders it unsuitable for use with instruments of small dispersion; some other light source must then be used. The spark spectrum of iron is convenient, and serves very well; a very good spectrum is given by an alloy of cadmium, tin, and lead as has been used by Hartley. The alloy is made by melting the metals together in molecular proportions, and its spectrum consists of a number of lines fairly equally distributed over the spectrum. Sparks from a coil with a Leyden jar in parallel are passed between two poles of the metal in question.

Some difficulty is often found in obtaining a standard spectrum which is sufficiently rich in lines in the red and orange regions of the spectrum. The iron arc contains many lines in these regions, but it is necessary to employ very strong electric currents in order to bring them out with sufficient intensity to make the photographing of them feasible. A current of at least 10—15 amperes is required, and under these circumstances the iron poles burn away very fast. The wave-lengths of the lines in the arc spectrum of iron have been measured by Kayser and Runge[1] to as far as $\lambda = 6750$. The spectrum of the new gas neon is also very rich in red rays,

[1] *Abhand. Berl. Akad.*, 1888. Also Watts' *Index of Spectra*, Appendix C, p. 1.

and therefore this gas serves extremely well as a standard for the red, orange, and yellow regions of the spectrum. The wave-lengths of the principal lines belonging to this gas are as follows :[1]—

6402·40	6266·66	6128·63	5974·73
6383·15	6217·50	6096·37	5944·91
6334·65	6182·37	6074·52	5882·04
6328·38	6163·79	6030·20	5852·65
6304·99	6143·28	5975·78	5764·54

When the standard of comparison has been chosen it is necessary first to take a photograph of its spectrum and calibrate it, as it were, by marking as many as possible of the lines of known wave-length, preferably writing the wave-lengths against them upon the plate; this saves endless trouble in future work, and the plate serves as a reference plate.

The recognition of the lines may best be carried out by comparison with one of the standard maps which are now published. For example, in the case of the arc spectrum of iron, the various lines may be identified by reference to Kayser and Runge's wave-length map of this spectrum. An exceedingly valuable reference book also is the atlas of spectra,[2] published by Hagenbach and Konen. If only a small portion of any spectrum has to be identified, it may be found difficult to do this at first sight. This difficulty of course disappears if the instrument possesses an attachment for photographing a wave-length scale alongside the spectrum. If such attachment be not available, then it may prove an advantage to photograph the unfamiliar spectrum with a more familiar spectrum alongside it. This will at once form a guide to the comparison with the standard map.

In any comparison with a standard map of a spectrum taken by means of a prism spectrograph, it must be remembered that as one proceeds along the prismatic spectrum towards the blue, the dispersion continually increases, so that a given linear

[1] Baly, *Phil. Trans.*, **202**. A. 183 (1903); and also *Proc. Roy. Soc.*, **72**, 84 (1903). Also Watson, *Proc. Roy. Soc.*, **81**. 181 (1908).

[2] *Atlas of Emission Spectra of Most of the Elements.* A. Hagenbach and H. Konen. Authorised English Translation by A. S. King. W. Wesley and Son, London, 1905, pp. vii. + 70; with 28 plates. £1 7*s*.

distance on the plate represents a smaller and smaller change in the wave-length and *vice versâ*.

It hardly need be mentioned that the wave-length scale attachment referred to above cannot be expected to serve as the basis of an accurate measurement of the wave-length of the lines. This can only be done by the method of interpolation described.

A description may be here given of the micrometer apparatus used in all linear measurements of photographs of spectra.

The most common type in use is the travelling microscope, which consists of a microscope mounted on a slide which accurately works in grooves, and is actuated by a micrometer screw. The length of travel of the slide is usually about six inches, which is quite sufficient for all ordinary work. The micrometer screw, which is cut and corrected as described on p. 36, is mounted on the frame of the instrument, and works in bearings so that it cannot move backwards or forwards; it is provided with a large divided drum-head and also a milled wheel for turning it. The drum-head is, as a rule, divided into a hundred divisions, which can easily be read to a tenth of a division, so that, if the screw is cut with a pitch of one millimetre, the movement of the microscope can be read to a thousandth of a millimetre. The whole is fixed to a massive stand in order to have the instrument as rigid as possible. Under the microscope is a support upon which the plate rests, and there is also provided a travelling mirror for illumination. The microscope proper is of quite low power, usually about twenty diameters; if a higher power be used the spectrum lines will become too magnified and difficult of measurement. The instrument is shown in Fig. 59.

In the eyepiece of the microscope, which is of the Ramsden design, one or two spider webs are fixed, one of which in taking a reading is adjusted upon the centre of the spectrum line. Under the best conditions of definition and sharpness of spectrum lines it is possible to determine the position of a line to 0·001 mm. Kayser[1] has designed a similar micrometer

[1] *Handbuch der Spectroscopie*, i. 644.

which is provided with certain mechanical arrangements, by means of which the reading of the micrometer and the intensity of the lines can be printed upon paper tapes; this is done by pressing certain keys similar to those of a typewriter so that the eye need not be removed from the microscope during the measurement of a plate.

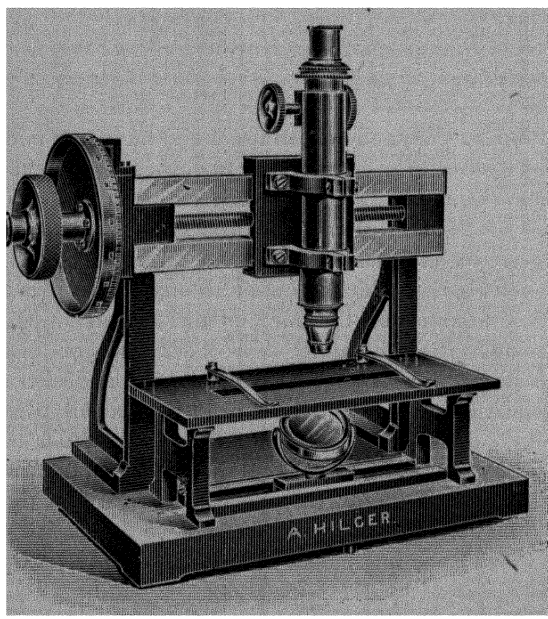


FIG. 59.

When only small linear distances have to be measured very good results can be obtained by the use of an ordinary travelling wire micrometer eyepiece (see page 112) fitted to a low-power microscope. The range of this instrument is, of course, very limited, being only a few millimetres on the plate, but it serves very well in interpolation measurements when the reference lines in the standard spectrum are situated close together.

In Fig. 60 is shown the Zeiss stereo-comparator, an instrument eminently suitable for measuring spectrum plates. The

fundamental principle of the instrument lies in the stereoscopic comparison of the unknown spectrum with a standard. It is too complex to describe in detail.

In the older forms of instrument two microscopes are employed, involving the use of both eyes. In the modern form of this instrument the two microscopes have been superseded by a Blink microscope, as is shown in Fig. 60.

Before proceeding to measure any photograph for the determination of wave-length, it is necessary to test each one

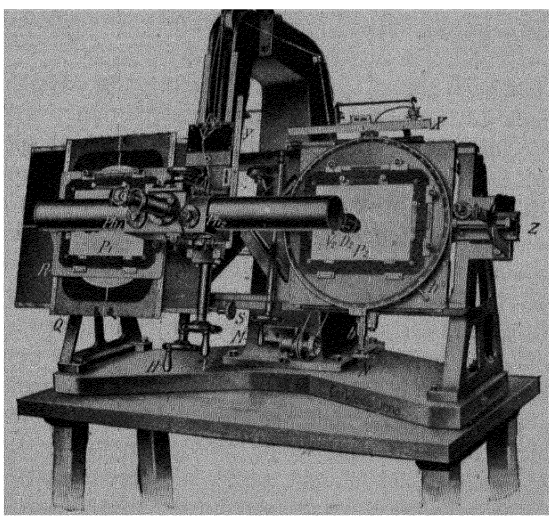


FIG. 60.

with the view of finding whether the standard and the unknown spectra are correctly situated with regard to each other. In order to permit of this being done, it is advisable to arrange that the unknown spectrum should show some known lines; for example, in the case of a gas in a vacuum tube a small quantity of hydrogen may be allowed to be present, or, again, in the case of spark spectra the air lines will serve the same purpose.

In spark spectra also one electrode may consist of a metal whose spectrum is perfectly known, while the other electrode

consists of an unknown substance. These known lines are picked out and their wave-lengths determined by reference to the standard spectrum. If the values so found agree with the known values, well and good; if not, the plate is of little use. It is true that we may construct a table of errors to be applied to the new spectrum, but this is a risky proceeding. When some good plates have been obtained in which the two spectra are correctly placed, these may be measured. It is first of all advisable to write on each plate the wave-lengths of as many as possible of the lines of the standard spectrum which may be found by comparison with the reference plate described above.

As has been stated several times before, the wave-length of any line is determined by measuring its position relatively to two lines, one on each side of it, in the standard spectrum. Although the dispersion continually increases in the spectrum as the blue is approached, yet in practice, if the two reference lines be situated close enough together, a simple linear interpolation will give the wave-length of the unknown line with sufficient accuracy. It is important, therefore, that the standard spectrum should contain as many lines as possible, so that, whatever be the wave-length of the unknown line, there will always be found lines in the standard situated sufficiently close to it to render its accurate measurement possible. It is advisable in actual work to select more than two of the lines in the standard, which should all be measured together with the unknown line; the wave-lengths of all should be computed by interpolation between those of the two extreme lines taken in the standard, so that the values found for the intermediate standard lines can be compared with the known values. This puts a check upon the accuracy of the measurements.

For the values of the wave-lengths of the lines of any spectra which have been measured the reader is referred to the tables published by Marshall Watts. A complete set of these was first brought out under the title of *Index of Spectra*, in which the values were referred to Ångström's Normal Map. The table for each substance included the

values found by the best experimenters, together with the brightness of the lines, and also the values of the oscillation frequency in each case. Watts has kept this invaluable work up to date by a series of appendices brought out as occasion required, so that the latest and best values can always be found. Appendix A is now bound up under the same cover as the index itself, but the other appendices may be obtained separately. In these addenda, of course, it will be found that the wave-lengths are based upon Rowland's map.

Although, as was stated on page 48, the Rowland standard is in process of being superseded by the new international standard based upon interference measurements, yet it can hardly be said at the moment of writing that it is possible to make use of a standard spectrum, the whole of the wave-lengths of which have been measured in terms of the new standard. Kayser[1] has published measurements of about 380 lines in the spectrum of the iron arc between the limits $\lambda = 6495$ and $\lambda = 4118$, which are based on the international standard, these being known as tertiary standards (see page 48). Further, Fabry and Buisson[2] have published wave-lengths of about 40 lines in the arc spectrum of iron between $\lambda = 4118$ and $\lambda = 2373$; but these, owing to their not having yet been repeated by other observers, have not been officially adopted as secondary standards. It can be seen, therefore, that there still remains some difficulty in the way of those who wish to express their measurements in terms of the new standard. On the other hand, it is of course possible to use standard wave-lengths on the Rowland scale, and afterwards reduce these to the new international standard with the help of a table of corrections. Such a table is given by Birge, see page 607.

Care must be taken in making the measurements to adjust the plate properly under the microscope, and to see that the direction of travel of the microscope is parallel to the spectrum, or rather the junction of the two spectra.

Another very important point to be remembered is the necessity of guarding against backlash in the measuring

[1] *Astrophys. Journ.*, **32**. 217 (1910).
[2] *Ibid.*, **27**. 169 (1908).

instrument, for all these instruments show it to a certain extent; the nut working upon the micrometer screw and carrying the microscope is never tightly clamped upon the screw, with the result that if, after turning the screw in one direction, the motion be reversed, an appreciable fraction of a whole turn will have to be given to the screw before the nut starts moving back. For this reason it will be found that with a travelling micrometer different readings will be obtained, if one approach the line from first one side and then the other. It is necessary, therefore, in measuring the lines, always to approach them all from the same side, that is, of course, the side nearest the starting-point.

In making an actual measurement, the cross-wire in the eyepiece is moved forwards until it be judged to bisect the chosen line; if by any chance it be moved too far, it must be brought back some distance and the line approached again. When a sufficient number of lines in the standard spectrum have been selected for the purpose of comparison with the lines to be measured in the unknown spectrum, the first of these is carefully adjusted under the cross-wire of the eyepiece of the micrometer, when set at zero. It is a good plan to label the chosen standard lines in some way, so that they can be recognised through the microscope, as otherwise mistakes may occur when the standard is very complex. When the first standard line is properly adjusted, the microscope is moved along the whole length of spectrum required, or as much as is possible, each chosen standard line and each unknown line being measured on the way.

A considerable amount of trouble is saved by using a travelling microscope with a long travel, even with prism photographs, because of the fewer times that the plate has to be moved and readjusted under the zero of the instrument. If, however, a micrometer with a very short travel is employed, as, for example, a travelling wire micrometer eyepiece, then the photograph must be frequently moved, and a new standard line adjusted under the zero of the instrument. In calculating the wave-lengths from the measurements of the lines,

proportional parts are taken between two standard lines which are not very far apart. For example, the following may serve as a typical record of measurements of a spectrum, the standard of comparison being the arc spectrum of iron :—

Scale reading of micrometer.	Wave-lengths of standard iron lines	Proportional parts of wave-lengths.	Wave-lengths.	Errors.
0	3821·32	0	(3821·32)	
337		1·82	3823·14	
420		2·27	3823·59	
604	3824·58	3·27	3824·59	+ 0·01
934		5·04	3826·36	
1024		5·53	3826·85	
1229	3827·96	6·62	3827·94	− 0·02
1561		8·42	3829 74	
2047		11·04	3832·36	
3727		20·11	3841·43	
3814		20·58	3841·90	
4092	3843·40	{(22·08) 0}	(3843·40)	
4829		3·98	3847·38	
5045		5·15	3848·55	
5339	3850·11	6·73	3850·13	+ 0·02
5413		7·14	3850·54	
6104		10·83	3854·23	
6518	3856·49	13·09	3856·49	0·00
6891		15·10	3858·50	
7356		17·61	3861·01	
8216	3865·65	(22·25)	3865·65	

The first column contains the scale readings of the micrometer, and the second column the wave-lengths of the iron lines which were measured *en route*. In the third column are the proportional parts expressed in wave-lengths; these have been calculated in two sections, between the two iron lines $\lambda = 3821{\cdot}32$ and $\lambda = 3843{\cdot}40$, and between $\lambda = 3843{\cdot}40$ and $\lambda = 3865{\cdot}65$. The first proportional part is therefore equal to—

$$\tfrac{337}{4092} \times (3843{\cdot}40 - 3821{\cdot}32) \text{ Ångström units,}$$

and the second to—

$$\tfrac{420}{4092} \times (3843{\cdot}40 - 3821{\cdot}32), \text{ and so on.}$$

The fourth column contains the computed wave-lengths; these are obtained by addition of the proportional parts to 3821·32 in the first section, and to 3843·40 in the second section. The wave-lengths of the intermediate iron lines are calculated along with the rest, and the fifth column contains the errors in these wave-lengths. It will be readily seen that these errors will give a general idea of the accuracy of one's work, for the presumption is, *ceteris paribus*, that the same order of error is affecting the measurements in the unknown spectrum.

In Fig. 61 is reproduced a photograph of two spectra in juxtaposition, which may give an illustration of the method of interpolation described above. The spectrum on the right hand is part of the arc spectrum of iron, while the other, the arc spectrum of copper, may serve as the unknown, the wave-lengths of which have to be determined. The plate is mounted under the microscope so that the junction of the two spectra is in the middle of the field of view, and also that the travel of the microscope is parallel to this line of junction.

For a determination of the wave-lengths of the lines in a spectrum Hartmann's interpolation formula is exceedingly useful. The accuracy of the results given by any interpolation formula depend, of course, on the range of wave-lengths over which it is used. If this range be not too great then the results are surprisingly accurate. Although for the determination of unknown wave-lengths with the highest accuracy it is preferable to work by the method of linear interpolation between a number of standard lines as already described, yet the Hartmann formula is capable of giving results sufficiently accurate for many purposes. It is particularly suited, for example, for the recognition of all the lines in a standard spectrum such as that of the iron arc.

The formula in its most general form is as follows :—

$$\lambda = \lambda_0 + \frac{c}{(\mu - \mu_0)^{\frac{1}{a}}}$$

where λ_0, c_1, μ_0, and a are constants. Hartmann, however, has pointed out that if two great ranges of wave-lengths are not

Plate I.

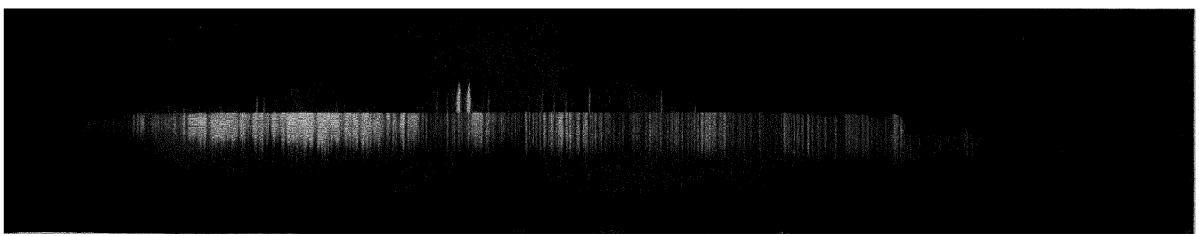


Fig. 61.

[*To face p.* 158.

required, the constant a, which is about 1·2, may be omitted, which simplifies the calculations very considerably. In the place of the indices of refraction μ we may use the angular deviation as given by the prism, or, what comes to the same thing, the linear distances between the lines in a photographed spectrum. If we read the linear distances in a photographed spectrum by means of a travelling micrometer, these readings may be substituted in the formula, which then may be written—

$$\lambda = \lambda_0 + \frac{c}{n_0 - n}$$

or

$$\lambda = \lambda_0 + \frac{c}{n - n_0}$$

according to the direction in which the plate is measured; n is the reading of the lines on the linear scale defined by the micrometer. Hartmann [1] further points out that λ_0 is a constant for any spectroscope, and may be determined once and for all, while the constant n_0 simply represents some definite point on the linear scale.

The calculation of the three constants λ_0, c, and n_0 is very simple; it is only necessary that the wave-lengths and scale readings of three lines be known. In the table below are given the scale readings and the wave-lengths of the lines in a stellar spectrum photograph which are taken from Hartmann's paper. If we select three of these, the constants may at once be found. Let us take, for example, the three lines, the wave-lengths of which are $\lambda = 370{\cdot}96$, $\lambda = 414{\cdot}39$, $\lambda = 486{\cdot}17$, and the corresponding scale readings $n = 0$, $n = 101{\cdot}513$, and $n = 195{\cdot}729$, respectively. We then have the three equations

$$370\,96 = \lambda_0 + \frac{c}{n_0 - 0} \quad \ldots\ldots \quad (1)$$

$$414{\cdot}39 = \lambda_0 + \frac{c}{n_0 - 101{\cdot}513} \quad \ldots \quad (2)$$

$$486{\cdot}17 = \lambda_0 + \frac{c}{n_0 - 195{\cdot}729} \quad \ldots \quad (3)$$

[1] *Astrophys. Journ.*, **8**. 218 (1898).

then by subtraction of (1) from (2)

we have $$43{\cdot}43 = \frac{c}{n - 101{\cdot}513} - \frac{c}{n_0}$$

By multiplying up and rearrangement of terms

we get $$n_0^2 - 101{\cdot}513 n_0 = \frac{101{\cdot}513}{43{\cdot}43} c = 2{\cdot}33739c \quad . \quad . \quad (4)$$

Similarly, by subtraction of (2) from (3)

we have $$n_0^2 - 195{\cdot}729 n_0 = 1{\cdot}69889c \quad . \quad . \quad . \quad (5)$$

Subtract (5) from (4)

we have $$94{\cdot}216 n_0 = 0{\cdot}63850c$$
whence $$c = 147{\cdot}56 n_0.$$

Substitute this value of c in equation (1)

then $$370{\cdot}96 = \lambda_0 + 147{\cdot}56$$
whence $$\lambda_0 = 223{\cdot}40.$$

Again, substitute this value of λ_0 in equation (2)

then $$414{\cdot}39 = 223{\cdot}40 + \frac{147{\cdot}56}{n_0 - 101{\cdot}513}$$
whence $$n_0 = 446{\cdot}414 \text{ and } c = 65872.$$

In this way we have obtained the values of the three constants; from these the wave-lengths of all the remaining lines may be calculated from their scale readings by means of the formula—

$$\lambda = 223{\cdot}40 + \frac{65872}{446{\cdot}414 - n}$$

These calculated wave-lengths are given in the second column of the table, and the differences between these and the true values are given in the fourth column.

Scale reading.	λ in μμ (calc.).	λ in μμ (obs.).	Errors.
0	370·96	370·96	—
5·336	372·75	372·71	+ 0·04
5·529	372·81	372·77	+ 0·04
10·134	374·39	374·36	+ 0·03
11·504	374·86	374·85	+ 0·01
14·698	375·98	375·95	+ 0·03
15·291	376·19	376 15	+ 0·04
16·425	376·62	376·58	+ 0·04
22·612	378·83	378·80	+ 0·03
24·557	379·54	379·50	+ 0·04
25·780	380·00	379·97	+ 0·03
29·343	381·34	381·31	+ 0·03
35·905	383·86	383·85	+ 0·01
36·547	384·12	384·10	+ 0·02
42·761	386·59	386·58	+ 0·01
45·902	387·86	387·86	± 0·00
50·040	389·58	389·57	+ 0·01
51·796	390·32	390·32	± 0·00
52·401	390·58	390·58	± 0·00
56·460	392·32	392·30	+ 0·02
57·620	392·83	392·82	+ 0·01
63·266	395·32	395·30	+ 0·02
65·167	396·18	396·17	+ 0·01
74·555	400·54	400·52	+ 0·02
82·883	404·62	404·60	+ 0·02
86·430	406·38	406·39	− 0·01
93·748	410·19	410·19	± 0·00
101·513	414·39	414·39	—
111·722	420·21	420·21	± 0 00
115·891	422·70	422·70	± 0·00
123·144	427·16	427·17	− 0·01
128·804	430·80	430·80	− 0·00
133·741	434·07	434·07	± 0·00
139·993	438·37	438·37	± 0·00
142·999	440·50	440·50	± 0·00
175·785	466·80	466·80	± 0·00
195·729	486·17	486·17	—

It will be seen on reference to the column of errors that there is a general trend beginning with an error of 0·04μμ and ending with no error at all. Hartmann has also calculated the wave-lengths of these lines in his paper, using three wave-lengths just as was done above. He, however, does not state which lines he used, and it happens that the scale reading of the first line on the list was slightly wrong in Hartmann's measurements, which accounts for the general trend of errors

in the above table. I give the results of my calculations, however, because they show very conclusively what is to be expected if one of the three lines chosen happens to have been inaccurately read with the micrometer. It is hardly necessary to point out that it would be a very simple matter to construct a curve of errors from the above values by means of which they could be smoothed out to give an equally distributed error. This is a very much simpler matter than a series of calculations to find out which three lines give the most even distribution of error.

In exactly the same way may the formula be applied to the measurements of the deviations given by a prism. For example, we may take the wave-length curve reproduced on page 147, and calculate its constants.

Three readings on this curve are—

$$\lambda = 7800 \quad D = 47^\circ \ 0' = 2820 \text{ minutes.}$$
$$\lambda = 5400 \quad D = 48^\circ \ 20' = 2900 \quad ,,$$
$$\lambda = 4200 \quad D = 50^\circ \ 20' = 3020 \quad ,,$$

For the sake of simplicity we may subtract 2820 from these readings of minutes, and then we have 0, 80, 200, or more simply 0, 8, 20, if we adopt ten minutes as the unit. From these equations we readily find the constant to be $\lambda_0 = 2400$, $c = 54000$, and $D_0 = -10$. These will then be found to fit the curve with a very fair accuracy.

These examples will doubtless suffice to show how the formula is applied and how serviceable it can prove.

An interesting application has been made of this formula by Fowler and Eagle.[1] If a prismatic photograph of a spectrum be copied by means of a camera lens, then it is possible to obtain the lines in the copy distributed according to their wave-lengths, *i.e.* it is possible to obtain a normal spectrum. This is done by setting the spectrum plate and the plate on which the image is received at certain angles to the axis of the lens of the copying apparatus. Fowler and Eagle show how these angles may be calculated if the focal length of the lens

[1] *Astrophys. Journ.*, **28**. 284 (1908).

be known, and also the constants of Hartmann's formula for the spectrum in question.

In measuring the lines in a spectrum notes should be made of the intensity or brightness in each case. The estimation of the intensity of lines in an emission spectrum is troublesome, owing to there being no satisfactory method of comparison; as a general rule, at the present time we mark the lines of greatest brightness as having an intensity of 10, and the weakest as having an intensity of 1; the other lines are then given an intensity varying from 9 to 2, depending upon their estimated brightness. This is the standard fixed by the British Association. In other countries different systems are frequently used; for example, sometimes the intensity of the brightest lines is put = 1, and the weakest = 10, thus reversing the above. The estimation of brightness is thus arbitrary, and it will be found that observers sometimes differ considerably in the values they assign to the intensity of a line. It must not be forgotten that sometimes a line of an emission spectrum is reversed in a photograph, the centre portion of the line being wanting on the plate. In measuring such a reversed line, it is needless to point out that the middle of the transparent centre must be taken, as this, of course, represents the centre of the true line. There are present in the spectra of certain metals, lines which are diffused upon one side only, the other side being perfectly sharp and well-defined. When these lines undergo self-reversal, the position of the true centre of the line is often very difficult to estimate, and great care must be taken to avoid making serious errors. No rule can be given for finding the centre of such a line; one can only be guided by the general appearance of the line. The accuracy of measurement of such lines, and all diffused lines generally, is clearly very much lower than in the case of fine and well-defined lines.

A simple and ingenious method of approximately determining the wave-lengths of lines from photographs of prismatic spectra has been devised by Edser and Butler. This method consists in photographing a series of interference fringes,

[1] *Phil. Mag.*, **46**. 207 (1898).

adjacent to the spectrum, to be measured; these interference fringes are produced by Fabry and Perot's method, which consists in causing a beam of white light to pass through a film of air bounded by two parallel sides of half-silvered glass. When this light is examined in a spectroscope, a continuous spectrum is seen, crossed by a series of interference fringes, the theory of which will be dealt with at length in Chapter IX., p. 317. A sufficiently accurate interference apparatus can be made by taking two pieces of good plate-glass about 3 inches square, which are each half silvered on one face;[1] the plates are then carefully dried and mounted together, the two silvered faces turned towards one another. The plates are fastened together by a little wax placed all round the edges, when perfect adjustment can be obtained by simply pressing the plates together with the fingers. A preliminary adjustment for parallelism is made as follows: a spot of light or an incandescent electric lamp is viewed through the silvered surfaces; a long train of images due to multiple reflections is generally visible. These images are brought into coincidence and then, on examining a sodium flame through the apparatus, interference bands will generally be visible. The final adjustment for parallelism is made with the help of these bands which should be made as broad as possible. In carrying out this adjustment, the film is held as close as possible to the eye, because for a parallel air film viewed normally the interference bands are formed at an infinite distance. The perfection of the results finally obtained will depend greatly on the accuracy of this adjustment.

Directions for making a simple interference apparatus suitable for this purpose are given by Barnes.[2]

The slit of the spectroscope is illuminated by a slightly convergent beam of light from an arc lamp, and the plates are placed in front of the slit, and as near to it as possible; under these circumstances the spectrum will be found to consist of a

[1] See Appendix, and also p. 320. By half silvering is meant the deposition of a silver layer which is transparent to light and yet is dense enough to reflect a considerable portion.

[2] Nature, **80**. 187 (1909).

series of bright lines separated by black intervals. The best results will be obtained when the plates are in such a position that the slit is parallel to the direction of the interference bands seen with sodium light. The closeness of the bands depends upon the thickness of the film between the silvered surfaces. It is well to introduce some common salt into the arc in order to obtain the D lines, as well as the H and K lines superimposed upon the fringes. By means of draw slides, or screens upon the slit, these interference bands are photographed adjacent to the spectrum which is to be measured.

As the interference bands are due to the interference of the directly transmitted ray, and that twice reflected from the surfaces of the film, it follows that, if d be the thickness of the air film, and μ the refractive index (supposed independent of wave-length)—

$$2\mu d = n\lambda_0 = (n + 1)\lambda_1 = (n + 2)\lambda_2 \ . \ . \ . \ = (n + m)\lambda_m$$

where λ_0, λ_1, λ_2, λ_m, etc., are the wave-lengths corresponding to the bright bands, and n is some whole number. We have, therefore—

$$n\lambda_0 = (n + m)\lambda_m,$$

whence

$$n = \frac{m\lambda}{\lambda_0 - \lambda_m} \quad . \ . \ . \ . \ . \ . \ . \quad (1)$$

where the band corresponding to λ_m is the mth towards the violet from that corresponding to λ_0. We have, also, therefore—

$$\lambda_r = \frac{n\lambda_0}{n + r}, \quad . \ . \ . \ . \ . \ . \quad (2)$$

where λ_r is the wave-length corresponding to the rth band counting from the band λ_0.

As an example, Edser and Butler found, that on a particular photograph the following figures were obtained:—

Scale-reading 90·2, wave-length 5328·5(λ_0),
,, ,, 402·3, ,, ,, 3968·6(λ_m).

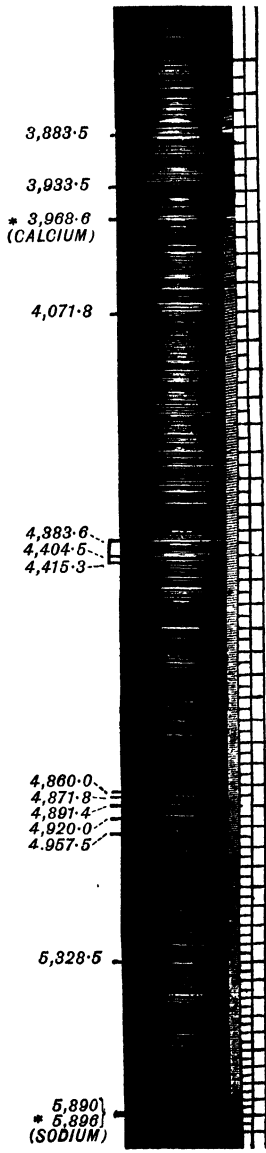


FIG. 62.

Then, in equation (1)—

$$m = 402{\cdot}3 - 90{\cdot}2 = 312{\cdot}1$$

and

$$\lambda_0 - \lambda_m = 1359{\cdot}9,$$

and therefore

$$n = 910{\cdot}8.$$

Again, to find the wave-length of the line whose scale reading is 371·2. Then, in equation (2)—

$$r = 371{\cdot}2 - 90{\cdot}2 = 281$$

and

$$\lambda_r = \frac{910{\cdot}8 \times 5328{\cdot}5}{910{\cdot}8 + 281}$$
$$= 4072{\cdot}2$$

The true wave-length of the line was 4071·8, giving an error of + 0·4 tenth metres. With a finer scale more accurate results can be obtained.

When many lines have to be measured a graphical method may be adopted. If we write $\frac{1}{\lambda} = \mathrm{L} =$ the frequency, we obtain the simple relation $\frac{n+r}{\mathrm{L}} =$ constant, or $\mathrm{L} = \mathrm{K}(n+r)$. In other words, the oscillation frequency is a linear function of r, *i.e.* the relation between L and r may be expressed by a straight line. The frequencies of a few lines at each end of the photograph are plotted against their

scale readings, and a straight line is drawn through the points thus obtained. From this straight line the oscillation frequency of a line can be found at once from its scale reading.

There is no need to take a separate photograph of the interference scale for every spectrum to be measured, for it is clear that this will be always the same, provided that the adjustments be not altered in any way. If the D lines are superposed on the original interference scale, and occur in every succeeding spectrum photograph, it is only necessary to fit the interference scale on to the spectrum photograph so that the D lines coincide; the position of the spectrum lines can then be read on the scale with perfect accuracy.

A prism photograph, with the bands adjacent to it, is shown in Fig. 62.

CHAPTER VI

THE DIFFRACTION GRATING

General Theory.—The elementary theory of the production of spectra by means of the diffraction grating was treated in the introductory chapters, and it was shown that the general wave-length equation has the form—

$$n\lambda = b(\sin i + \sin \theta), \quad . \quad . \quad . \quad . \quad (1)$$

where n stands for the number of the order of the spectrum, λ the wave-length, b the grating space, i the angle of incidence, and θ the angle of diffraction. When the incident rays are normal to the grating the equation is simplified to the form—

$$n\lambda = b \sin \theta.$$

Equation (1) readily gives an expression for the dispersion of a grating, for, if we assume the angle of incidence to be constant, then by differentiation we have—

$$nd\lambda = b \cos \theta d\theta$$

and thus

$$\frac{d\theta}{d\lambda} = \frac{n}{b \cos \theta}.$$

The dispersion of a grating, therefore, is equal to the number of the order of the spectrum divided by the product of the grating space into the cosine of the angle of diffraction. It is evident from this that the dispersion reaches a minimum value when $\cos \theta$ is a maximum, that is to say, when $\cos \theta = 1$, *i.e.* when $\theta = 0$. We see, therefore, that, when the observing telescope is placed perpendicular to the plane of the grating, the dispersion is a minimum and is equal to $\frac{n}{b}$.

Under these circumstances $d\theta = \text{const.} \times d\lambda$, and therefore

small changes in λ produce proportional changes in θ, or, in other words, the spectrum obtained is perfectly normal. Although this is only strictly true when $\cos\theta = 1$, yet, as $\cos\theta$ varies so little from this with small changes in θ, it holds good for some distance on each side of the normal. It is quite easy to calculate how far it is possible to work from the normal within a given limit of accuracy. For example, if the accuracy required is 1 part in 10,000, it is necessary that $\cos\theta$ do not have a smaller value than $1 - 0{\cdot}0001 = 0{\cdot}9999$, and, therefore, that θ have no larger value than 48′. The spectrum is thus normal within 1 part in 10,000 when the angle of diffraction is less than 48′; similarly, it may be found to be normal with an accuracy of 1 in 1000 when the angle of diffraction is less than $2^{\circ}\ 34'$.

The values of the dispersion when $\theta = 0$ may be calculated for gratings having the usual values of b. As at present made the Rowland gratings are usually ruled with 20,000, 14,438, or 10,000 lines to the inch, that is, 7874·1, 5684·4, or 3937·1 to the centimetre. The dispersions of the three gratings (when $\theta = 0$) are, therefore, $n \times 7874{\cdot}1$, $n \times 5684{\cdot}4$, and $n \times 3937{\cdot}1$. As an example, we may calculate the angular difference between the two D lines in the second order with a 20,000 line grating. Taking the difference in wave-length between the lines as $0{\cdot}006 \times 10^{-5}$ cm., the angle between them will be $2 \times 7874{\cdot}1 \times 0{\cdot}006 \times 10^{-5} = 0{\cdot}000945$, which is 3′ 15″ of arc.

It can readily be seen from equation (1) that the spectra of different orders are superposed upon one another, for, with any position of the observing telescope, that is, with a fixed value of i and θ, it follows that $\lambda^{I} = 2\lambda^{II} = 3\lambda^{III} = 4\lambda^{IV}$, etc., where λ^{I}, λ^{II}, λ^{III}, λ^{IV}, etc., are the wave-lengths in the first, second, third, fourth, etc., orders. The different orders are thus superposed upon one another, and the wave-lengths are inversely proportional to the numbers of the orders. On wave-length of 9000 A.U. in the first order are superposed 4500 in the second order, 3000 in the third, 2250 in the fourth, and similarly for other wave-lengths in different orders. It also follows in the same way that the linear lengths of the spectra are proportional to the numbers of the orders.

An expression for the resolving power of a grating was first given by Lord Rayleigh.[1] The resolving power of a spectroscope is defined as ratio $\frac{\lambda}{d\lambda}$, where $d\lambda$ is the difference in the wave-lengths of two lines just separated by the instrument, and λ the mean wave-length of the pair (*vide* p. 74, *et seq.*). Lord Rayleigh obtained the value of this expression as follows:—

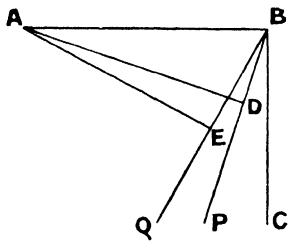


FIG. 63.

If in Fig. 63 AB represents the whole grating, and BP the principal direction of the diffracted rays for the wave-length λ in the nth spectrum, then, if the perpendicular AD be drawn, the length BD, or the relative retardation of the rays from the extreme grating apertures, will be equal to $mn\lambda$ if m be the number of apertures in the length AB. BQ is then drawn so that the projection of AB upon BQ, that is to say BE, is equal to $mn\lambda + \lambda$. Now, BQ will be the principal direction for a wave-length $\lambda + d\lambda$, and therefore BE must equal $mn(\lambda + d\lambda)$.

It follows that—

$$mn\lambda + \lambda = mn(\lambda + d\lambda),$$

whence

$$\frac{\lambda}{d\lambda} = mn = r; \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or the resolving power of a grating is equal to the product of the number of apertures and the order of the spectrum. That the resolving power, or defining power, as it might be called, of a grating, depends upon the number of apertures follows from the elementary theory. If the retardation between the secondary waves from two adjacent apertures be equal to any odd number of half wave-lengths, they will mutually interfere; if, however, the retardation be not exactly equal to an odd or even number of wave-lengths, interference will take place

[1] *Phil. Mag.* (4), 47. 193 (1874).

between the waves from apertures which are not adjacent to one another. For example, if the retardation be equal to one-hundredth of a wave-length, the waves from the first and fifty-first apertures, the second and fifty-second, etc., will interfere, and, therefore, if the apertures be sufficiently numerous, total interference will take place, except when the retardation between the waves from adjacent apertures be equal to an exact number of whole wave-lengths; the greater the number of apertures, therefore, the better the interference on each side of a bright line, that is to say, the better the defining power of the grating. Again, if we start from equation (1) and multiply both sides of this equation by m, the number of rulings in the grating, we have—

$$mn\lambda = f(\sin i + \sin \theta)$$

where $f = bm$ = the width of the grating, being the product of the width of the grating spaces into the number of them.

By differentiation (sin i being constant)—

$$mnd\lambda = f \cos \theta d\theta,$$

and

$$mn = f \cos \theta \frac{d\theta}{d\lambda}.$$

Now, $f \cos \theta$ is the diameter of the beam of diffracted rays leaving the grating, and calling this a as before (p. 75)

we have—

$$mn = a\frac{d\theta}{d\lambda}.$$

But from equation (2) $mn = \frac{\lambda}{d\lambda} = r$,

we see, therefore, that the resolving power of a grating is equal to the product of the aperture into the dispersion, and that the grating is quite comparable with other optical instruments.

If now in the equation $mn\lambda = f(\sin i + \sin \theta)$, r be substituted for mn,[1] then—

[1] Wadsworth, *Phil. Mag.* (5), **43**. 317 (1897).

$$r\lambda = f(\sin i + \sin \theta)$$

and

$$r = \frac{f}{\lambda}(\sin i + \sin \theta) \quad . \quad . \quad . \quad . \quad (4)$$

This is an expression for the resolving power, which is independent of the number of rulings, and only dependent upon the aperture, and the position into which the grating is turned. The maximum value of r in (4) is obtained when $i = \theta = 90°$, in which case—

$$r_{max} = 2\frac{f}{\lambda}.$$

This theoretical maximum cannot, however, be obtained, as with very large values of the angles of incidence and diffraction the angular aperture of the grating becomes very small, and the light is reduced to a minimum. In practice the largest value of i when $\theta = 0$ is about 60°, and, in the Littrow type of instrument, when $i = \theta$ the value lies between 45° and 50°. The practical limit of resolving power lies, therefore, between $\frac{7}{8}\frac{f}{\lambda}$ and $\frac{3}{2}\frac{f}{\lambda}$. Taking the upper limit, we have for a 5½-inch grating and $\lambda = 5500$ A.U. a resolving power of 375,000; that is to say, this grating should resolve lines whose wavelengths differ by 0·015 A.U. This, of course, is based on the assumption that the slit is infinitely narrow; this is never true in actual work, and the effect of this factor will be treated in Chapter X.

It follows from equation (4), $r = \frac{f}{\lambda}(\sin i + \sin \theta)$, that, since θ and f are independent, the resolving power of a grating depends upon the extent of the ruled space, not upon the number of rulings in that space. From equation (2), $r = mn$, it would appear that r varies directly as m; but this equation assumes λ as constant, so that n is dependent upon m and θ. Hence the two equations are quite consistent.

It is of little use to increase the number of lines in a given space, because, for example, if two gratings be used of the same size, but one containing twice as many rulings as the other,

the first order spectrum will be obtained with the first grating in the same position as the second order spectrum with the second grating; the resolving power will be identical in the two spectra. It thus follows that, provided the values of i and θ do not change, increasing the number of lines in unit length of grating surface does not increase the resolving power.

At the same time, it may be noted that there are certain advantages to be derived from using a grating containing a great number of rulings rather than one which contains fewer. One is thereby enabled to work in the lower orders and still obtain high resolving power; as stated above, a grating with 20,000 lines to the inch will give the same resolving power in the first order as a grating of same size with 10,000 lines to the inch in the second order, because the values of the angles of incidence and diffraction are the same in each case. Now, two very decided advantages would be obtained by using the 20,000 line grating and working with the first order. First, in all probability the amount of light will be greater in the first than in the second order, and second, there is less complication arising from superposition of spectra in the first order than in the second. Further consideration, perhaps, will render this second advantage more explicit. If we work in the first order spectrum we shall have the region from 2000 to 4000 A.U. practically free from contamination with higher orders, because superposed on it will be the second order spectrum from 1000 to 2000 A.U., which cannot under ordinary circumstances be photographed. The region from 4000 to 7000 A.U. will have superposed upon it the wave-lengths 2000 to 3500 A.U. in the second order, the third order being still photographically inactive. It is possible, therefore, to photograph the first order spectrum without any contamination with higher orders, from 2000 A.U. to at least 4000 A.U., and from 4000 A.U. to 7000 A.U., by using an absorbing layer of plate-glass, which will entirely cut off the superimposed second order.

When working in the second order, however, the contamination by the spectra of other orders is very troublesome, because it is impossible to photograph the second order in any region without the use of absorbing layers; in those regions

where contamination by the third order is not prevalent, photographically active portions of the first order are superimposed, which, of course, cannot be removed by absorption, as there is no substance at present known which will absorb the higher wave-lengths and transmit the lower wave-lengths.[1] The great advantage accruing from the use of the first order spectrum, especially for work in the ultra-violet region, is thus very marked, and for this reason, as well as for the greater brightness of the first order spectrum, a grating with a greater number of rulings in unit length is to be preferred to one with a lesser number.

The brightness of the spectra of different orders next claims our attention; in this case we must deal with an ideal grating, that is to say, a grating which consists of alternate perfectly opaque and transparent portions, the theory of which was first worked out by Lord Rayleigh.[2] The grating, however, in practical use does not possess truly opaque portions, but translucent portions, so to speak, produced by cutting grooves on a glass or polished metal plate. Furthermore, these grooves may vary in shape, nature, and size from grating to grating and therefore the illumination obtained very often varies considerably from that produced by an ideal grating. The theory of the effect of varying the nature of the ruling has been worked out by Rowland very fully, and the abnormal results obtained in practice can be mathematically accounted for.

To consider the illumination produced in any spectrum given by a grating, let us first deal with that produced by a plain aperture, and afterwards find the effect of the ruling. Let AB in Fig. 64 represent any linear aperture, and let it receive plane waves perpendicularly to itself. All the secondary waves transmitted by the ether particles in AB in the perpendicular direction BC agree completely in phase, and therefore when they are all brought to a focus by a lens their resultant

[1] Wood (*Phil. Mag.*, **5**. 257 (1903)) has found that a gelatine film dyed with nitrosodimethylaniline absorbs portion of the visible spectrum and transmits the ultra-violet. This, however, does not modify the conclusions drawn in the text, as the use of such a screen very materially reduces the light, and is, therefore, not to be recommended.

[2] *Phil. Mag.* (4), **47**. 193 (1874).

will attain its highest possible value. In a direction BP, making a very small angle with BC, the agreement in phase will be disturbed. Drop the perpendicular AD, and then if BD equal one or any whole number of wave-lengths, there will be equal numbers of secondary waves at opposite phase proceeding in the direction BP, which, when brought to a focus by the lens, will have as resultant nil. If, however, BD be not equal to any multiple of λ, the resultant of the secondary waves will have some value which may be obtained as follows. In the first place, the phase of the resultant will necessarily always correspond with the phase of the secondary wave which issues from the ether particle or element in the middle of the aperture. If E be an ether particle lying in the aperture and EF the wave transmitted by the element at E, it is necessary to find the dis-

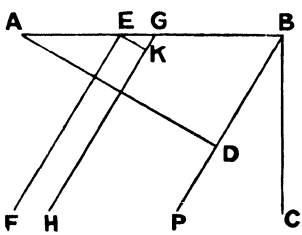


FIG. 64.

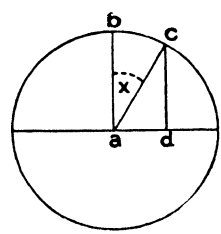


FIG. 65.

turbance produced at the focus of the lens by the elements lying along EA and EB; the sum of these will give the amplitude of the resultant at the lens focus. Consider the element at G, then clearly the secondary wave GH is retarded upon the wave EF by the amount GK, that is to say, the vibrations leaving G are a little later in phase than the vibrations simultaneously leaving E. Let the radius *ab* in Fig. 65 represent the amplitude of the vibration due to the wave from the element E, and the arc *bc* the short space of time the wave leaving the element G is behind this, then the perpendicular *cd* represents the amplitude of the vibration due to the element G. Let the angle $bac = x$, this being the angular retardation of the wave from the element G; now $cd = ab \cos x$, and, if the amplitude *ab* of the central wave be put equal to unity, $cd = \cos x$; that

is to say, the amplitude of the vibration from the element G is equal to the cosine of the angular retardation. The amplitude of the resultant, therefore, at the focus of the lens, is equal to the sum of all the disturbances $\cos x \times \frac{dy}{AB}$, where $\frac{dy}{AB}$ is the ratio of the size of the element at G to the whole aperture AB.

Now if R be the angular retardation between the extreme waves from the elements at A and B, then clearly we shall have—

$$\frac{R}{AB} = \frac{x}{y},$$

when x is the relative angular retardation of two elements separated by a distance y.

By differentiation and rearrangement of terms—

$$\frac{dx}{R} = \frac{dy}{AB},$$

substituting $\frac{dx}{R}$ for $\frac{dy}{AB}$ in the expression for the amplitude, we see that the amplitude of the resultant is the sum of the disturbances $\cos x \times \frac{dx}{R}$.

Let E be considered as the centre of the aperture AB; then as R is the angular retardation between the waves from the extreme elements at A and B, $\frac{R}{2}$ is the angular retardation between the element at A and B respectively and the element at E. It follows that, considering the elements lying on each side of the central one at E, x must increase as one gets further from E, until it reaches $\frac{R}{2}$ on one side and $-\frac{R}{2}$ on the other side. In order to find the amplitude of the resultant vibration at the focus of the lens, it is therefore necessary to sum all the disturbances $\cos x\, dx \div R$, when x has all possible values between $-\frac{R}{2}$ and $+\frac{R}{2}$. The resultant amplitude is,

therefore, given by $\int_{-\frac{R}{2}}^{+\frac{R}{2}} \cos x \, dx \div R$ if the amplitude in the principal direction BC = 1. This expression on integration $= \sin \frac{R}{2} \div \frac{R}{2}$, which is the amplitude required.

Considering the interference bands produced by such an aperture AB, the intensity of the central image when R = 0 is equal to unity; the first minimum corresponds to the condition that BD = λ, that is to say, that R = 9π, when the resultant amplitude is zero. The first maximum obtains when BD = $\frac{3}{2}\lambda$ and R = 3π; the amplitude is then equal to $\frac{2}{3\pi}$, and the intensity to $\left(\frac{2}{3\pi}\right)^2$. For the second minimum R = 4π, and thus the amplitude is again zero; similarly the second and third, etc., maxima have an intensity of $\left(\frac{2}{5\pi}\right)^2$, $\left(\frac{2}{7\pi}\right)^2$, etc. It is evident that the illumination falls off very rapidly on each side of the central image; for example, if AB be 25 mm. and λ be 5000 A.U., the angle θ corresponding to the first minimum (BD = 5000 A.U.) will be about 4″.

The effect of the ruling may be examined, and let us suppose the grating to consist of transparent bars of width a, alternating with opaque bars of width d. In the principal direction BC, the secondary waves are, of course, in complete agreement of phase, but their amplitude is diminished in the ratio of a to $a + d$. The central image of a line of light obtained with a grating is the same as if the rulings were absent, with the exception that the intensity is less in the ratio of a^2 to $(a + d)^2$. As regards the maxima on each side of the central image, these occur when the retardation between corresponding waves from adjacent apertures is equal to any multiple of λ, that is, when BD in Fig. 65 is equal to $mn\lambda$, where n equals the number of the maximum counting from the centre (the order of spectrum), and m the number of apertures. On either side of the maxima the illumination is distributed according to the same law as for the central image, and vanishes when the retardation amounts to $mn\lambda = \lambda$.

In considering the brightness of the maxima the effect of each aperture of the grating is the same. When the aperture AB was plain and had no rulings the angular retardation R between the two extreme elements was equal to $2\pi\frac{z}{\lambda}$, where z = BD, the projection of the aperture upon the direction BC; in the present case R becomes equal to $2\pi\frac{az}{(a+d)\lambda} = \frac{2an\pi}{a+d}$ where $n = \frac{z}{\lambda}$ = order of spectrum. Substituting this value for R in the integral deduced above, we have for the ratio of brightness—

$$B_n : B_0 = \left(\int_{-\frac{an\pi}{a+d}}^{+\frac{an\pi}{a+d}} \cos x\, dx \div \frac{2an\pi}{a+d}\right)^2$$
$$= \left(\frac{a+d}{an\pi}\right)^2 \sin^2 \frac{an\pi}{a+d},$$

where B_n and B_0 are the brightness of the nth spectrum and of the central image respectively.

If B represents the brightness of the central image when the whole of the grating aperture is transparent,

then $$B_0 : B = a^2 : (a+d)^2$$

and $$B_n : B = \frac{1}{n^2\pi^2}\sin^2\frac{an\pi}{a+d}.$$

As the sine of an angle can never be greater than unity, it follows that under the most favourable circumstances only $\frac{1}{n^2\pi^2}$ of the original light can be obtained in the nth spectrum. If now $a = d$, then the formula becomes—

$$B_n : B = \frac{1}{n^2\pi^2}\sin^2 n\frac{\pi}{2};$$

so that when n is even, B_n vanishes, and when n is odd, $B_n : B = \frac{1}{n^2\pi^2}$. Under these circumstances the first order spectrum has an intensity of about $\frac{1}{10}$ of the original light, the second is wanting, and the third $\frac{1}{90}$ of the original. In general

it is clear that the brightness of a spectrum vanishes when $\sin \frac{an\pi}{a+d} = 0$, which is the case when $\frac{an\pi}{a+d} = \pi, 2\pi, 3\pi$, etc. The spectra will therefore vanish for which $n = \frac{a+d}{a}, 2\frac{a+d}{a}, 3\frac{a+d}{a}$, etc. If, for example, $a = \frac{1}{4}d = \frac{1}{5}(a+d)$, then the 5th, 10th, 15th, etc., spectra will be wanting. Finally, if a be small compared with $a + d$, then, except for the higher orders, the above expression may be simplified to—

$$B_n : B = \left(\frac{a}{a+d}\right)^2,$$

that is to say, the brightness of all the spectra is the same.

The above equations show that in no case can the brightness of a spectrum exceed that of the central image; it must be remembered, however, that this result depends upon the hypothesis that the lines of the grating act by opacity, which in practice is very far from being true. In an engraved grating there is no opaque material present by which light can be absorbed, and therefore the effect depends upon the difference of retardation due to the alternate parts. If, for example, a grating were composed of equal alternate parts, both alike transparent but giving a relative retardation of half a wavelength, the central image would entirely be extinguished, while the first spectrum would be four times as bright as if the alternate parts were opaque. In the case of metal gratings the case is similar, and effects are produced by the reflections from the grooves, so that the character of the latter has great influence.

Rowland[1] has obtained an expression for the brightness of the lines of the spectra, which shows that the intensity is a function of λ as well as of n, so that the distribution of intensity in any grating spectrum may vary with the wavelength, and the sum of all the light in any one spectrum of a white source need not be equal to white light. On the basis

[1] "Gratings in Theory and Practice," *Astronomy and Astrophysics*, **12**. 129 (1893).

of this work he was able to explain the fact, often observed, of the concentration of light into one spectrum to the detriment of the others, and also the excessive brightness of one particular colour in one spectrum. Rowland points out that if the diamond make a single groove the lower orders will be the brightest, but if it rule several lines at once then the higher orders can be brighter. Asymmetry in the ruling produces asymmetry in the spectra.

It will generally be found, therefore, that a grating gives unequal spectra, that is to say, certain spectra brighter than others; very often this is noticeable on comparing the spectra obtained on each side of the normal.

It is important also to notice that the resolving power of a grating depends upon the accuracy of the ruling, which must be very high in order to ensure good results. For example, Rayleigh [1] compares two gratings which have the same amount of ruled space, but one with 1000 lines and the other with 1001 lines. Since the wave-lengths of the two D lines are practically different by a thousandth part, it is evident that the first grating would produce the same deviation for the D_1 line as the second grating would for D_2. If now the two gratings were combined to form one, the D lines would not be resolved, so that in a grating which is required to resolve the D lines there must be no *systematic* irregularity to the extent of a thousandth part of the grating space, though single lines may be out of position to a much larger amount. In a later paper [2] Rayleigh says, "It can make but little difference in the principal direction corresponding to the first spectrum, provided each line lies within a quarter of an interval from its theoretical position. But to obtain an equally good result in the nth spectrum, the error must be less than $\frac{1}{n}$th of this amount. It must not, however, be supposed that errors of this magnitude are unobjectionable in all cases. The position of the middle of the bright band representative of a mathematical line can be fixed with a spider line micrometer within a small fraction of the width of the

[1] *Phil. Mag.* (4), **47**. 193 (1874).

[2] *Encyclop. Britt.*, 9th ed., **24**. Article: "Wave Theory," p. 438.

band, just as the accuracy of astronomical observations far transcends the separating power of the instrument."

As regards the effect produced by errors of ruling, those arising from periodic errors may be mentioned. By periodic errors is meant the continually repeating of some false ruling; this usually arises from some defect in the ruling machine, which occurs at every revolution of the screw. The effect of errors of this kind is to produce false images of lines, which are called "ghosts." With a good grating these ghosts are often non-existent, but they may in cases assert themselves so much as to render a grating useless. It is the bright lines which most readily, of course, give rise to ghosts, and the latter may be recognised by their appearing as weak lines symmetrically placed on each side of the brighter lines. Rowland[1] has investigated the general theory of the effect of errors in the ruling of gratings; as regards the ghosts arising from periodic errors, he found that the intensity of the ghosts of the first order is proportional to the square of the order of the spectrum considered, and to the square of the relative variation from the true grating interval. Small spacing errors produce diffused light about the spectrum lines, which is taken from the lines themselves (*cf.* Bell, *vide* p. 44), and its amount is proportional to the square of the relative spacing error and the square of the spectrum order. A periodic error takes a certain quantity of light from the principal lines and distributes it symmetrically as a system of lines. The intensity of the ghosts and of the diffused light rapidly increases with the order of the spectrum. Rowland has calculated the relative brightness in three cases of the first order ghosts, which are as follows :—

Relative error.	Relative brightness of ghosts in—		
	First order.	Second order.	Third order.
$\frac{1}{25}$	$\frac{1}{63}$	$\frac{1}{18}$	$\frac{1}{7}$
$\frac{1}{50}$	$\frac{1}{252}$	$\frac{1}{63}$	$\frac{1}{28}$
$\frac{1}{100}$	$\frac{1}{1008}$	$\frac{1}{252}$	$\frac{1}{112}$

[1] *Loc cit.*

In the first column is given the relative error, that is to say the relation between the irregular spacing and the correct spacing. It will be seen that in the first case very strong lines will give visible ghosts in the first order, while in the third order the ghosts will have as much as one-seventh of the brightness of the principal lines—enough, perhaps, to render the grating useless. In the second case the ghosts will be visible in the third order, and barely so in the second; while in the third case the ghosts will not be visible in the first three orders.

The Concave Grating.—This type of grating was first produced by Rowland in 1882, and consists of a grating ruled upon a polished spherically concave surface of speculum metal, the rulings being equally spaced upon the chord of the arc, not upon the arc itself. It was found that, in the case of such a grating, if the grating and slit are placed upon the circumference of a circle which has as radius half the radius of curvature of the grating, the spectra are also focussed round the circumference. There is thus no need for lenses with these gratings—a fact which at once shows their immense superiority over the ordinary plane gratings. When mounted by Rowland's method, with the eyepiece or photographic plate at the centre of curvature, so that the spectra are normal, this grating has proved to be one of the finest spectroscopic machines ever produced.

Theory of the Concave Grating.—For the complete theory of the concave grating some larger text-book must be consulted, for it is too mathematical to find a place here. Certain theoretical points in connection with the practical working may be given. In the first place, to find the focal curve.

Let AB be a single element on a curved grating, XY; and let P be a point emitting light. PA and PB represent rays incident upon the element AB, making an angle of incidence i with the normal. These rays are therefore diffracted, and are focussed at the point Q, making an angle of diffraction θ. By the general grating equation we have, if AB is put as usual $= b$, $n\lambda = b(\sin i - \sin \theta)$; $\sin \theta$ being negative because P and Q are on opposite sides of the normal. Let AC and BC be

the normals at A and B; these will meet at the point C, which is the centre of curvature of the grating.

Considering the two rays PA and PB, these are incident at angles i and $i + di$, that is to say, the angles PAC, PBC are equal to i and $i + di$ respectively; similarly the two angles of diffraction QAC, QBC are equal to θ and $\theta + d\theta$ respectively. Let us further denote the angles at P, C, and Q by the letters x, y, and z, then in the two triangles PAE and CBE $x + i = y + i + di$, and similarly in the triangles CAF, QBF $y + \theta = z + \theta + d\theta$,

therefore $di = x - y$

and $d\theta = y - z$.

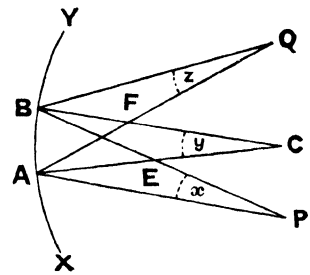


FIG. 66.

Now, if the light from P be homogeneous, it will be seen that, since Q is the focus of the diffracted rays from P, $\sin i - \sin \theta$ in the equation $n\lambda = b(\sin i - \sin \theta)$ is a constant; by differentiation, therefore—

$$\cos i di - \cos \theta d\theta = 0.$$

By substitution of the values found above for di and $d\theta$, we have—

$$\cos i(x - y) - \cos \theta(y - z) = 0.$$

By putting AP $= r$, AC $= \rho$, AQ $= s$, and AB $= b$, we have—

$$x = \frac{b}{r}\cos i,\ y = \frac{b}{\rho} \text{ and } z = \frac{b}{s}\cos \theta.$$

By substitution of these values in the last equation we have—

$$\cos i\left(\frac{b \cos i}{r} - \frac{b}{\rho}\right) - \cos \theta\left(\frac{b}{\rho} - \frac{b \cos \theta}{s}\right) = 0;$$

multiplying out and dividing throughout by b—

$$\frac{\cos^2 i}{r} - \frac{\cos i}{\rho} - \frac{\cos \theta}{\rho} + \frac{\cos^2 \theta}{s} = 0,$$

whence

$$s = \frac{r\rho \cos^2 \theta}{r(\cos i + \cos \theta) - \rho \cos^2 i}$$

Now, the distance r and the angle i are the polar co-ordinates of the point P, and similarly s and θ are the polar co-ordinates of the point Q, so that if the point P move along any curve, the point Q will correspondingly move along another curve defined by this equation. The curve described by Q is, of course, the focal curve of the grating. If, now, P always move round a circle having a diameter equal to ρ, then of course—

$$r = \rho \cos i.$$

Substituting this value of r in the last equation we have—

$$s = \rho \cos \theta,$$

that is to say, the point Q will also move upon a circle with diameter equal to ρ. In other words, when the source of light and the grating are placed upon the circumference of the circle described with the radius of curvature of the grating as diameter, the spectrum will always be brought to a focus upon that circle.

In mounting a concave grating it is necessary that this condition be fulfilled, and Rowland's method was described in Chap. II., p. 39. The mounting of a small grating is shown in Fig 67.

Let us consider again the wave-length equation—

$$n\lambda = b(\sin i + \sin \theta).$$

We may substitute for θ the equivalent ratio $\frac{p}{\rho}$, where p is the length of arc of the focus circle corresponding to the angle of diffraction θ, and ρ is the radius of curvature of the grating,

therefore $$n\lambda = b \sin i + b \sin \frac{p}{\rho}.$$

Differentiating, sin i being constant,

$$nd\lambda = \frac{b}{\rho} \cos \frac{p}{\rho} dp$$

$$\frac{dp}{d\lambda} = \frac{n\rho}{b \cos \frac{p}{\rho}}.$$

This shows us that $\frac{dp}{d\lambda}$, or what may be called the linear

dispersion of the spectrum, is, at any given position of the instrument, proportional to n, or the order of the spectrum. This is only another way of expressing the fact that the various orders of spectra are superposed, each superposed wave-length

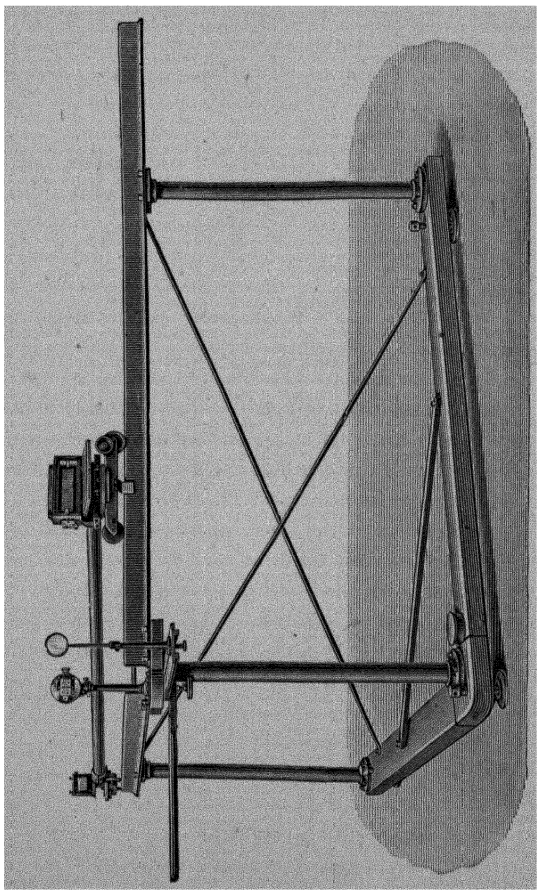


FIG. 67.

being inversely proportional to its order. This has already been proved before. Furthermore, the equation shows that the dispersion is a minimum when $p = 0$, *i.e.* at the centre of curvature of the grating; the linear dispersion is then equal to

$\frac{n\rho}{b}$, and is constant; that is to say, the spectrum is normal at this point. It is possible to give p quite a large value and still find the spectrum normal, and it has been proved[1] that the error in normality is equal to $\frac{bp^3}{24n\rho^3}$; the error is therefore proportional to the cube of the linear distance from the centre of the photographic plate. An example may be given of this. In the case of the largest Rowland concave grating at present in the market, $b = 0{\cdot}000127$ cm. and $\rho = 650$ cm., and putting the maximum allowable error at $\frac{1}{1000}$ Ångström unit, then we have ($n = 1$)—

$$p^3 = \frac{1 \times 10^{-11} \times 24 \times (650)^3}{0{\cdot}000127}$$

and $p = 8$ cm. nearly.

It is, therefore, possible to photograph 16 cm. of the first order spectrum (8 cm. on each side of the centre) perfectly normal within this error, which is, in fact, the greatest attainable accuracy with our present measuring apparatus.

Similarly, it can be found that with the same grating the deviation from normality at the ends of a 50 cm. photograph is only 0·03 A.U. in the first order. The distances are closely proportional to these with the smaller gratings, as may readily be found from the above expression.

If now we consider the spectra produced at the centre of curvature of the grating, *i.e.* when $\theta = 0$, we have—

$$n\lambda = b \sin i,$$

and

$$\sin i = \frac{n\lambda}{b}.$$

But the distance from slit to eyepiece (AE in Fig. 15, p. 39) is equal to $\rho \sin i$, and if ρ again be put equal to the radius of curvature, this distance therefore $= \frac{\rho n\lambda}{b}$, that is to say, in any given order it is directly proportional to the

[1] Kayser, *Handbuch der Spectroscopie*, i. 466.

wave-length. It is possible, therefore, to mark off on the grating rail a linear scale on which the wave-lengths may be approximately read off from the position of the eyepiece. It is important to notice that this scale is the same as the normal scale of the spectrum obtained upon the photographic plate at the centre of curvature; for if the distance from slit to eyepiece be put $= g$, then $\frac{dg}{d\lambda} = \frac{\rho n}{b}$, which is the value of the linear dispersion upon the photographic plate $\frac{\rho n}{b \cos \frac{p}{\rho}}$, when $\cos \frac{p}{\rho} = \cos \theta = 1$, *i.e.* when $\theta = 0$. This constant $\frac{\rho n}{b}$ is called the scale of the instrument, and for the largest gratings of 650 cm. focus and 20,000 lines to the inch it is equal to 5118100 in the first order; a change in wave-length of 1 A.U. means therefore a change of position on the plate of about 0·5 mm. in the first order, and n times this in the nth order. It follows from this, and what has gone before, that it is possible with Rowland's largest gratings to photograph upon one plate a range of 320 A.U. normally, with a maximum error of $\frac{1}{1000}$ A.U.

It may again be pointed out here that this scale is perfectly constant over the whole range of the instrument, so that all photographs taken with it are absolutely comparable with one another, a fact which alone upholds the immense superiority of the concave grating over any other spectroscopic instrument.

It must not be forgotten that this method of mounting puts a limit upon the spectra which can be observed. As a general rule, the largest workable value of the angle of incidence is about 70°; above this the angular aperture of the grating falls so rapidly as materially to decrease the illumination. We have, therefore—

$$n\lambda = b \sin 70^\circ,$$

and

$$\lambda = \frac{0{\cdot}94b}{n}.$$

The practical maximum value of λ in the first order with a

20,000 line grating is about 12,000 A.U.; in the second order, 6000 A.U.; in the third, 4000, and so on. With a 10,000 line grating the practical limits will be twice the above.

It is thus necessary, in working with rays of great wave-length, to make use of gratings ruled with comparatively few lines to the inch; it is preferable, on the other hand, to use closely ruled gratings when work is to be done upon the ultra-violet spectra, since it is in this way possible to get greater resolving power in the first order, the first order being dealt with on account of the greater freedom occurring here from overlapping of the higher orders.

We have, lastly, to deal with the astigmatism of the concave grating. Since the grating in Rowland's mounting is always more or less obliquely situated with regard to the incident light, the spectrum obtained from a point source of light is always more or less widened out, so that a spectrum of lines of greater or less length is obtained with a point as the light source. The greater the obliquity—that is to say, the greater the angle of incidence—the more pronounced is the widening. This widening is parallel to the ruling of the grating, and depends upon their length and upon the angle of incidence. It has been shown[1] that the length of the lines when a point source is used is equal to—

$$\sin i \,.\, \tan i \,.\, l,$$

where l is the length of the rulings on the gratings. In the case of Rowland's largest grating $l = 5$ cm., the length, therefore, of a line at 6000 A.U., given in the first order, with a point source, is $0{\cdot}25l = 1{\cdot}25$ cm., since the angle i would be 28° 12′. If a slit be used as the source of light, every point will be drawn out into a line, and these linear images overlapping one another give a line considerably longer than the original slit. Kayser gives as the length of the brightest portion of the spectrum lines—

$$\frac{s}{\cos i} - \sin i \,.\, \tan i \,.\, l,$$

[1] Kayser, *Handbuch der Spectroscopie*, i. 463.

and for the whole length of the lines—

$$\frac{s}{\cos i} + \sin i \,.\, \tan i \,.\, l,$$

where s is the length of the slit.

As a result of this astigmatism, "dust lines," which arise from the presence of particles of dust between the slit jaws, are not formed in the spectrum; these horizontal dust lines are brought to another focus.

This property of the concave grating renders it impossible to obtain two sharply defined adjacent spectra for comparison

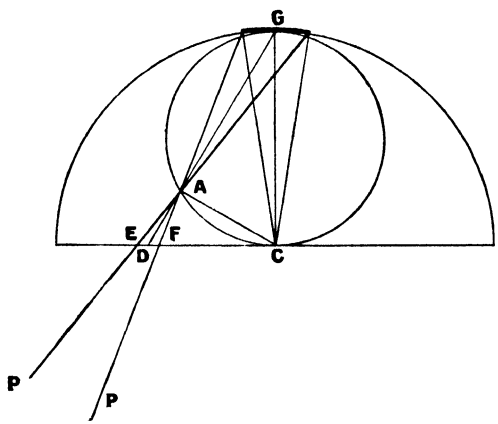


FIG. 68.

by means of the draw slides upon the slit, or a comparison prism, as described upon p. 58, for prism apparatus. For such comparison a mechanical method is usually used (*vide infra*, p. 212). Sirks,[1] however, has shown that a comparison prism can be used if it be placed a certain distance away from the slit. This may be seen from Fig. 68, where G is a grating with a radius of curvature equal to GC; the slit is at A, and the incidence angle i = AGC. A beam of light is shown coming from PP, passing through the slit at A, and focussed by the grating G at C. Now the slit A produces a vertical image at C, and there is also a horizontal focus line at EF, so that a

[1] Sirks, *Astronomy and Astrophysics*, **13**. 763 (1894).

horizontal wire stretched across the incidental beam of light at EF will be focussed as a horizontal line on the plate at C. It therefore follows that if a very narrow right angle prism be placed horizontally at EF, a sharply defined narrow horizontal strip will be cut out of the centre of the spectrum at C. A second source of light can be thrown in through this prism, with the result that the chief spectrum at C will have a narrow and sharply defined comparison spectrum running horizontally along its centre. It is clear that the size of the prism and its distance from the slit varies with every position of C; these may readily be calculated. First, the distance DA—

$$DA = DG - AG;$$

now $$DG = \frac{\rho}{\cos i}, \text{ where } \rho \text{ as usual} = GC$$

and $$AG = \rho \cos i,$$

therefore $$DA = \frac{\rho}{\cos i} - \rho \cos i = \rho \sin i \tan i.$$

Secondly, the length of face EF. If the total width of the grating be $= d$, then—

$$\frac{EF}{d} = \frac{DA}{AG}$$

and $$EF = \frac{\rho d \sin i \tan i}{\rho \cos i}$$

$$= d \tan^2 i.$$

The Michelson Echelon Diffraction Grating.—This grating was designed by Michelson with a view of obtaining an instrument of very high resolving power, which, at the same time, would give spectra of great brilliancy. In the case of the ordinary diffraction grating, the illumination falls off very rapidly as one mounts into the higher orders; with the echelon grating the light is all concentrated into the high orders; the resolving power is very great with the echelon, because the relative retardation between the extreme rays entering the telescope is extremely great, and, just as in the ruled grating, the resolving power may be said to depend upon the retardation between the rays from the extreme apertures.

The echelon grating is made by setting together a series of perfectly parallel glass plates of equal thickness, which decrease in size by an equal amount, as is shown in Fig. 69. The beam of parallel light is incident normally on the top plate in the diagram, and the rays, after passing through, are brought to a focus by a lens. The pencils *a*, *b*, *c*, etc., coming from the different elements of the grating are retarded upon one another by reason of the difference in the velocity of the light through the glass and air, and thus interference is set up at the focus of the lens, and a spectrum is produced. It will be seen that the relative retardation between the rays from the two extreme elements is very great, and therefore the order of spectrum obtained is very high ; and since the direction in which the spectra are obtained is in the direction of propagation of the light, the brightness of these spectra is very considerable.

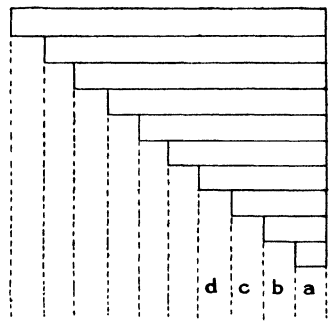


FIG. 69.

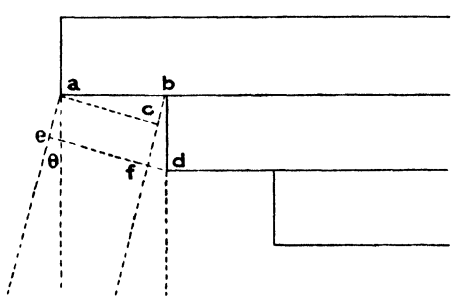


FIG. 70.

Dispersion.—The analytical expressions for the production of the spectra are readily obtained, as may be seen from Fig. 70, where only two adjacent apertures are drawn, which are quite sufficient for the purpose.

Let $ab = s$ be the breadth of an aperture, and $bd = t$ the thickness of each plate. The angle of diffraction, θ, of the spectra observed is very small, and if n be the order of the spectrum observed, then the relative retardation of the rays of two interfering pencils will be equal to $n\lambda$. Evidently, therefore, the relative retardation between the rays leaving a and d must be equal to $n\lambda$, and, therefore, we may put—

$$n\lambda = \mu bd - ae = \mu t - ae,$$

where μ represents the index of refraction of the glass for wave-length λ, *i.e.* the relative velocity in air and glass.

Now $\quad ae = bf - bc = bd \cos\theta - ab \sin\theta$

therefore $\quad n\lambda = \mu t - t\cos\theta + s\sin\theta.$

But θ is extremely small, so that $\cos\theta$ may be put $= 1$ and $\sin\theta = \theta$, and thus we have—

$$n\lambda = (\mu - 1)t + s\theta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By differentiation with respect to λ, n being constant—

$$nd\lambda = td\mu + sd\theta$$

and

$$\frac{d\theta}{d\lambda} = \frac{1}{s}\left(m - t\frac{d\mu}{d\lambda}\right).$$

Substituting for n its approximate value $\frac{(\mu - 1)t}{\lambda}$, from (1) ($\theta$ being extremely small), we have—

$$\frac{d\theta}{d\lambda} = \frac{t}{s\lambda}\left[(\mu - 1) - \lambda\frac{d\mu}{d\lambda}\right]$$

$$= \frac{bt}{s\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where b represents the coefficient within the square brackets, which, it will be noticed, is entirely a function of the glass employed, and may be calculated from its optical constants. It lies between 0·5 and 1·0 for most glasses.

Equation (2) gives the dispersion of an echelon grating, and shows that the dispersion of a grating of a given glass for light of a given wave-length is independent of the number of steps, and varies directly as the thickness of the plates, and inversely as the breadth of aperture of each element.

By differentiation of equation (1) with respect to n keeping λ constant—

$$\lambda dn = s d\theta$$

and
$$\frac{d\theta}{dn} = \frac{\lambda}{s};$$

putting $dn = 1$

then
$$d\theta_2 = \frac{\lambda}{s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $d\theta_2$ is the change in deviation occurring in passing from one order to the next; that is to say, the angle between the images of the same line in two consecutive orders is equal to $\frac{\lambda}{s}$. This separation of orders is, therefore, only dependent upon the wave-length and the width of step.

Resolving Power.—If $d\theta_3$ represent the angular limit of resolution, that is to say, the angular separation of two lines which are just seen separated in the telescope, then (*vide* p. 75)—

$$d\theta_3 = \frac{\lambda}{a}$$

where a is the effective aperture of the telescope object glass; but this is equal to the sum of the width of all the steps $= ms$, m being the number of elements;

therefore
$$d\theta_3 = \frac{\lambda}{ms}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By substitution of this value of $d\theta$ in equation (2),

we have
$$\frac{\lambda}{a\lambda} = r = \frac{bmt}{\lambda}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

The resolving power of an echelon grating is thus proportional to the total thickness of glass traversed, and for a given wave-length is independent of the thickness of the plates or width of the steps.

A comparison of equations (3) and (4) shows that the angular limit of resolution is $\frac{1}{m}$th of the angular separation of two consecutive orders.

The Intensity of Illumination.—Evidently this is a maximum when $\theta = 0$, because this is the principal direction of propagation of the light; if this be put equal to unity, the intensity in oblique directions will be found from the expression—

$$I = \frac{\sin^2 \pi \frac{s}{\lambda} \theta}{\left(\pi \frac{s}{\lambda} \theta\right)^2}$$

which is deduced in exactly the same way as the similar expression on p. 177. From this it is evident that the illumination vanishes when $\theta = \frac{\lambda}{s}$; but by equation (3) the angle between the images of the same line in two consecutive orders is also $= \frac{\lambda}{s}$. If, therefore, a line be obtained in the position $\theta = 0$, the images of the same line in the next lower and the next higher orders will vanish.

As an example of the application of the above formulæ, an echelon recently made by Hilger may be chosen. For this instrument the various constants were—

$t = 10$ mm.
$s = 1$ mm.
number of plates $= 20$;

optical constants—

$\mu_C = 1{\cdot}5706 \quad \lambda = 6{\cdot}5631 \times 10^{-5}$ cm.
$\mu_D = 1{\cdot}5746 \quad \lambda = 5{\cdot}8930 \times 10^{-5}$ cm. (mean of D_1 and D_2)
$\mu_F = 1{\cdot}5845 \quad \lambda = 4{\cdot}8615 \times 10^{-5}$ cm.
$\mu_{G'} = 1{\cdot}5927 \quad \lambda = 4{\cdot}3410 \times 10^{-5}$ cm.

The value of $\frac{d\mu}{d\lambda}$ for this glass at $\lambda = 5{\cdot}8930 \times 10^{-5}$ as calculated from Cauchy's formula as shown on p. 74 is -7113 by interpolation between μ_C and μ_F. Substituting this and the values of μ_D and λ for the D line in the coefficient $(\mu - 1) - \lambda \frac{d\mu}{d\lambda}$, b_D is found to be equal to $0{\cdot}5746 + 0{\cdot}0419 = 0{\cdot}6165$.

Dispersion.—From equation (2)—

$$\frac{d\theta}{d\lambda} = \frac{bt}{s\lambda}$$

therefore $\frac{d\theta}{d\lambda} = 104615$ at wave-length 5893 A.U.

putting $d\lambda = 0{\cdot}1$ A.U. $= 1 \times 10^{-9}$ cm.

$d\lambda = 0{\cdot}0001046$ radian

$= 22''$ of arc.

That is to say, that the angle between two rays which differ in wave-length by 0·1 A.U. is 22″ of arc.

Separation of Orders.—From equation (3)—

$$d\theta_2 = \frac{\lambda}{s} = 0{\cdot}0005893 \text{ radian}$$

$$= 2' \text{ of arc.}$$

This being the angle between the images of the same line in consecutive orders.

Angular Limit of Resolution.—From equation (4) this is $\frac{1}{m}$th of the separation of orders. Now the number of plates was twenty, but the aperture of the telescope object glass is 1 mm. larger than the largest plate, so the number of effective apertures is $21 = m$;

therefore $d\theta_3 = 6''$ nearly,

this being the angle between two rays in the neighbourhood of D which can just be seen separated. From equation (4*a*) the difference in wave-length of two such rays which can just be separated—

$$d\lambda = \frac{\lambda^2}{bmt} = \frac{5{\cdot}893^2 \times 10^{-10}}{0{\cdot}6165 \times 21 \times 1}$$

$$= 0{\cdot}027 \text{ Ångström unit.}$$

Therefore the instrument will resolve lines which differ in wave-length by 0·027 A.U.

Finally, the resolving power is equal to $\frac{bmt}{\lambda} = 218330$.

In the modern form of the echelon, the plates, after having been thoroughly cleaned, are carefully clamped together and

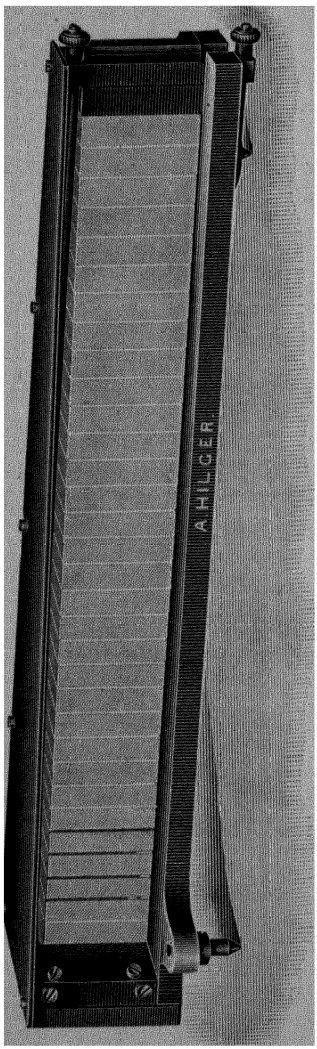


FIG. 71.

mounted on a stand, provided with levelling screws. It is hardly necessary to point out with what accuracy the plates must be worked, and with what care they must be handled. As usual with gratings, the plates are so mounted that the apertures are parallel to the slit. An echelon with thirty-two plates is shown in Fig. 71.

It is necessary in making use of an echelon grating that the light be submitted to a preliminary analysis, by means of a prism, before it is allowed to enter the echelon apparatus, on account of the very small angle between two successive orders of spectra. For this purpose the most convenient form of auxiliary spectroscope is the constant deviation instrument described on p. 122. With this apparatus the eyepiece is removed, and the telescope object glass so adjusted as to focus the image of the slit upon the slit of the echelon instrument; by simply turning the constant deviation prism any desired line can be brought on the echelon

slit, without any further adjustment. The echelon spectroscope is similar to any ordinary spectrometer, in that it possesses a collimator and telescope; it is, as will readily be seen from what has gone before, essentially a direct-vision instrument; it should be provided with a centre table which can be rotated to a small extent, and, further, there should be an arrangement by means of which the echelon can be swung out of the field of view.

In Fig. 72 is shown an echelon spectroscope, with a constant deviation spectroscope for the preliminary analysis of the light. The echelon itself is at A, and the telescope and collimator at B and C respectively; the slit is shown at D. E is the constant deviation instrument, with its collimator and telescope; it will be noticed that the latter has no eyepiece, but is brought close up against the echelon slit, so that this slit may be in the focal plane of the telescope objective. All the necessary adjustments can be carried out from the eyepiece end of the echelon; the handle F regulates the echelon slit, the handle G rotates the constant deviation prism, while the handle H adjusts the echelon itself. The arrangement for swinging the echelon out of the field of view is not shown in the illustration; this is only used in the preliminary adjustments.

The adjustments of the apparatus are very simple and straightforward. In the first place, it is necessary to see that the telescope of the auxiliary spectroscope is in an exact straight line with the collimator and telescope of the echelon instrument; and in the second place, that the object glass of the auxiliary telescope correctly focusses the image of the slit upon the echelon slit. A sodium flame is then brought in front of the auxiliary slit, and the prism turned until the D lines are brought upon the echelon slit; on looking through the echelon telescope with the eyepiece removed, the object glass should appear equally illuminated all over, with, perhaps, two slight and symmetrical black strips to the right and left; if this is the case the instrument is in adjustment.

A line that it is required to examine may now be brought upon the echelon slit, and, following on the theory given above, different phenomena may be seen on looking through the echelon

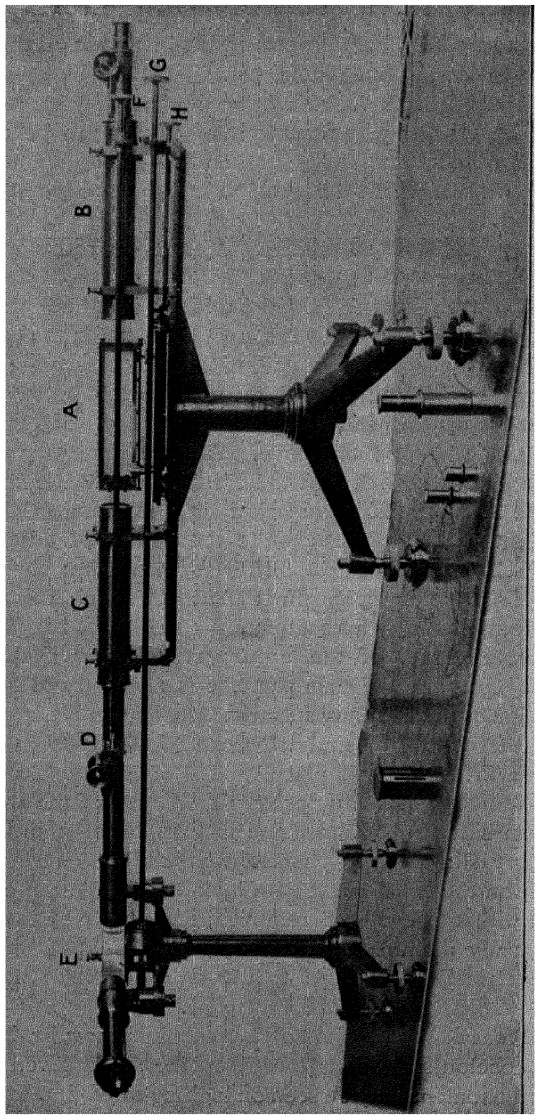


FIG. 72.

telescope. For example, if the line be seen under the condition $\theta = 0$, then it will appear as a single very bright line in the middle of the field, with a series of very faint lines diminishing in intensity on each side of it. The two neighbouring orders on each side are now absent $\left(\text{since } \theta = \frac{\lambda}{s}\right)$, and the faint lines are the next higher orders to these—very faint, because they are visible under larger values of θ. This condition may not be realised, and there may be seen two equally bright lines, which are two successive orders of the same line, and at the same time the series of faint lines on each side. Again, the condition may lie between the above two, so that two lines of unequal brightness are seen. It is important to notice that on each side of the centre of the field there is a dark point corresponding to the condition that $\theta = \frac{\lambda}{s}$; between these dark points is a region equivalent to twice the distance between two consecutive orders. It is this region that should be examined, and the fainter lines lying outside the two dark points will not in any way interfere. By a slight rotation of the echelon on its vertical axis any required condition can be obtained, and a number of orders can be made to cross the field of view. It will be found during the rotation of the echelon that there is one position at which the direction of motion of the lines in the field is reversed; the echelon is then normal to the incident light, which is the best position for work.

The chief objection to this grating lies in the small value of the separation of consecutive orders of spectra. The objectionable nature of this makes itself felt, when lines are examined which have a considerable breadth of their own. For example, in the case of the grating given above, the angular separation of consecutive orders is about 2′ of arc, or 0·0005893 radian, while the dispersion is 104615 at D, *i.e.* $d\theta_1 = 0{\cdot}0001046$ radian when $d\lambda_1 = 0{\cdot}1$ A.U. The greatest possible breadth, therefore, of a line in the neighbourhood of D which can be observed without two orders overlapping is about 0·56 A.U.

The Echelette Grating.—One of the most important problems connected with the grating is the question of the distribution of intensity amongst the spectra of the different orders. Practically no rigorous investigation has been made owing to the impossibility of determining the actual form of the groove in a ruled grating. Wood [1] has recently attacked the problem by making gratings with grooves of such large size as to make a determination of their exact form a matter of certainty, and then investigating the energy distribution by means of the long heat waves. By employing the residual rays from quartz as discovered by Rubens and a grating with say 1000 lines to the inch, it is evident that we should have about the same ratio of wave-length to grating space as in the case of a Rowland grating with 14,000 lines to the inch and red light. Thus gratings with constants varying from 0·1 mm. to 0·01 mm. could be studied by means of the residual rays or narrow regions of the infra-red spectrum isolated by means of a rock-salt prism. Wood has succeeded in preparing such gratings, and it has been shown by him in conjunction with Trowbridge that they are singularly adapted for study of the infra-red spectrum. For by means of such gratings a much greater resolving power can be obtained than has hitherto been found possible for such long wave-lengths. It is found that in these gratings a larger percentage of the energy is thrown into the first or second spectra and thus they may be regarded as reflecting echelon gratings of comparatively small retarding power, and Wood has proposed the name of echelette, to distinguish them from the ordinary grating or the Michelson echelon. The method finally adopted for their manufacture was as follows: A sheet of polished copper plate such as is used by photo-engravers for the half-tone process was gold plated and polished. A carborundum crystal was used for the ruling point. The crystals were selected by breaking up the mass of the substance as it comes from the furnace, the natural edge of the crystals being so straight that they rule a groove with optically perfect sides. It is hardly necessary to point out that the success of the grating depends

[1] *Phil. Mag.*, **20**. 770 and 886 (1910).

upon this fact. In the ruling everything depends on the nature of the edge and the angle at which the crystal is set, *i.e.* the tilt forwards or backwards with respect to the direction of the ruling. When the ruling is properly carried out the groove is formed simply by a compression of the gold surface, no metal being removed. Since the angle of the carborundum crystal is 120° the sides of the groove approximately enclose this angle, and according to the position of the crystal so the grooves may be obtained of various shapes. The crystal is mounted so as to rule a groove with one edge at an angle of 20° or less with the original surface, and it is found that such a grating when illuminated with infra-red radiation of longer wave-length than say 3μ behaves like an ideal grating, and gives spectra similar to those given by an ordinary grating which throws practically all the light into one or two orders on each side of the central image.

A complete investigation of these gratings is being carried out by Trowbridge and Wood,[1] the results of which have therefore not yet been published, but the investigation has been carried sufficiently far to indicate that the method gives reliable experimental data regarding the relation between the form of the groove and the distribution of energy. In practice it is found that owing to the diffraction of the radiation from the reflecting plane, it is not possible to concentrate all the energy into one single spectrum, but with a properly sloped edge as much as 70 per cent. of this can be utilised.

The application of these gratings to the study of radiations such as the residual rays of quartz is described by Trowbridge and Wood[2] in a third paper, and their superiority in resolving power as compared with a rock-salt prism is manifest; for example, the quartz residual rays which Coblentz found to consist of two closely situated maxima at $8{\cdot}5\mu$ and 9μ were now found to consist of two maxima of equal intensity at $8{\cdot}41\mu$ and $8{\cdot}90\mu$ sharply separated by a minimum with an intensity of one-third that of the maxima. This minimum is therefore very much more

[1] *Phil. Mag.*, **20**. 886 (1910).
[2] *Ibid.*, 898 (1910).

pronounced than appears from Coblentz's method. Similarly in the case of the carbon dioxide radiation from the bunsen burner the radiation at 4·4μ is undoubtedly resolvable into two maxima at 4·3μ and 4·43μ respectively. The dispersion of these gratings has been compared with that of rock-salt and fluorite prisms, and it has been found that between 4μ and 5μ it is nearly 17 times that of a 60° rock-salt prism and 4 times that of a fluorite one. Between 8μ and 9μ the Echelette grating has a dispersion of 5·4 times that of the rock-salt prism. The grating space of the grating used was 0·0123 mm.

CHAPTER VII

THE RULED GRATING IN PRACTICE

The Plane Grating.—As already described in the introduction (p. 41), there are several methods in which a plane grating may be used. Generally speaking, however, except in cases of absolute measurement, the plane grating is not so serviceable as the concave grating for wave-length determinations; recently by far the best absolute determinations have been made by the interference methods of Michelson, and of Fabry and Perot, so that a plane grating may be considered as of little use in accurate work. They still, however, find a use for ordinary work, especially the very excellent copies which may now be purchased very cheaply. The following directions are given as showing the methods of work with these instruments.

The general equation, as before stated, is—

$$n\lambda = b(\sin i + \sin \theta) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where θ is positive or negative according as the incident and diffracted rays are on the same or opposite sides of the normal. This equation can be written in the form—

$$n\lambda = 2b \sin \frac{i+\theta}{2} \cos \frac{i-\theta}{2};$$

and since $i + \theta$ is equal to the angle of deviation which may be called ϕ,

therefore $$n\lambda = 2b \sin \frac{\phi}{2} \cos \frac{i-\theta}{2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From this equation it is clear that the larger the value of the term $\cos \frac{i-\theta}{2}$, the smaller the value of the term $\sin \frac{\phi}{2}$,

and that when $\cos \frac{i-\theta}{2}$ has a maximum value, $\sin \frac{\phi}{2}$, and therefore the angle ϕ, will have a minimum value. The term $\cos \frac{i-\theta}{2}$ has a maximum value of 1 when $i - \theta = 0$, *i.e.* when $i = \theta$; it therefore follows that the deviation obtained with a grating is a minimum when the angles of incidence and diffraction are equal to one another, and that under these conditions the general wave-length equation is simplified to the form—

$$n\lambda = 2b \sin \frac{\phi}{2}. \quad \ldots\ldots \quad (3)$$

In the case of a transmission grating the condition of minimum deviation is readily enough obtained by so setting the grating that the incident and diffracted rays make equal angles with the normal. With a reflecting grating, however, minimum deviation can only be obtained in the Littrow type of apparatus, in which the incident and diffracted rays pass through the same telescope (*vide* p. 124).

The position of minimum deviation with a grating has a certain advantage in that the definition is always very much improved, but at the same time it is rather laborious in practical work. It was, however, used by Mascart in his determinations of absolute wave-length.

The above equations are sufficient for all the methods of measurement of wave-length with plane gratings. There are five of these methods, differing slightly from one another (*vide* p. 42). In the first two methods the grating is set perpendicularly to the collimator or the telescope, and thus in equation (1) either i or θ is made equal to zero, and so we may write the equation as—

$$n\lambda = b \sin \phi,$$

where ϕ is the angle of deviation.

In the third method the grating is not set perpendicularly to either the telescope or the collimator, and therefore equation (1) is applicable.

The fourth method is that of minimum deviation described

above; and the fifth method is to fix the collimator and telescope firmly at some known angle to one another and to rotate the grating.

In equation (3) the term $i - \theta$ evidently represents the angle between the incident and diffracted rays, and thus the angle between the collimator and the telescope; if this be known, it will only be necessary to determine the value of ϕ or the deviation in order to find λ from equation (3).

In all cases of mounting plane gratings for purposes of measurement of wave-length, a spectrometer must be employed; for the first, second, and third methods the spectrometer must be provided with a rotating telescope, the amount of whose rotation can be measured, and the same for the fourth method with transmission gratings. With the fourth and fifth method, using reflecting gratings, a spectrometer table must be used, by means of which the necessary amount of rotation given to the grating can be measured.

In the first two methods, where the grating is set perpendicularly to the collimator and the telescope respectively, an ordinary spectrometer is employed such as was described for a prism on p. 116; the adjustment of the apparatus as regards illumination is precisely the same as in the case of the simple prism apparatus; there is, however, in all cases of grating mounting an additional adjustment which must be attended to, namely, to see that the rulings on the grating are parallel to the slit, for otherwise the definition will be hopelessly ruined.

It is very convenient to have the grating mounted upon a table provided with three levelling screws, as this enables the necessary adjustments for verticality, etc., to be readily made. When a grating has been properly adjusted, the spectra should not rise or fall in the field of view of the telescope when the grating is rotated on its vertical axis.

If the first method of working be adopted, then, after all the preliminary adjustments have been satisfactorily made, the grating is turned until it is normal to the collimator. When this is the case the angle of deviation for any line will be the same on each side of the normal, and therefore the

position of the grating may be tested in this way. In the case of a transmission grating, the cross-wire in the telescope eyepiece is first fixed upon the image of the slit obtained straight through the grating and the reading taken; the telescope is then turned until the image of some line is brought upon the cross-wire and the reading taken; the telescope is then turned back until the same line in the same order on the other side of the normal is brought upon the cross-wire. The two angles of deviation must be equal; if they are not, the grating is turned one way or the other until equal angles are obtained. When this is the case the wave-lengths of any lines may be found from the equation $n\lambda = b \sin \phi$. In this way, by taking readings on each side of the normal, greater accuracy is obtained. If a reflecting grating be used it will, of course, be necessary to take the reading of the direct image before the grating is put in place; the deviation in this case will, of course, be the angle between the collimator and the telescope when fixed on the line in question, and will be equal to the difference between 180° and the angle through which the telescope is turned from the direct image to the line in question.

The second method is preferably restricted to reflecting gratings, and evidently in this case the grating must be so placed that the telescope, when fixed upon the line in question, bisects the angle between the incident rays from the collimator and the reflected rays. This method possesses the inconvenience that the grating must be adjusted for every line measured.

In the third method the grating is not necessarily placed in any particular position, but the angles of incidence and diffraction are both measured and the wave-length found from the general equation—

$$n\lambda = b(\sin i + \sin \theta).$$

This method, of course, has not such a probable accuracy as the first, owing to the fact that two angles have to be measured in place of one; it was, however, used by Ångström in his work. The methods of measurement are as follows, with a transmission grating: When the grating has been put

in position, the telescope is turned until the cross-wire is brought upon the direct image and the reading taken; similarly a reading is taken of the reflected image. The angle between these readings subtracted from 180° gives the angle between the incident and reflected rays, and half this latter angle is the angle of incidence. From these data the reading of the telescope when normal to the grating can readily be found; from this reading to the reading on the diffracted ray gives the angle of diffraction. Care must be taken to note the sign of this angle θ, it being positive when the incident and diffracted rays are on the same side of the normal, and negative when they are upon opposite sides. The values found are then substituted in equation (1), whence the wave-length can be found. Exactly similar procedure holds in the case of the reflecting grating. Equation (2) may also be employed when it becomes necessary to measure the angle of deviation ϕ, that is to say, the angle between (*a*) the diffracted ray and (*b*) the transmitted ray in the case of a transparent grating, and the reflected ray with a metal grating. The angle $i - \theta$ in the case of a transmission grating is obtained as follows: Readings are taken of both the reflected ray and the diffracted ray; the angle between them substracted from 180° is the angle $i - \theta$. In the case of a reflecting grating $i - \theta$ is the angle between the incident and diffracted rays, and may be readily found by reading the direct image before the grating is put in place.

The fourth method, namely, that of minimum deviation, can be used with a transmission grating, and has the advantage of better definition, but is very cumbersome owing to the fact that the grating has to be specially adjusted for each line measured. The condition for minimum deviation as shown before is obtained when the angles of incidence and diffraction are equal; in practice the grating is so turned that the angle of deviation becomes equal to the angle between the incident and reflected rays. This method is not often made use of with plane reflecting gratings, owing to the fact that a Littrow type of apparatus is necessary, and as a rule these are made with concave gratings.

The fifth and last method, which was used by Bell in his

later determinations of absolute wave-length, consists in working with the telescope and collimator permanently clamped at some known angle with each other. This angle, of course, is the angle $i - \theta$ in equation (2), and, since this is determined once for all, it is only necessary to measure the angle $i + \theta$ or the deviation. For this purpose it is necessary that the grating be mounted upon a spectrometer table so that its rotation can be measured. In an experiment the grating is so turned that the reflected image of the slit is adjusted upon the cross-wires in the eyepiece of the telescope, when the reading of the rotating grating table is made. The grating table is then turned until the spectrum line required is brought upon the cross-wires, when the reading is again taken. Twice the angle through which the grating has been turned is equal to the angle of deviation. By substituting the value of this angle and the angle between the collimator and telescope in equation (2) the wave-length may be obtained.

A word may perhaps be said here concerning the value of b or the grating space. It will be remembered that this refers to the length of one aperture on the grating plus one adjacent dark space. This may very readily be found from the number of lines which are known to be ruled; Rowland gratings are now always ruled, except in special cases, with 20,000, 14,438, or 10,000 lines to the inch, and have therefore grating spaces respectively of 0·00127 mm., 0·001759 mm., or 0·00254 mm. It will be quite sufficient to take these as perfectly correct for all ordinary work; it is only in cases when very great accuracy is required that the correctness of these numbers comes into question,[1] and under these circumstances, as before pointed out, attention should be turned to other methods of measurement.

It was first shown by Rayleigh that replica gratings can be produced from a ruled grating by simple photographic methods. It is now possible to obtain commercially replicas of Rowland gratings at a very reasonable cost, which are casts in celluloid taken from a good-ruled grating. These are generally known under the name of Thorp's gratings, after the discoverer of the

[1] See page 44, *et seq.*

process. Thorp's method has been improved upon by R. J. Wallace,[1] who used gun-cotton in place of celluloid. He dissolved this in amyl acetate, using only the very best quality of gun-cotton, and then poured the solution into water. The precipitated gun-cotton is filtered off and thoroughly dried. The dried cotton is again dissolved in amyl acetate, and the resulting collodion is poured over the grating, care, of course, being taken that all dust is kept away. It is then allowed to dry very slowly, and the film carefully removed from the grating and mounted on a piece of plate-glass, the latter having been previously coated with a film of hard gelatine.

It has recently been found possible to convert these transmission into reflecting replicas by coating them with a very thin metallic film. This is done by Houllevigue's[2] method, and the application of this method to the replica grating is described by Gehrcke and Leithäuser.[3] The metallic deposit is produced by submitting the replica to the kathode rays in a very high vacuum, using a platinum kathode, and the process takes about two hours. The reflecting grating has exactly the same properties as the original.

One of the most convenient mountings for using a plane grating is that known as the Littrow mounting, which is a simple modification of that already described and shown on page 125. This method consists in placing a lens in front of the grating to render the incident light parallel and rotating the grating until the diffracted light is returned along the direction of incidence, and is focussed by the same lens.

The Mounting of the Concave Grating.—A brief description has already been given of Rowland's method of mounting the concave grating in so far as was necessary to show how the necessary condition was secured of the grating, slit, and eyepiece, or camera, always being placed upon the circumference of the same circle, namely, the circle having the radius of curvature of the grating as its diameter. A description of Rowland's apparatus at the Johns Hopkins University has

[1] *Astrophys. Journ.*, **22.** 123 (1905).
[2] *Comptes Rendus*, **135.** 626 (1902).
[3] *Verh. der Deutsch. Phys. Gesell.*, **11.** 310 (1909).

been given by Ames,[1] from which the following details are taken:—

AB and AC (see Fig. 73) are heavy wooden beams 6 × 13 inches cross-section, and 23 feet long. AB is rigidly fixed, while AC has a slight freedom of rotation about A, controlled by screws at C. The rails for the two carriages carrying the grating, and the camera, are fastened to these beams by screws

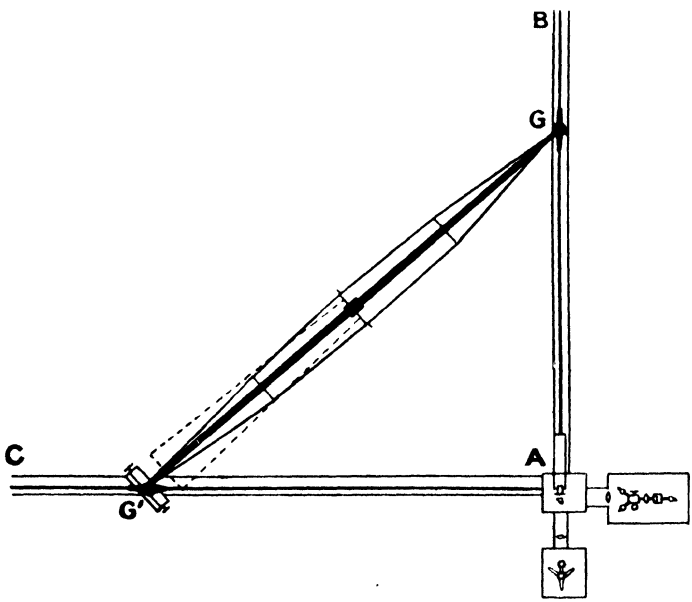


FIG. 73.

(see Fig. 74) which admit of adjustment, so that the rails may be straightened if the beams warp. They are made of $\frac{1}{2}$-inch angle iron, although a board made of any hard wood might be used. GG' is a 4-inch tubular wrought-iron girder braced by a truss, and pivoted at the two ends, directly over the rails, on the two iron carriages. The length of the girder is approximately equal to the radius of curvature of the grating, and there

[1] *Phil. Mag.* (5), **27**. 369 (1889).

is a range of adjustment of about 6 inches. To the ends of the girder tube are fastened two thick metal plates, and these rest upon the two carriages; these plates are bored to fit over a vertical pin, which is fixed upon the top of each carriage. The carriages each have two brass wheels placed about 1½ feet apart, and these, resting on the rails, enable the girder to be easily moved from one position to another.

One of the carriages carries the grating holder, and the other the camera. The grating holder is shown in Fig. 75; it is made of brass, and consists of a heavy platform, carrying an upright frame, B, which can move in slots on A. Fastened to the two sides of B are two lugs, P, between which the square brass plate C is held by pins, and in this way the plate C can be turned on a horizontal axis. This motion is governed by the screw S. At

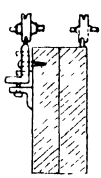


FIG. 74.

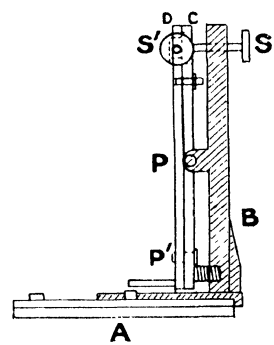


FIG. 75.

the lower end of C is a pin, P′, on which is fitted a second brass plate, D, which thus can revolve on the axis P′. This motion is controlled by the screw S′, and a spring which is not shown in the diagram. The grating itself stands on two projections from the bottom of D, and is held up against D by soft wax, thus being free from all manner of constraint. The camera box consists of a fixed wooden frame, B, Fig. 76, and a box, A, which can be removed. The photographic plate is placed in A in suitable slots, and is pressed firmly by wooden buttons against pieces of hard rubber, so that it is bent to the proper radius. There is in B a frame which can be moved vertically by a rack and pinion; and to this A is fastened by dowel pins on the bottom and hooks on the top. On the back

of the camera box B is hinged a board, C, which can be held firmly in place by hooks. This board carries a brass plate, Fig. 77, having a longitudinal opening of a width equal to the thickness of the plate, and capable of revolution round a horizontal central axis. By means of stops this revolution is

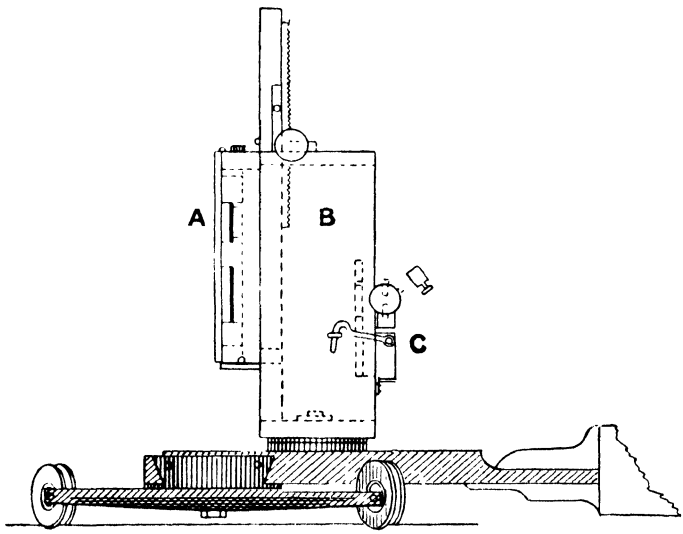


FIG. 76.

confined to 90°. This plate is used for the comparison of spectra.

The slit used in all grating apparatus must, necessarily, be provided with an arrangement whereby it can be rotated in its own plane, on account of the fact that it is essential for the slit aperture to be truly vertical and parallel to the rulings on the grating. The slit of Rowland's apparatus is shown in Fig. 78 in front elevation and side sectional elevation; as will be seen from the figures, it can be rotated in its own plane by the lower adjusting screw, while the upper screw is for the

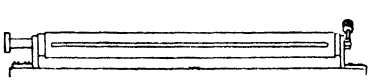


FIG. 77.

regulating of the slit opening. A V-shaped sliding diaphragm is placed over the slit for use with the light of the sun, in order to stop down the solar image, as otherwise the definition may be spoiled by the rotation of the sun.

It is necessary that hoods of black cloth be used to keep out stray light, both at the slit and at the camera box, the latter preferably extending halfway to the grating, for although the apparatus is placed in a dark room lighted only through ruby glass windows, a certain quantity of stray light is sure to be present.

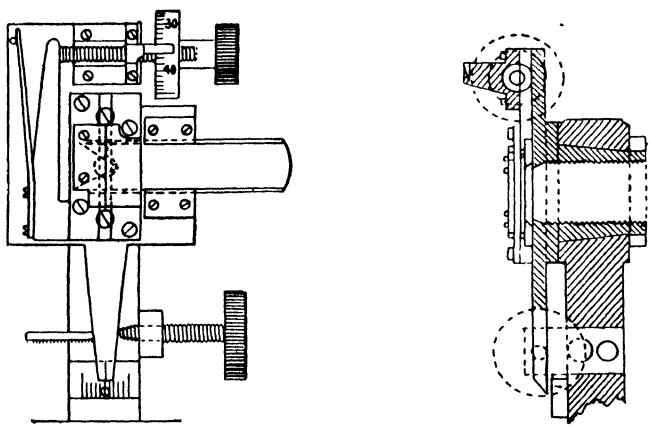


FIG. 78.

Kayser, in describing his method of mounting,[1] considers that the fact that the carriages have only two wheels does not ensure their being rigid, that is to say, a small amount of bending of the carriages backwards or forwards is, in his opinion, quite possible with Rowland's arrangement. He therefore uses four-wheeled carriages, two of which run on the rails, while the other pair run on a flat-topped beam fixed parallel to the beam carrying the rails. The wheels are about 2 feet apart, and the weight of the carriages is about 110 lbs. The girder in Kayser's apparatus is a bridge structure, made

[1] *Handbuch der Spectroscopie*, i. 474.

of hoop-iron, and carries light wooden frames, over which black cloth is stretched.

It is often necessary, of course, that a grating apparatus be erected in a light room, when it becomes necessary to box the whole apparatus in, and a method of doing this has been devised by Adeney and Carson for the large grating in the Royal University of Ireland.[1] Their arrangement is shown in

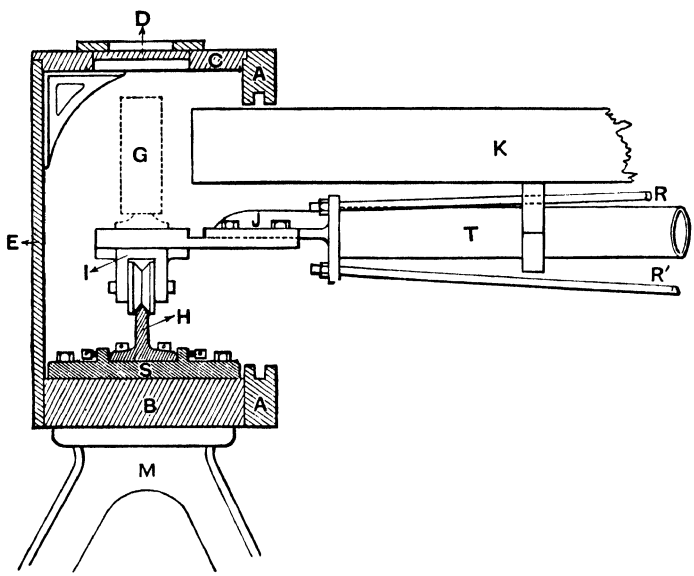


FIG. 79.

Figs. 79, 80, and 81, which are taken from their paper. The whole of the grating rail is enclosed on the outer side, and the top as shown at E and D in Fig. 79; AA are two grooved pieces, into which a series of sliding panels can be inserted from either end. K is a wooden rectangular tube, along which the diffracted rays pass to the plate; it is shown in sectional elevation in Fig. 80. As can be seen, the side of this box was grooved for the reception of sliding panels, which extended for

[1] *Proc. Roy. Soc.*, Dublin (1), 8. 711 (1898)

about half the length; the necessity for this is clearly shown in Fig. 81, where the dotted line IA represents the side of K, which must be open in order to allow the free passage of the light from the slit to the grating. The amount of opening necessary in the side of K varies, of course, with the position of the camera.

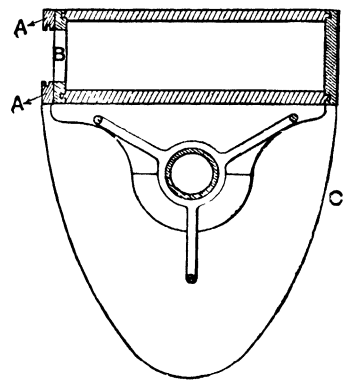


FIG. 80.

The following is a description of the mounting of the 10-foot focus grating at University College, London, which was made in the department, and may perhaps serve as a guide to any one who wishes to make his own mounting.

The whole apparatus is carried on three cast-iron columns, 4 inches in diameter, and 8 feet in height. Each of these columns has a base about 1 foot square, which is securely bolted down to the concrete floor by four $\frac{3}{4}$-inch bolts, one at

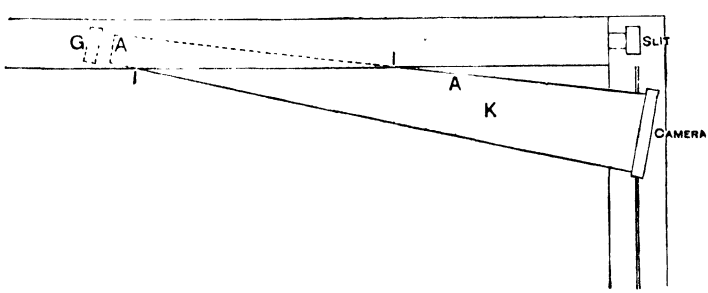


FIG. 81.

each corner, and on the top of each column is rigidly fixed a cap with a flat surface for the support of the beams. The columns are erected at about 10 feet from each other, and so placed as to include as nearly as possible a right angle. Resting on

these and bolted to the caps are two steel girders 5 × 5 inches of I cross-section, and a little over 11 feet long. The girders are thus set as nearly as possible at right angles to one another, and both rest on, and are bolted to, the cap of the centre column. This forms the main support of the apparatus. The two rails on which the camera and grating carriages run are of steel 2 × 2 inches of ⊥ cross-section, and 11 feet long. Each rail is supported by fourteen $\frac{3}{8}$-inch levelling screws, which are placed at distances of a foot apart, alternately on each side of the centre web, and two at each end. The lower ends of the screws are turned to sharp points, which are hardened, and rest on the steel girders. Moreover, each screw is provided with a locknut to clamp it in position when the rail is level. In fitting up the apparatus, when the two rails had been adjusted with sufficient accuracy to a right angle, and properly levelled, each of the screws was smartly hit with a hammer, and thus the sharp-pointed ends punched for themselves small sockets in the girders. After this had been done the rails were again tested with a level and again adjusted.

In this way, since the points of the screws rest in the sockets, no lateral shifting of the rails is possible unless they are lifted in any way, and this is obviated by firmly fixing them down by two angle pieces at each end of the two rails, which are held by screws into the steel girders. The centre webs of the rails were planed, which gives a sufficiently level surface for the carriages to run upon. By this method of mounting, certain conveniences are obtained, notably in the lightness of the rails themselves. This lightness has no disadvantage, for, supported as they are at such close intervals by the levelling screws, there can be no possibility of any sinking of the rails in any way under the weight of the carriages.

The slit is mounted on a special casting shown in Fig. 82 in side and front elevation. The slit itself is mounted upon a tube which slides into a flanged tube, and this flanged tube is screwed to the annular plate C. This plate C is about 3 inches outside diameter, and about $\frac{5}{16}$ inch thick. The upright standard which supports C is of + cross-section, as is shown in the diagrams. The bottom block D, which is about

4 inches long, is slotted in order to admit the centre web of the grating rail. The plate C was faced up in a lathe, and the slot in the base was planed out so as to be true and square to it, this being, of course, necessary in order to bring the slit into correct alignment with the grating, when the base is fitted over the grating rail. As can be seen from the diagram, three screws are set in each side of the base, which serve to clamp

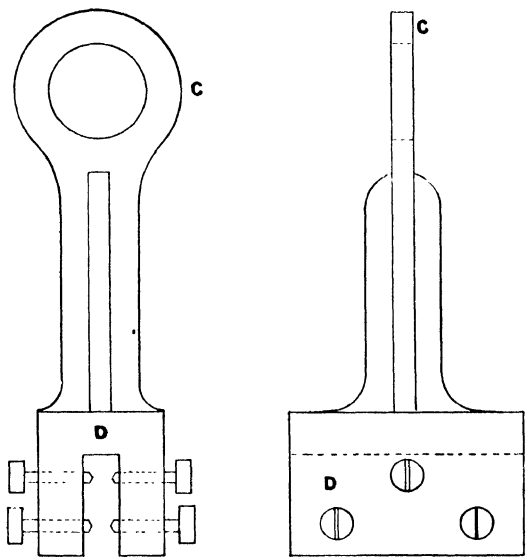


FIG. 82.

the apparatus in position on the rail, and by their means the position of the slit can be adjusted with great accuracy.

The two carriages which carry the grating and camera are identical in construction, and are shown in Fig. 83, in plan and side and end elevation. AA are two iron castings, 12 inches long, 2 inches wide, and $\frac{1}{4}$ inch thick; they widen, as shown, at the top, in order to offer more substance to the screws. These castings are planed on their top edges, and they form the sides of the carriages. The top B is a planished brass plate, 12 × 3 inches, and $\frac{1}{4}$ inch thick, and this is screwed

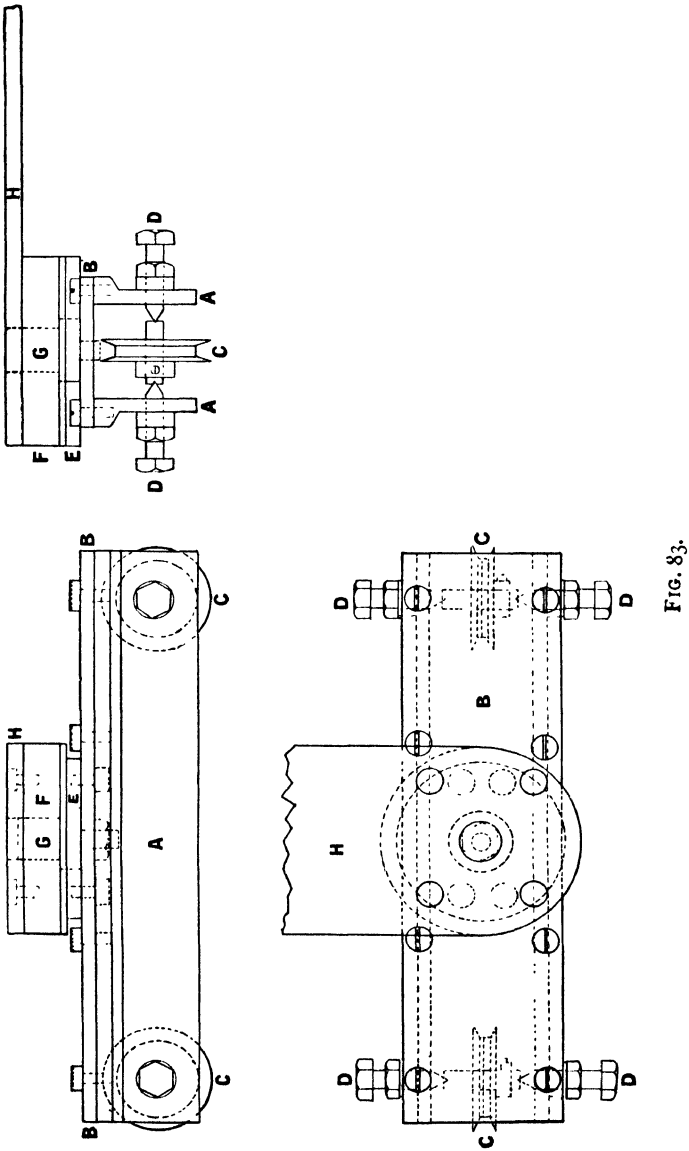


FIG. 83.

down on to the planed top edges of the side pieces by four screws on each side. The two wheels CC are gun-metal, and are about 2 inches in diameter, and are mounted on $\frac{3}{8}$-inch steel axles. These wheels are supported by the $\frac{3}{8}$-inch set-screws DD, which pass through bosses on the cast-iron side pieces. These set-screws are pointed, and the ends of the axles of the wheels are drilled to receive them; the screws also carry locknuts to clamp them in position. The distance between the centre of the wheels is about 10 inches, the side pieces extending about 1 inch at each end beyond the set-screws. The large vertical bearing, by means of which the beam connecting the two carriages is supported in each case, consists of two gun-metal discs, 4 inches in diameter, which work against one another round a centre steel pin. The construction of the joint is shown on the carriage at EFG. E and F are the two gun-metal discs, the lower one, E, being $\frac{3}{8}$ inch thick, and the upper one, F, $\frac{3}{4}$ inch thick. The centre steel pin is shown at G, and is $\frac{7}{8}$ inch in diameter where it passes through F, and $1\frac{1}{4}$ inch where it passes through the disc E. Below E it is turned down to $\frac{3}{8}$ inch, and, passing through the brass top of the carriage B, it is screwed and nutted underneath. Both of the discs are accurately turned and bored out to fit the steel pin, and to work with the greatest possible smoothness against one another. The lower disc E is fastened by four screws on to the carriage top, as is shown in the plan, while the upper disc F, as shown at A, Fig. 84, is fastened to a plate forming part of the beam connecting the two carriages. Fig. 84 is a diagram, drawn to quarter of the scale of Fig. 83, of the construction of this beam, and shows half of the beam in elevation and in plan. As mentioned above, the upper disc of the carriage bearing is shown at A; the disc is fastened by screws to the plate H, which is of mild steel, 14 × 4 inches, and $\frac{3}{8}$ inch thick, and is planed on both sides. As shown in the plan, this plate H is rounded off at the end over the disc in order to make the appearance as neat as possible. A $\frac{7}{8}$-inch hole was drilled in the mild steel plate, as shown, to admit the top of the steel pin of the bearing, which projects through the top disc, as shown at G,

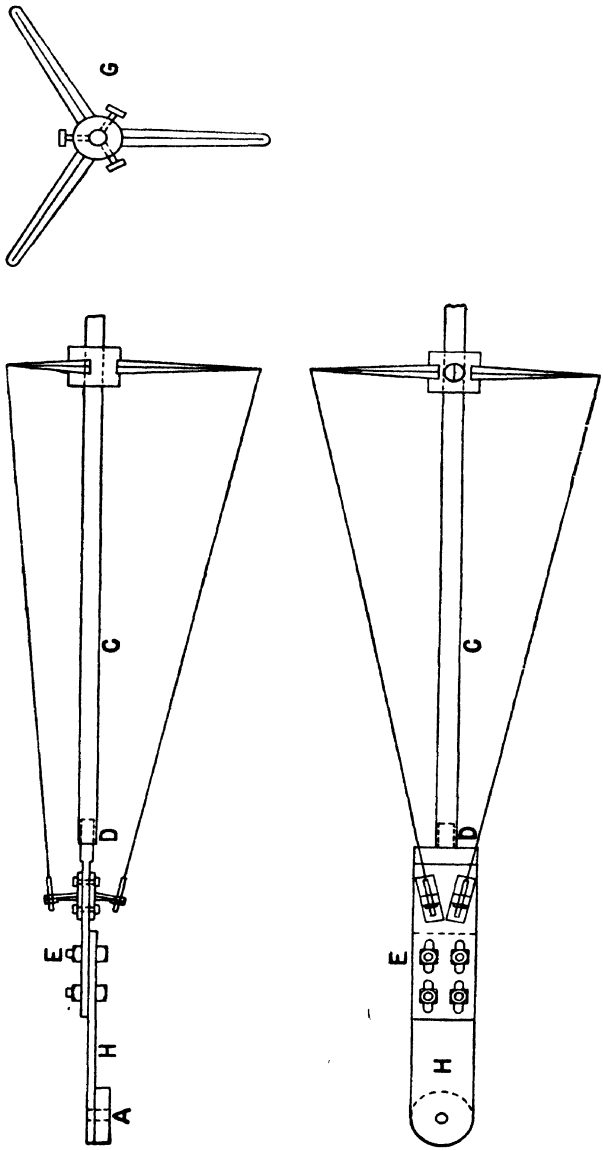


FIG. 84.

Fig. 83. This was arranged simply as a matter of convenience in fitting the apparatus together. The beam itself, as shown in Fig. 84, is very simple in construction, and was designed to be as light and, at the same time, as rigid as possible. It is made of bicycle tubing, stayed with three steel wire. This tube, which is marked C in the figure, is 7 feet 2 inches long, and 1 inch in diameter, and about $\frac{3}{64}$ inch thick in the walls. At each end this tube is brazed on to a lug, D, which projects about 2 inches from a cast-iron plate, E, which is 4 inches wide—the same as the mild steel plate—about 1 foot long, and $\frac{1}{2}$ inch thick. These cast-iron plates were planed on the under sides, and the lugs carefully turned in a lathe so as to be true to the planed surfaces, and just to fit the bicycle tubing. The brazing of the two ends of the tubing on to the lugs was one of the most difficult operations of the whole mounting, for it was absolutely essential to obtain the planed surfaces of the cast-iron plates at each end of the beam perfectly true to one another. The whole success of the mounting depended on this, and care was especially taken to guard against any twist. This operation was successfully carried out, and the two planed surfaces are almost absolutely true to one another.

The three staying wires are made of the best stout piano wire, and are carried from brackets on the cast-iron plates at each end over a three-winged support in the middle of the tubing. As can be seen in the diagram, two of the brackets are on the top of the cast-iron plates, and one underneath. Their design is quite simple, and sufficiently indicated in the figure. They are of gun-metal, and are fastened by a screw at each end into the cast-iron plates. The three stay wires at each end are brazed into $\frac{1}{4}$-inch bolts, which are about 4 inches long, and screwed the whole length. These bolts pass through holes drilled in the brackets, and are nutted at the back. There is thus 4 inches of adjustment at each end of the wires to take up stretching. The three-winged support for the wires in the middle of the beam is a gun-metal casting, and is shown at G, Fig. 84. Each wing is 10 inches long, and the whole is so placed that one wing points vertically downwards, while the other two enclose rather a wider angle than

symmetry requires—it is about 130°. This was done in order to prevent any interference with the spectrum as it passes between them. The centre block of the casting was bored out so as to fit the bicycle tube, and three set-screws symmetrically placed serve to hold it in position. The three wires are very tightly stretched, care being taken that no distortion is caused to the beam by reason of any unequal tension in the wires. As regards the joining of the beam to the mild steel plates, this is done in each case by four $\frac{1}{2}$-inch bolts. Both the cast-iron and the mild steel plates at each end of the beam are slotted, to allow of some latitude in the length

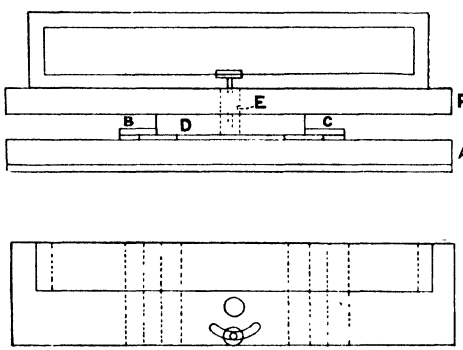


FIG. 85.

of the beam, which may be required when the final adjustments are being made.

The supports carrying the camera in one case and the grating mounting in the other case are of necessity somewhat different. At the camera end of the beam, a planished brass plate, 18 inches long, $4\frac{1}{2}$ inches wide, and $\frac{1}{4}$ inch thick, is screwed to the mild steel plate exactly at right angles to the beam, and so placed that its centre is exactly over the centre of the steel centre pin of the bearing. This brass plate carries a mahogany board of the same area, but 1 inch thick. This is shown at A, Fig. 85, and in this diagram are drawn the complete camera fittings, the most important of these being the adjustments for focussing. The adjustment normal to the

grating is obtained by the use of the brass slides, shown at B and C. These are $4\frac{1}{2}$ inches long, and are made of $\frac{3}{16}$-inch brass. Each bearing consists of brass strips, B and C, $1\frac{1}{2}$ inch wide, which are screwed to the mahogany board, but are separated from it by distance pieces of half their breadth. The strips therefore project about $\frac{3}{4}$ inch over the distance pieces, and thus form a groove into which the corresponding brass fittings on the upper board D exactly fit. A rotary adjustment is also possible between small limits, and is obtained as follows:—

In the centre of D is erected a $\frac{1}{2}$-inch brass pin, E, which fits into a brass tube carried by the upper board F. This allows a rotary motion to be given to F, the amount of which is controlled by a set-screw into the lower board D, passing through the slot shown in the plan. The board F forms the support of the dark slide. A mahogany frame, G, is fastened by screws on to the top of F, and has a clear opening of 14 × 4 inches, and is 2 inches deep. The dark slide is tightly held up against this frame by two brass hooks at the sides, and good contact between the two is ensured by strips of velvet glued to the back edges of the frame. The dark slide requires no special description. It is made to carry plates 12 × 2 inches, which are specially made of thin glass, and are bent to the required curve, namely, a circle of 5 feet radius. This is accomplished in the usual way, by fixing two carefully cut templates in the slide, and pressing the plate against these by rubber pads on the back of the dark slide. It should be said, of course, that the back is detachable, and that when a plate has been put in, the back is fastened down by catches, and forces the plate round the templates.

As regards the mounting of the grating on its carriage, a $\frac{3}{16}$-inch planished brass circular plate, 8 inches in diameter, is screwed down to the mild steel plate (H, Figs. 83 and 84), centrally over the bearing on the carriage, and on to this plate is screwed the bottom plate of the grating mounting. This is a plate about $5\frac{1}{2}$ inches in diameter, and has three radial slots cut in it, in which the three levelling screws of the grating table rest.

This completes the description of the actual mounting of the grating apparatus, and it only remains to describe the covering in of the apparatus, the method of which is as follows. Two boards, 18 × 6 inches, and 1 inch thick, are fastened, one across the top and the other across the bottom of the cast-iron and mild steel plates at E, Fig. 84, at the camera end of the beam. Both these boards are recessed to admit the bolts and plates just sufficiently to allow them to meet, and they are screwed firmly together.

These two boards serve as a support for two iron brackets, which are screwed to the top board. Two similar brackets are also erected just behind the grating, on the 8-inch circular brass disc mentioned above. Four thin iron strips about 1 inch wide are stretched along the beam, two between each outside pair of brackets, and are kept in tension by bolts and nuts. The bolts are brass, and are soldered to the iron strips, and pass through holes in the brackets. These four bands, one at the top and bottom of each bracket, form a support for two thicknesses of satteen, which are stretched tight and stitched all along each strip.

In order to keep the iron bands in their position, that is to say, to keep them from closing together when the satteen is stretched over them, distance pieces are placed at suitable intervals between the upper pair and the lower pair of bands. These distance pieces are quite light, being only of wood 1 inch square, and are held in their positions by screws through holes drilled in the iron strips.

The two brackets at the camera end are placed about 3 inches in front of the frame against which the dark slide is placed, and the space between is covered by satteen, which is quite loosely stretched between the brackets and the frame, to allow of a certain amount of adjustment in the position of the dark slide for purposes of focussing.

In order to admit the passage of the light from the slit to the grating, the satteen between the two iron strips opposite the slit is cut away, just as far as is necessary to admit the light from the slit when the camera is brought near to the slit. It follows, therefore, that when the camera is moved to the

other end of its rail, the grating becomes exposed to the ordinary light of the room through this opening. The exposed portion is covered over with a dark cloth, this being found quite sufficient to make it light-tight.

Seeing that the four iron strips have to be kept in considerable tension, in order to hold them moderately rigid, a certain amount of displacement will be caused to the beam by this means. An extra stay of steel wire was put underneath the beam, between two brackets, similar to those already described; this was found to counteract the strain set up by the iron strips.

For the covering in of the grating rail, a simple method has been adopted. A wooden framework was erected over the girder, which carries the rail. This framework is made of 2-inch square mahogany, and is about 1 foot wide, and 20 inches high. The top, the outer side, and the two ends, are covered with light wooden boards, about $\frac{1}{4}$ inch thick. The front side, that is to say, the side along which the beam has to pass, is filled in with two curtains, running on wires. Two wires are tightly stretched between the supports at each end of the frame, one at the top and one at the bottom. Two curtains—each capable of stretching along the whole frame, that is to say, about 11 feet—are threaded on these two wires. One end of each of these curtains is nailed to the frame support, one at each end of the girder, and one curtain is put on each side of the beam. It is evident from this that whatever the position of the beam may be, these curtains may be drawn right up to each side of it. This shuts out practically all light. Although the two wires which carry the curtains are placed as close as possible to the top and bottom of the frame, still a certain amount of light will necessarily be able to pass above and below them. As regards the top, this is easily obviated by a short curtain, which is nailed all along the top of the frame, and which, by simply hanging down, keeps all the light out. As regards the bottom, it might be arranged to have a short fringe stretched along the two curtains, which would answer the purpose, but it has been found more convenient to use ropes of twisted black cotton-wool, which are placed along the frame under the curtain. It would be possible, no doubt,

to have a light metal frame to run on the curtain wires, through which the beam could pass. If the two curtains were fastened to the two sides of this, the adjustment of the curtains would become automatic. This, however, has not been adopted, because it is such an easy matter moving the curtains by hand after the camera-carriage has been set in the right position.

Wadsworth[1] has devised several methods of mounting concave gratings, which partake of the fixed-arm type. These are, perhaps, more especially intended to adapt the instrument to astronomical purposes. One of these, however, may be described here, although it does not strictly belong to the fixed-arm type. This arrangement is shown in Fig. 86, and, as will be

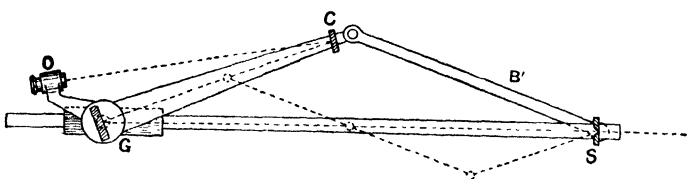


FIG. 86.

seen, the principle is the same as in Rowland's mounting; it differs from this, however, in that the diffracted rays from the grating G do not travel direct to the eyepiece, but are reflected by a plane mirror, C, to the eyepiece or plate at O. The grating is mounted upon a sleeve which slides over the rod GS, and the two ties CG and CS are linked together at C, and pivoted at G and S respectively. The slit is fixed at S, and the spectra are made to pass in front of the field of view in the eyepiece, by sliding the grating sleeve along its rod.

Wadsworth[2] has also devised a special mounting to utilise the astigmatism of the grating, as pointed out by Sirks, which is as follows. Let G, Fig. 87, be the position of the grating, s the slit, r the source or the reflecting prism, and O the observing eyepiece, placed normal to the grating, and at a fixed distance ρ from it, as in Rowland's mounting. Then

[1] *Astrophys. Journ.*, **2**. 370 (1895). [2] *Ibid.*, **3**. 46 (1896).

the slit must lie always on the circle $Os''ss'$ of radius $\frac{\rho}{2}$, while the source r lies at the intersection of Gs produced and the line Or, drawn at right angles to GO.

Then $$Gs = 2GQ \cos i = \rho \cos i$$

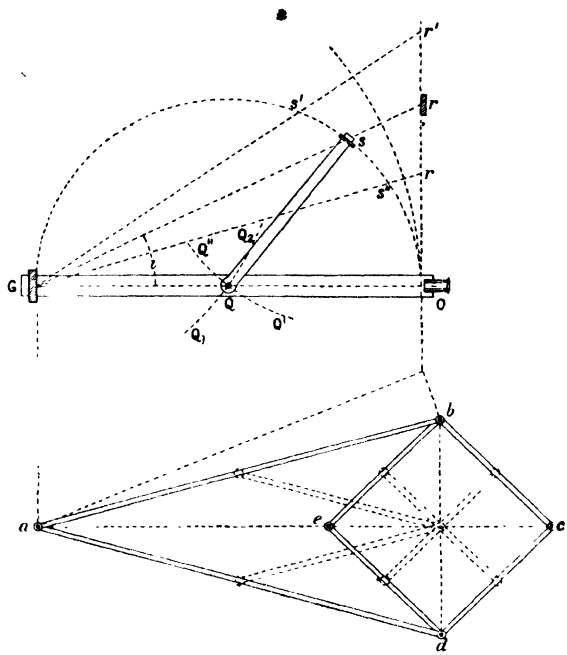


FIG. 87.

and $$Gr = \frac{\rho}{\cos i}, \text{ or } sr = Gr - Gs = \frac{\rho}{\cos i} - \rho \cos i.$$

To satisfy these conditions it is necessary to mount the slit on the end of an arm of length $\frac{\rho}{2}$, pivoted at Q, and also we must have from the geometry of the circle $Gs \times Gr = (GO)^2 = \rho^2 =$ constant.

This can be obtained by means of the Peaucellier linkage

shown in Fig. 87 ; in it we have $ae \times ac = ab^2 - be^2$, which, to satisfy the above condition, must equal ρ^2.

Hence, if we place the source or comparison prism at C, and pivot the vertices e and a to the ends s and G of the links Qs and QG respectively, the desired conditions will be obtained, and we will have the simple mountings shown in Fig. 88. We may either fix the pivot at G, the pivot at s, or the pivot at r in position. If G is fixed, Q may also be fixed, in which case O also remains fixed ; but the slit and comparison prism r slide along the line Gsr, while this line itself rotates about the pivot G. A simpler arrangement, therefore, is obtained by fixing either the pivot s or the pivot r, leaving

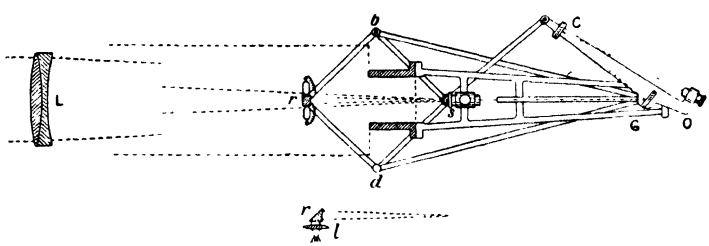


FIG. 88.

Q free. Then the grating and comparison prism, or the grating and slit, slide along the bar Gsr, which remains fixed, and the point Q describes a curve Q′QQ″ (if s is fixed) or Q_1QQ_2 (if r is fixed), whose centres at any instant are at G and s. The eyepiece O will, therefore, describe a similar curve of twice the radius about G as a centre, and, in order to avoid this large range of motion, as well as the long arm GO, we may place a reflecting plane mirror at C (Fig. 88), and return the rays to an eyepiece O near G. In Fig. 88 the slit is fixed at s, so that the comparison prism at r and the grating move ; in the diagram a vacuum tube is shown at r as a comparison source.

A very advantageous method of mounting the concave grating has been devised by Eagle.[1] The mounting is of the Littrow auto-collimating type similar to that used for the plane

[1] *Astrophys. Journ.*, **31**. 120 (1910).

grating, except that no lens is used. This method of mounting has the advantages of occupying a very small space, and being about half the cost of the Rowland mounting. Furthermore, spectra on either side of the normal may be used with equal facility, and higher orders can also be obtained. The definition obtained by it is, if anything, better than that obtained in the Rowland mounting, and also greater brilliancy gained, especially in the higher orders, owing to the fact that the astigmatism is much reduced. On the other hand, the instrument does not remain in automatic focus, but this difficulty is not serious, since the focussing of the instrument for any particular region is a perfectly simple matter. Although the spectrum obtained with this mounting is not quite normal, the deviation is sufficiently small to make it generally practicable to employ a simple linear interpolation formula, and to draw a curve of errors. It will be remembered that such a curve is always to be recommended, even in the case of the Rowland mounting. Finally, owing to the small space occupied, it is easy to have the surrounding box covered with some non-conductor of heat so that the temperature may be kept constant during long exposures.

The Adjustment of the Concave Grating.—Ames[1] gives the following directions for the adjustments of the various parts of the apparatus. First, the two beams are made as level as possible, and placed at right angles by the 3, 4, 5 rule. Distances from the intersection of the rails proportional to 3 and 4 are accurately marked out on the two beams respectively, and the beams adjusted until the distance between the two points thus found is proportional to 5. Next, the axes at the ends of the girder must be made parallel, while the girder is under stress; for this purpose the girder is supported at its two ends, and the axis adjusted by the control screws until the axes are vertical. The camera, grating, and slit are now put into position at the proper height, care being taken that the grating is so placed that the brightest spectra are observed, for, as was pointed out before, the spectra obtained with a grating are generally brighter on one side than on the other. A candle

[1] *Phil. Mag.* (5), **27**. 369 (1889).

is held at the centre of the camera-box, immediately over the axis of the carriage, and the grating is turned, and the girder lengthened, until the flame and its image coincide. In this way the grating is placed perpendicularly to the girder, and the girder itself is given the proper length. To adjust the camera so that it is perpendicular to the girder, a piece of plate glass is fastened to its face, and a candle is held on the girder near the grating. The camera is then turned until the flame and its image come into line. Light from some source is now thrown on to the slit so as to illuminate the whole grating, and the spectrum is observed at the camera, and, if necessary, the grating is tilted more or less until the spectrum is seen in the middle of the camera. The girder is then moved about, and if the spectrum thereby tends to rise or fall, the grating is revolved in its own plane by the side screw of its holder (S', Fig. 75) until this is corrected. Finally, the slit is revolved until the best definition is secured. The instrument should now be in perfect adjustment, which may be tested as follows: an exposed and developed photographic plate, of which the emulsion has been partly scraped off so as to give it a lattice-work appearance, is put in the camera-box, emulsion side towards the grating. The spectrum is then observed with an eyepiece, and at any position of the girder the emulsion on the plate and the spectrum ought always to be in the same focus Generally, however, this will not be the case, and from the theory of errors developed in the earlier part of his paper, Ames recommends a slight adjustment of the grating around its vertical axis, for this generally corrects the above defect.

Kayser[1] gives a rather more detailed account of the methods of adjustment which he has himself employed, and which may be quoted here.

In the first place, he considers Ames's 3, 4, 5 rule to be insufficiently accurate, and recommends the use of a theodolite placed exactly over the intersection of the rails; he then adjusts the beams until the angle measured between them is exactly equal to 90°. For the adjustment of the grating and camera over the axes of their carriages, small pointed metal

[1] *Handbuch der Spectroscopie*, i. 475.

pins are fitted exactly in the centre of the axes, holes having been bored in the centres when the axes were first made. By means of a plumb-line the surface of the grating and the emulsion of a plate in the camera are brought over these points. Kayser also gives a more accurate method for the adjustment of the length of the girder and the position of the grating. An exposed and developed plate is taken, and about 1 cm. from the middle a cross is cut in the emulsion, and exactly the same distance on the other side of the centre a portion of the emulsion is scraped off, and some scratches made on the glass, with a diamond. The plate is then put in position in the camera, and a small totally reflecting prism is fastened with soft wax to the outside of the plate behind the cross. A beam of light from a side source is thrown through the cross on to the grating, and, if the adjustments are correct, the image of the cross should be focussed on the clear glass, and thus the scratches and the image of the cross should be seen together in perfect focus through an eyepiece. The grating must be turned and the length of the girder altered until this condition is secured.

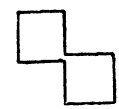


FIG. 89.

A convenient method for the testing of the adjustments is to cover the grating with a diaphragm shaped as in Fig. 89, which leaves two opposite quarters exposed. Clearly these portions of the grating will give a continuous line if the adjustments be correct, and two slightly displaced lines if they be not correct; in the latter case, from the positions of these displaced lines, the amount of error in the focus may be calculated.

Practical Use of the Concave Grating.—From what has already been stated under the theory of the grating in the last chapter, it is necessary, if the instrument is required for accurate work based on the overlapping of the spectra, that the grating be carefully examined with respect to the distribution of the light in the various orders; for it is quite possible for a grating to give an incomplete spectrum in a given order, for example, the visible portion may be very bright, and the ultra-violet very weak. Further, as pointed out by Ames,

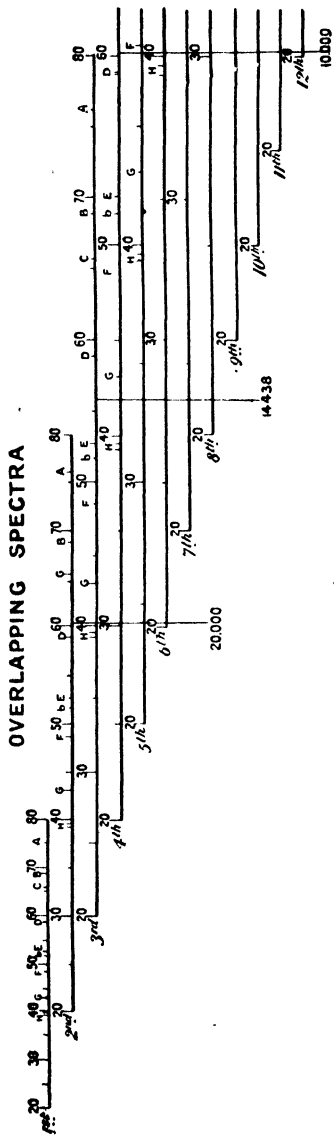


FIG. 90.

different portions of the grating may give spectra of varying brightness, and these imperfections must be guarded against for accurate work.

As regards choice of grating, it is only when work is to be done with the camera in the ultra-violet that it becomes necessary to use a 20,000 line grating, and as, further, a 10,000 line instrument has the advantage in point of definition and cheapness, therefore, for ordinary work the latter or a 14,438 line should be chosen. The practical ranges of the various-sized gratings were given before on p. 187, but they may be given more fully here. Fig. 90 is a diagram of the overlapping spectra as obtained with the various instruments. The extent of the first five spectra reached is given in the following table :—

Lines per inch.	First spectrum.	Second spectrum.	Third spectrum.	Fourth spectrum.	Fifth spectrum.
10,000	Entire	Entire	Entire	To 6000	To 4800
14,438	Entire	Entire	To 5760	,, 4330	,, 3460
20,000	Entire	To 6000	,, 4000	,, 3000	,, 2400

These limits are taken at the centre of the photographic plate. At the end of the plate, of course, the limit is somewhat greater. With a grating of 21·5 feet radius, the width of the spectrum varies from $\frac{1}{4}$ inch to 4 inches.[1]

The scales may readily be calculated from the formulæ on p. 187, and for the largest size grating of 650 cm. focus they are given by Ames as follows:—

Lines per inch.	First order.	Second order.	Third order.	Fourth order.
10,000	0·26	0·51	0·77	1·03
14,438	0·37	0·75	1·12	1·50
20,000	0·52	1·03	1·55	2·07

The numbers given for the various orders represent the linear distance in millimetres on the photographic plate, corresponding to a change of wave-length of one Ångström unit—this being, of course, at the centre of curvature of the grating. For gratings of shorter radii these numbers are simply to be multiplied by the ratio of the radii.

When in observing a particular spectrum it is required to cut off the overlapping spectra, certain absorbing media may be used, these being placed, of course, between the slit and the light source. The following are recommended by Ames, and the regions of spectra given are those transmitted by the absorbents.

[1] See p. 188.

Greenish plate glass	3300–8000
Saturated solution of salicylic acid in alcohol in quartz cell	3500–8000
Aesculin, 0·25 per cent. aqueous solution with one drop of ammonia to each 30 cc.	4100–8000

This must be freshly prepared, as it rapidly oxidises to a brown colour.

Potassium ferrocyanide	4400–8000
Primrose or aniline yellow	5000–8000
Fluorescein or gold chloride	5200–8000
Chrome alum, Malachite green, *Bitter almond green, Brilliant green	3200–3700 and 4600–5200
Cobalt chloride	3400–4500
Gentian violet, strong	3600–4600 and 6000–8000
Potassium permanganate	3900–4600 and 5800–8000

As an example, when photographing in the fourth order with a 10,000 line grating, the following absorbing solutions are used:—

At 3800 Cobalt chloride in water.
„ 4000 Cobalt chloride or Gentian violet in water in a glass cell.
„ 4200 Potassium permanganate or Gentian violet in water.
„ 4400 Aesculin or Potassium permanganate.
„ 4600 Aesculin.
„ 4800 Aesculin and Malachite green in water.
„ 5000 Aesculin and Potassium ferrocyanide.
„ 5200 Aesculin and Potassium ferrocyanide.
„ 5400 Aesculin and Primrose.

It is advisable that before the use of any absorbent an experimental photograph should be taken in order to observe its effect.

For regions beyond the C line and into the infra-red, special absorbents are required, and amongst others the following may be mentioned as having been used by Abney—a solution of potassium bichromate, or a solution of iodine in carbon bisulphide.

Wood[1] has discovered that nitrosodimethylaniline, when in thin layers, has an absorption band between the limits $\lambda = 5000$ and $\lambda = 3900$, but beyond the latter it is transparent to as far as $\lambda = 2000$. This substance may be used, therefore, in order to photograph the ultra-violet spectra free from overlapping higher orders. For this purpose a gelatine film, stained with the nitroso body, is fairly suitable, but a better way is to make a solution in glycerine, and use it in a quartz cell; as the glycerine is acted upon by ultra-violet light, Wood recommends the use of a small quartz cell, made by cementing two quartz plates together with a space between of 0·5 mm. This cell should be cemented to the bottom of a thistle funnel with a very small bore. By filling the thistle funnel with the glycerine solution, a flow takes place through the cell at the rate of about a drop every two minutes. The exposure must be much increased when using the screen, and varies from two to twenty times the ordinary, according to the density of the screen. In the case of weak spectra, the increased time of exposure rather precludes the use of this substance, and under these circumstances it is necessary to take comparison photographs for the purpose of recognising the ultra-violet lines. Two photographs are taken—one of the complete overlapping spectra, and the other with the ultra-violet portion cut off by means of suitable absorbents; the lines present in the first photograph and absent in the second are the ultra-violet lines.

On account of the astigmatism of the concave grating, the usual method of comparing spectra by throwing the images of the two sources adjacent to one another on the slit is not possible, as the two spectra will overlap so considerably. Rowland's method is to employ the mechanical device described

[1] *Phil. Mag.* (6), **5**. 257 (1903).

on p. 212, which consists of a metal plate with a horizontal slot cut in it exactly equal to the width of the plate (Fig. 77). When in use this plate is turned to a vertical position, and a photograph taken of the spectrum from some source through the slot; the plate is then turned through 90° to a horizontal position, and the comparison spectrum photographed. When the plate is developed, it will be found to have the comparison spectrum with a narrow band of the first spectrum along its centre. In case of any possible movement of the camera during the process, the first spectrum is usually given half the correct exposure, then the second is taken, and finally the first again to complete its exposure; in this way any chance movement of the camera will be detected.[1]

Measurement of Wave-length by means of the Concave Grating.—As has already been explained, the concave grating can be employed for the determination of wave-lengths with great accuracy in relation to a chosen standard by Rowland's method of coincidences, which is based upon the simple relation between the overlapping orders and the normality of the spectra observed.

The standard adopted by Rowland was the value for the D_1 line taken by him as a weighted mean of Bell's and other measurements.

In the following table are given the values of the coincidences between this line and points in different orders. The table reads downwards—that is to say, the vertical columns give the coincidences:—

Order	1	5896·156			
„	2	2948·078	5896·156		
„	3	1965·385	3930·771	5896·156	
„	4		2948·078	4422·117	5896·156
„	5		2358·462	3537·694	4716·925
„	6		1965·385	2948·078	3930·771
„	7			2526·924	3369·232
„	8			2211·059	2948·078
„	9			1965·385	2620·514
„	10				2358·462

The table, therefore, shows that on the D_1 line in the first

[1] *Vide* p. 240.

order are superposed 2948·078 in the second order, and 1965·385 in the third; and again on D_1 in the third order are superposed 4422·117 in the fourth, 3537·694 in the fifth, and so on.

The method of working is as follows: photographs are taken of the D_1 line in as many orders as the grating allows; in the case of the 20,000 line grating, this can only be done in the first two orders, but with a 10,000 grating, D_1 can be photographed in the first four orders. Care is taken that the D_1 line is approximately in the centre of the plate. On each side of the D_1 line on the photographs will be found a number of lines in different orders, and if the orders to which these lines belong be found by the use of absorbents, then their wave-lengths may be approximately obtained by measuring their distance from the D_1 line on the plate, and by calculation from the scale of the instrument. Ames's values of these scales were given above; it must, of course, be remembered that these can only be quite approximate, and that therefore the wave-lengths we have obtained from our measurements can only be correct to a first approximation.

After this has been done these new lines are again all photographed in different orders from before, in such a way that two, at least, of them are obtained on every plate within the range of normality. The distance between them is measured on the new plates, and from the approximate wave-lengths found in the first place more accurate values are obtained of the scale of the instrument. This more accurate scale value is used for a recalculation of the wave-lengths of the chosen lines on the first plates to a second and closer approximation. With these new values the scale of the instrument is again calculated from the second set of plates, and so on until the limit of accuracy is reached. This limit is of the order of 0·003 A.U., with the best apparatus, and this Kayser considered to be the mean error of his wave-lengths of the principal lines in the arc spectrum of iron.

An accurate value of the scale of the instrument may be obtained by measuring the whole distance from D_1 in the first

order to D_1 in the second order. For this purpose a complete series of photographs are taken of the normal spectrum from end to end, and the linear distance between these two lines measured, working from plate to plate. The change in wave-length between the two lines is, of course, 5896·156 A.U. in the first order, and from this the scale may be obtained. Lines between the two may be measured, and their wave-lengths found, from which the scale may be checked from plates containing more than one of these lines, as described above.

Rowland,[1] in his work on the solar spectrum, determined—

1. The wave-lengths of fourteen lines in the visible spectrum by measurements with a travelling micrometer eyepiece, and these were used as primary standards.

2. The solar standards were measured from one end of the spectrum to the other many times, and a curve of error drawn to correct these primary standards.

3. Flat gratings were also used.

4. Measurements of photographs were made which had upon them two portions of the solar spectrum of different orders. The blue, violet, and ultra-violet spectra were compared with the visible portion, giving many checks on the first series of standards.

5. Measurements were made on photographic plates having the solar spectrum in coincidence with metallic spectra; often of three orders giving the relative wave-lengths of three parts of the spectrum.

Often the same line in the ultra-violet had its wave-length determined by two different routes back to two different lines in the visible spectrum. The agreement of these in nearly every case to 0·01 A.U. showed the accuracy of the work.

6. Finally the important lines had from ten to twenty measurements on them connecting them with their neighbours, and many points in the spectrum both visible and invisible; and the mean values bound the whole system together so intimately that no changes could be made in any part without changing the whole.

Rowland expresses the accuracy of his map as follows:—

[1] *Phil. Mag.* (5), **36**. 49 (1893).

distribute less than 0·01 A.U. properly throughout the table as a correction, and it will become perfect within the limits 2400 and 7000 A.U.

Roland's wave-lengths are given, as measured in air, at 20° C. and 760 mm. pressure. As regards the influence of change of atmospheric conditions on the accuracy of the above method, it can readily be shown from Kayser and Runge's[1] values for the refractive indices of air that, within the limits of 15–25° C. and 740–780 mm. pressure, the errors produced lie within the greatest experimental accuracy, and may therefore be neglected.

As has been stated elsewhere (pp. 48 and 348) this method of coincidences has been proved by Kayser to be unreliable, and hence it cannot any longer be looked upon as being accurate enough for good work. There have been put on record standard spectra which have been measured with the greatest possible accuracy, and the measurement of unknown wave-lengths resolves itself into a comparison between known and unknown, very similarly to the method already described for prismatic apparatus, only with much greater accuracy. For this purpose comparison photographs are taken of the standard and unknown spectrum upon the same plates, and from the measurements of these plates the new wave-lengths can be found with very great accuracy. For work with gratings, either the solar spectrum may be used or the arc spectrum of iron. The latter is to be recommended for several reasons: in the first place, for the solar spectrum, one is dependent entirely upon meteorological conditions, which at times are by no means favourable to the experimenter; in the second place, in order to use the sunshine when it is available, it is necessary that the grating be so erected as to be able to receive the rays; in the third place, the lines in the solar spectrum are not necessarily sharp on account of changes in the solar atmosphere; and finally, account must be taken of the varying relative motion of the sun and earth. For these reasons the iron arc spectrum is to be recommended in

[1] *Ann. der Phys.*, **50**. 293 (1893).

most cases as the standard.[1] The wave-lengths of a few of the lines in this spectrum as determined by Fabry and Buisson on the new International Scale are given in Chapter IX., p. 351. Kayser has also published a list of these wave-lengths as tertiary standards (see p. 49); these last only extend from $\lambda = 6494$ to $\lambda = 4198$.

In order to obtain the comparison photographs, it is to be recommended that the two spectra, known and unknown, be perfectly superposed upon one another to ensure the greatest possible accuracy. This is simple enough when arc spectra are to be measured, because one pole of the arc is then made of iron, and the other pole of the substance whose spectra is to be measured. When the spectrum of this compound arc is photographed, it stands to reason that the two sets of lines are correctly placed with regard to one another. In the case of other types of spectra, such as those of rarefied gases, the two spectra must be photographed separately, and in this case great care must be exercised in order to obtain the relative position quite correct. The chief point to be secured is that the whole of the grating be illuminated with the incident light, and for this purpose a condensing lens should be used to focus an image of the light source upon the slit.

The following method of procedure may be adopted. The iron arc is first put in such a position that the condensing lens (which must, of course, be made of quartz) can focus an image of it upon the slit. The slit is now opened and the lens taken away; then the arc is moved from side to side until it is found that the grating is illuminated in the centre. This is readily enough seen by looking through the camera at the grating with the naked eye, standing far enough back to focus the narrow spectrum produced. The slit is then closed to the working width, and the lens put in place, so as to focus an image of the arc on to the slit; it is then securely clamped in position. A plate is then put in the dark slide, and the latter fixed in position to the camera back, and a photograph taken. When the correct exposure has been given, without disturbing any part of the grating mounting, the arc is moved, and the

[1] See Chapter XVII., on Doppler's Principle.

second source of light put in place, so that its image is focussed on nearly the same part of the slit as was the image of the arc before, this being done without moving the condensing lens. The exposure of this spectrum is thus started, and when finished the plate will carry the two photographs quite correctly superposed, provided no shifting of the camera took place during the process. If due care be taken, there will be no need to expect this, but it is better that the unknown spectrum contain some lines whose wave-lengths are well known, to serve as a check against any possible shifting of the apparatus; if the wave-lengths of these lines found from the measurements of the photographs agree with the known values, then the relation between the spectra may be assumed to be quite accurate.

The temperature is an important factor in an accurate comparison between two spectra. A change of temperature can easily produce a serious error, owing more particularly to the expansion or contraction of the grating, and the consequent change in the grating space. It is absolutely necessary that the temperature be kept constant during the exposures, for the errors that may creep in are surprisingly large. The change in the wave-length is proportional to the change in the grating space produced by the temperature variation. For we have $\frac{d\lambda}{\lambda} = \frac{db}{b}$, where b is the grating space. Now $\frac{db}{b}$ is about 0·00002 for a change of 1° C., hence, in the first order, when $\lambda = 5000$, $d\lambda = 0{\cdot}1$ Ångström. Since a full-sized Rowland grating with 14,438 lines to the inch will resolve spectrum lines 0·13 Ångström apart, so a temperature change of 1° C. will make it impossible to resolve lines less than 0·23 Ångström apart. In the second order the variation in the position of the lines will be twice as great, and such a creep of the lines during the exposure will make any accurate measurements impossible even in the first order.

The photographs of the mixed spectra are then compared with plates previously taken of the same region of the iron arc spectrum, and of the unknown spectrum separately; in this way the unknown lines are picked out and marked, and also the standard iron lines, which are also marked. It is only necessary,

of course, to mark those iron lines which appear in the list of standards. It will be found a great convenience to rule a fine straight line with a needle along the whole photograph through the centre of the spectrum. Where the various lines, which have been picked out, cross this ruled line, they are marked, the two kinds in distinctive ways, *e.g.* the standard iron lines may be denoted by a fine black ink mark, and the unknown lines by a similar red mark. This is simply for the purpose of recognising these lines when measuring the plate, for the field of view of the travelling micrometer is always very small, and unless the marks are made close to the part measured they will not be seen.

The photograph is now ready to be measured, which process is perfectly straightforward, all the wave-lengths being calculated by interpolation between two standard lines, one at each end of the plate. Two standard lines in the iron spectrum are chosen, one at each extreme end of the plate, and one of these is adjusted under the cross-wires in the eyepiece of the micrometer when set at zero reading. Care should be taken that one of the cross-wires be set parallel to the spectrum lines, and that the line, ruled on the plate along the spectrum, be set so that it is parallel to the direction of travel of the micrometer, and visible at the top or bottom of the field of view. The plate is then measured along to the standard line at the other end and the readings taken on all the marked lines are noted, care being taken, of course, to distinguish between the known and the unknown. If the travel of the micrometer is not sufficiently long to reach over the whole length of the plate, then, when the limit has been reached, the instrument is turned back to the zero mark, and the last line measured is readjusted under the cross-wires as before; this is repeated until the final standard line is reached.[1]

The wave-lengths of all the lines that have been measured are then calculated by simple proportion between the wave-lengths of the two extreme standard lines, and the numbers obtained for the iron lines are compared with the standard

[1] It is necessary to guard against backlash or the screw of the micrometer: see p. 155.

values, and the differences between them noted. A curve of errors is then drawn, in which the ordinates mark the scale of errors and the abscissæ the wave-lengths. From this curve the corrections to be applied to the new wave-lengths may be read off, and these values duly corrected. By the drawing of this curve the following sources of error are corrected for; first, possible errors in the screw of the travelling micrometer; second, the errors arising from the fact that the whole of the spectrum is not normal; third, errors in the values of the wave-lengths of the standard lines; and lastly, constant errors in reading. In order to make the curve as accurate as possible, as many standard lines as possible should be measured; it may be noted, that if lines are measured in different orders, the errors should be reduced in proportion to the orders dealt with.[1] There remain, over and above these errors, chance errors of reading the position of the unknown lines; it stands to reason that these can only be guarded against by repeated measurements, preferably on different plates.

Perhaps the whole method of working would be made clearer by an imaginary example. Let us suppose that we have the spectrum of a gas to measure, and that our plates are 12 inches long, and that we are working with a 10-foot grating ruled at the rate of 14,438 lines to the inch. Each photograph will have a range of 750 A.U. in the second order, allowing for a little overlap. Four photographs of the following regions in the second order are taken of the iron arc spectrum, and the gas spectrum superposed—

1. $\lambda = 5900$ to $\lambda = 5150$
2. $\lambda = 5150$ to $\lambda = 4400$
3. $\lambda = 4400$ to $\lambda = 3650$
4. $\lambda = 3650$ to $\lambda = 2900$

It is clear that on the first three plates the following regions of the third order are also superposed:—

[1] In drawing this curve the lie of the points as regards the curve will give a very good idea of the general accuracy of reading; the closer they are situated to the curve when drawn, the greater the reliance that may be placed upon the readings of the unknown lines.

1. $\lambda = 3933$ to $\lambda = 3433$
2. $\lambda = 3433$ to $\lambda = 2933$
3. $\lambda = 2933$ to $\lambda = 2433$

On the fourth plate the third order may be discounted, as it has become very non-actinic. On the fourth plate, however, the first order is superposed from $\lambda = 7300$ to $\lambda = 5800$. These plates, therefore, contain the complete spectrum from $\lambda = 7300$ to $\lambda = 2430$. The above regions have been chosen simply with a view of showing how the superposition of orders may be made use of in dealing with the spectrum of a substance. Some of the lines in the above case would be measured only in the first order, and some in both the second and third orders, so that the probable accuracy of working would be by no means evenly distributed. This, however, does not invalidate the above as an example of the method.

A second set of plates are next taken of the same regions of the gas spectrum alone, without the superposition of the standard iron spectrum. A third set are lastly taken in the same places of the gas spectrum, using absorbing media to separate the different orders. Nos. 1 and 2 are taken through aesculin solution, which cuts off the third order; No. 3 is taken through glass, which also will remove the third order. In the case of No. 4, aesculin is again used, which only allows the first order to pass.

The three sets of photographs are dealt with as follows: On the first set the wave-lengths of as many lines as possible are measured, and calculated as directed above. These measurements and calculations are quite independent of the order to which the lines may belong, and we may consider as a hypothesis that they are all calculated out as if they belonged to the second order. The second set of plates are then measured, and the wave-lengths of all the lines calculated by proportional parts, as before, between two lines, one at each end of the plate, using the wave-lengths of these as determined on the first set of plates. A curve of errors is then drawn as described above, using the wave-lengths as determined on the first set of plates. In this way the wave-lengths of some

lines, which on the first plates were hidden behind iron lines, are measured, and further, some corrections may be found necessary in the case of the other lines. We now have all the lines measured and calculated out as if they belonged *in toto* to the second order. The second and third order plates are now compared, whereby the lines are sorted into their respective orders; the wave-lengths of the lines in the first and third orders are obtained by multiplying their hypothetical values in the second order by 2 and by $\frac{2}{3}$ respectively. It will be seen on reference to the extent of the plates in the different orders, that certains regions have been photographed in two orders, viz. $\lambda = 3933$ to $\lambda = 2900$ in the second and third orders, and $\lambda = 5900$ to $\lambda = 5800$ in the first and second orders. The values obtained for each line in the two orders should, of course, agree; in actual practice these determinations of the wave-lengths of the same line in different orders form a most valuable check upon the accuracy of the work.

Attention may again be drawn to the fact that the above is only given as an instance of the methods of work; one objection may be at once urged, namely, that as all three sets of plates are taken at the same places, certain lines are only measured at the ends of the plates, where the spectrum is not normal. But in actual work, if high accuracy were aimed at, many additional plates would be taken at different places from those given above, in order to measure as many lines as possible in at least two orders. Again, no mention is made of contamination by the fourth order in plates 1 and 2; with an average grating, as one gets into the higher orders the illumination falls off rapidly, so that it is unlikely that they would have any disturbing effect in the case of a faint spectrum such as that of a gas. In the case of the grating at University College, London, the fourth order is extremely weak. An important point also to remember in connection with this work with gratings, is that the wave-lengths of the important lines are determined in as many orders as possible, and it is in the searching for these lines in the higher orders that shows whether contamination from them is to be expected. If, for example, lines of intensity 10 were just visible in the fourth

order, and those of intensity 9 were not, it is evident that the wave-lengths of the strongest lines could be measured in the fourth order, and that no further contamination need be looked for.

Owing to the fact that the coincidences are not accurate, the above method must be modified to a certain extent. The important point to be remembered in any interpolation work is that where great accuracy is aimed at no interpolation is to be depended upon when made between lines in different orders. The essential difficulty at the present moment is that while the coincidence method has been shown to be untrustworthy, a complete set of closely situated standards throughout the whole spectrum on the new International Scale has not yet been published. Kayser's new iron arc wave-lengths only extend from $\lambda = 6494$ to $\lambda = 4118$, while, though they reach $\lambda = 2373$, Fabry and Buisson's values still show some rather large gaps in certain places.

CHAPTER VIII

THE EXTREME INFRA-RED AND ULTRA-VIOLET REGIONS OF THE SPECTRUM

As was described in Chapter II., the existence of the infra-red region was discovered by Sir W. Herschel in 1800, who, in testing the heating power of the different colours of the spectrum by placing a very sensitive thermometer in the path of the various rays, found that the heat intensity increased towards the red end, and finally reached a maximum at a point some distance beyond the end of the visible portion. It was Ampère, in 1835, who first concluded that these heat rays were of the same nature as the light rays in the visible portion of the spectrum, that they were both due to waves in the same medium, and only differed from one another in their wave-length. In 1840 Sir J. Herschel succeeded in proving the existence of Fraunhofer lines in this region of the solar spectrum, by projecting it upon a strip of dull black paper, moistened with alcohol. Had the spectrum been perfectly continuous, it is evident that the increase of temperature produced by the rays would have caused the alcohol to evaporate equally from those portions of the paper covered by the heat spectrum. In actual fact he found that this was not the case, but that damp spots were left in places, which fact clearly pointed to the existence of absorption bands in the solar spectrum.

In 1880[1] Abney published a map of the infra-red region of the solar spectrum from $\lambda = 7160$ to $\lambda = 10{,}000$ Ångström units, which he had obtained by photographic processes, with the help of gratings and prisms. The complete description of the method Abney employed in the preparation of the photographic plates sensitive to this region will be given at length in Chapter XI.; suffice it, therefore, to say here that the ordinary

[1] *Phil. Trans.*, 171. I, 653 (1880); and also 177. A, 457 (1886).

silver bromide emulsion appears red by transmitted light, and is, therefore, readily absorbent of the blue rays. Abney succeeded in the preparation of an emulsion which was blue by transmitted light, and which, therefore, absorbed the red rays. He found that such emulsions were sensitive to as far as wave-lengths of 20,000 A.U. The process of preparing the plates for this work is very troublesome, and as they very soon lose their sensitiveness to the red rays, this method of investigation has found very little application since the brilliant work of Abney himself. At the present time there are known methods of dyeing photographic plates in order to render them sensitive to the red end of the spectrum, and, indeed, there are upon the market certain brands of plates especially made for work in this region. Under certain circumstances it is possible to reach $\lambda = 9000$ A.U. by means of such plates. By use of what is known as the phosphoro-photographic method (see p. 373), it has been found possible to obtain photographic records of emission spectra to as far as $\lambda = 20{,}000$ A.U.

With the exception of the photographic methods, it may be said that all the modern instruments of measurement in this region depend upon the heat action of the rays. By means of the modern apparatus it has been found possible to penetrate an extraordinary distance into the infra-red region of emission spectra, and to detect radiations with a wave-length of 314μ (0·314 mm.). It may be said that the work in this region has been carried out in three directions; we have, first, the extension of the solar spectrum and the measurements of the wave-lengths of the Fraunhofer lines; secondly, the determination of the wave-lengths and indices of refraction of various media for rays of very long wave-length; and thirdly, the determination of the distribution of energy in the spectrum of an absolutely black body.

Without entering fully into the historical development of the methods of work, it is necessary to treat shortly of the means employed to determine the position which a particular ray occupies in this region—that is to say, the means employed to calibrate this region in terms of wave-lengths. In the case of a grating being used as the dispersing apparatus, then the

angles of diffraction give at once the wave-lengths, but when prisms are used one has no guide whatever towards the wave-length determination, for it is clearly impossible to extrapolate on a dispersion formula. In the latter case interference bands have been used, by counting which one can readily tell how far one is progressing into the unknown region. These were first made use of by Fizeau and Foucault[1] in 1847. Mouton, in 1879, published an account of some measurements of the wave-lengths of the long heat rays, in which he employed these interference bands. These bands were produced in the following way.[2] A quartz plate, cut parallel to its optic axis, is put between two Nicol prisms and perpendicular to the path of the light; the principal section of the quartz plate makes, therefore, an angle of 45° with the principal sections of the Nicols. Under these circumstances two interfering components are obtained, with a difference of phase which is equal to $\frac{e(\mu_e - \mu_0)}{\lambda}$ where e is the thickness of the plate, μ_e and μ_0 the indices of the extraordinary and the ordinary rays respectively, and λ the wave-length. When this expression equals $\frac{2k+1}{2}$, k being some whole number, then a black band will be produced. As k represents the order number of the fringe, it is only necessary to know it for one fringe, when it will be known for all, as it changes by one from fringe to fringe. From the above relation the wave-length corresponding to any band can be found from the equation—

$$\lambda = \frac{2e(\mu_e - \mu_0)}{2k+1}$$

if e, k and the indices of refraction are known.

It is clearly impossible to measure e by ordinary methods, and it is, therefore, necessary to use optical means. This Mouton effected by allowing the light from the last Nicol to fall upon the slit of a spectrometer provided with a grating, and by measuring the deviations produced for two bands, and from his knowledge of the wave-lengths corresponding, he was

[1] *Comptes Rendus*, **25**. 447 (1847). [2] *Ann. Chim. Phys.* (5), **18**. 145 (1879).

able to calculate the values of e and k. In order to do this it was necessary to know the values of $\mu_e - \mu_0$ for the wave-lengths dealt with; these were obtained from an interpolation formula derived from the well-known Cauchy dispersion formula—

$$\mu_e - \mu_0 = \alpha + \frac{\beta}{\lambda^2}, \text{ where } \alpha = 0{\cdot}0088205 \text{ and } \beta = 0{\cdot}0001093.$$

These constants were obtained from observations in the visible region, and cannot be used for extrapolation into the infra-red. When the values of e and k had been obtained, it became simply necessary to measure $\mu_e - \mu_0$ for the interference bands in the infra-red, from which the wave-lengths corresponding could be obtained at once. This Mouton carried out by means of an ordinary spectrometer, provided with a Thollon

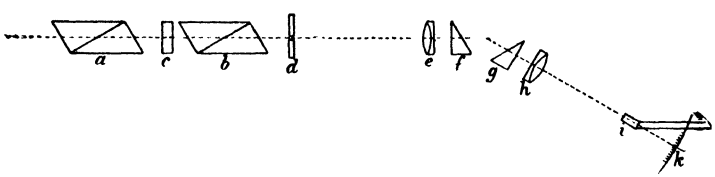


FIG. 91.

prism pair; a diagram of his apparatus is shown in Fig. 91. a and b are the two Nicols, and c the quartz plate; d is the slit of the spectrometer, f and g the prism pair, and i a delicate thermopile placed in the focus of the telescope lens. By means of the thermopile the positions of the black interference, or "cold," bands in the heat spectrum are detected. The rest of the apparatus explains itself.

In 1881 was published the first notice of Professor S. P. Langley's bolometer,[1] which was an exceedingly great advance upon any of the apparatus which previously had been used. This apparatus, which Langley called the actinic balance or bolometer, consists of an electrical resistance thermometer—that is to say, an instrument which measures temperature in

[1] *Amer. Journ. Science* (3), **21**. 187 (1881); *Chem. News*, **43**. 6 (1881); *Ann. Chim. Phys.*, **24**. 275 (1881).

terms of the change of electrical resistance of a very fine strip of metal. The elementary theory of the instrument is as follows:—

The current from a battery divides itself at A (Fig. 92) into two portions, one of which passes through a long bent strip of metal at *a*, and the other through an exactly similar strip at *b*; they both join at B and return to the battery. Evidently if the resistance of the two arms be equal, equal quantities of current will travel along each, but if the resistance of one be greater, less current will flow along that arm, and, consequently, a certain amount will flow through the galvanometer G, an amount directly proportional to the difference of resistance between the two arms. If now *a* and *b* be made of exactly the same length of similar strip, then their resistance will be the same when at the same temperature; in actual

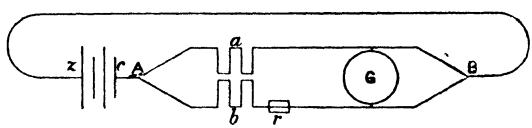


FIG. 92

practice this is often not absolutely secured, and a resistance box is introduced at *r*, to compensate for the slight difference in *a* and *b*, and also in the resistance of the two arms as a whole arising from slight differences in the two leading wires. Let us suppose now that the two strips *a* and *b* are at exactly the same temperature, and the resistance of the two arms absolutely equalised, then no current will flow through G; if, however, either *a* or *b* be heated, its resistance will at once increase, and the balance will be destroyed, with the result that the galvanometer needle will be deflected by an amount proportional to the difference in temperature between *a* and *b*. In practice *a* and *b* are both brought close together, so as to secure their both being affected equally by change of the room temperature; one alone is exposed to the radiation, the other being screened. The arrangement of the strips is diagrammatically shown in Fig. 93, there being an equal number of

strips in *a* and *b*, with half of those of *b* set on each side of

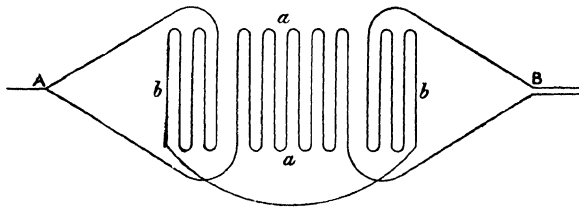


FIG. 93.

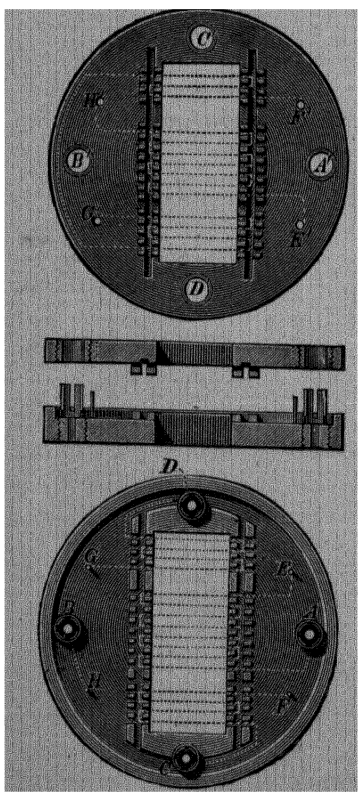


FIG. 94.

those of *a*. These strips, which are made of very thin steel or platinum, are arranged, according to the diagrams, upon ebonite frames, shown in Fig. 94, and these frames are mounted in a wooden or ebonite tube, as shown in Fig. 95 at B.

The arrangement of the strips upon the frames will be seen quite clearly from Fig. 94, where they are shown by the dotted lines. The central set of strips on each frame form one arm of the balance, and the outer sets form the other arm. The upper ebonite frame exactly fits upon the lower, and the strips upon each frame are so placed when the two discs are fitted together that those upon the one disc lie in the spaces between those upon the other disc. This arrangement is adopted in order to expose as much surface of the strips to the radiation as possible. The two discs fixed together are

mounted in an ebonite or wooden tube, as shown in B, Fig. 95. A screen, K, is mounted in the tube just in front of the discs, in order to protect the outer sets of strips from the radiation; diaphragms, as shown at SS, Fig. 95, are fixed to minimise the air currents inside the tube.

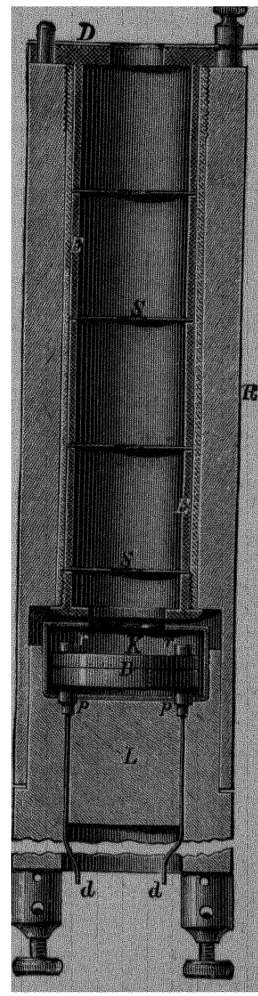


FIG. 95.

The apparatus shown in Figs. 94 and 95 is an old form; the design most recently employed by Langley is too complicated for reproduction on a small scale.[1] It may be pointed out that when the bolometer is in use a current of electricity is continually flowing through the arms, the amounts flowing through each arm being exactly balanced when at the same temperature.

The instrument described here is known as a surface bolometer—that is to say, one which exposes a considerable surface to the radiation; such an instrument is of no use for the measurement of spectrum lines. In this case the sets of strips as depicted above, are replaced each by one or more strips, mounted upon their edges so as to form a very narrow line, and expose as narrow a surface as possible to the radiation. The smaller the angular magnitude of the exposed strip, the more accurate will be the determinations of the position of spectrum lines. With the earlier forms of this apparatus Langley was able to measure a rise of temperature of 0·00001° C., and in his later apparatus he reached a

[1] *Annals of the Astrophysical Observatory, Washington*, vol. i.

sensitiveness of 0·000001° C. In the final form only one strip was exposed, which was 0·5 mm. broad and 0·002 mm. thick.

With these bolometers Langley investigated the heat spectrum of the sun, and at first measured the absorption caused by the earth's atmosphere. This was carried out by making observations with the sun high and low in the sky, and also by transporting the whole apparatus to a station on Mount Whitney, nearly 15,000 feet high.[1]

The first observations of the infra-red spectrum were made with the help of a flint glass prism as the dispersing apparatus, and a map of the new region was published,[2] in which the abscissæ were proportional to the deviations produced by the prism. In order to determine the wave-lengths of the absorption bands on this map the following device was adopted;[3] the rays from the sun were first diffracted by a grating and then refracted by a prism, and in this way the indices of refraction for rays of known wave-length were obtained; further, the prism served to separate the various superposed orders of spectra produced by the grating. A diagram of the apparatus is shown in Fig. 96. A beam of sunlight from a heliostat falls on to the concave mirror M, which focusses it upon the slit S_1 of a concave grating apparatus. This slit is protected from the great heat by a plate of iron, pierced with a hole, which is only a little larger than the slit. From the slit the rays fall upon the concave grating G, which focusses the spectral rays, as is known, on the dotted circle. At S_2, where the photographic plate, or eyepiece, is usually placed to observe the normal spectra, there is a second slit, which forms part of a prism spectrometer, of which the lenses are shown at L_1 and L_2, and the prism at P. The second lens focusses the image of S_2 upon the bolometer at B; the arm carrying the bolometer rotates round a centre under the prism, and there is an arrangement for always keeping the latter in the position of minimum deviation. The readings of the angle of deviation produced by the prism could be read accurately to 1′ of arc. The grating was one ruled by Rowland, with

[1] *Nature*, **26**. 314 (1882); *Brit. Ass. Rep.*, 1882, p. 459.
[2] *Phil. Mag.* (5), **15**. 153 (1883). [3] *Ibid.*, (5), **17**. 194 (1884).

18,050 lines, 142 to the millimetre, on a spherical mirror of 1·63 metres focus.

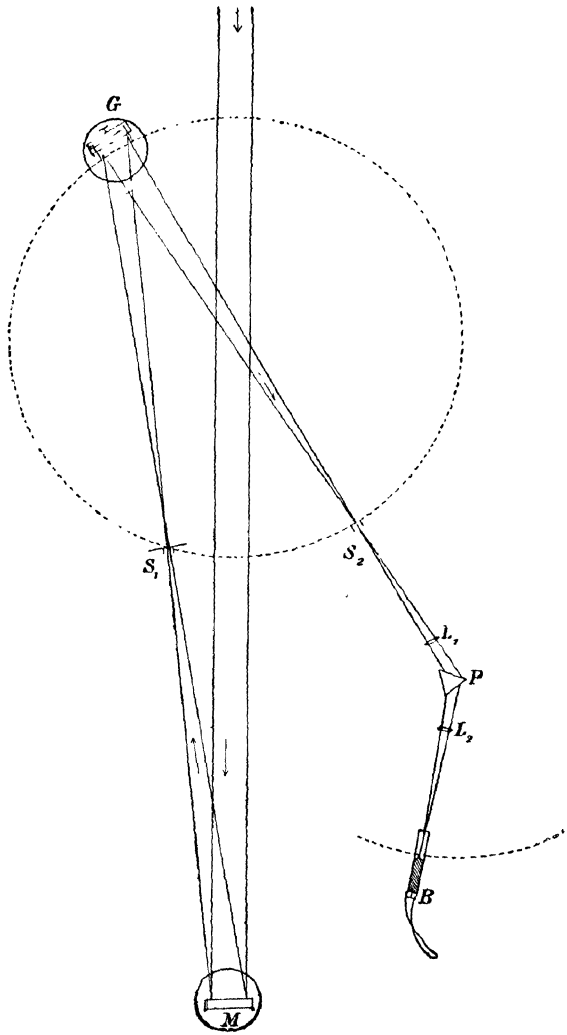


FIG. 96.

The method of experiment with the apparatus can be very shortly described, best in Langley's own words. "The apparatus having been previously adjusted, and the sunlight properly directed by the heliostat, the visible Fraunhofer line D_2 of the third spectrum of the grating was caused to fall upon the slit S_2 of the spectrobolometer. Then, according to the theory of the grating, there passed through this slit rays having the wave-lengths—

$0{\cdot}589\mu$, third spectrum,
$0{\cdot}888\mu$, second spectrum,[1]
$1{\cdot}767\mu$, first spectrum.

"The prism having been removed and the telescope brought into line, an image of S_2 was formed in the focus of the objective, and, on testing with the bolometer, the face of which was covered by a screen with a 2 mm. slit, a deviation of the galvanometer needle of 30 divisions was produced. The prism was then replaced, and then the angles of deviation were sought for the three rays. The first, *i.e.* D_2, gave a deviation of $47^\circ\ 41'$, and the third was found by turning the bolometer little by little about the position where the ray was expected, until the maximum heat effect was obtained. The slits were then narrowed in order to increase the accuracy of reading, and finally, the deviation for the ray $\lambda = 1{\cdot}767\mu$ was found to be $45^\circ\ 10'$. Proceeding in this way the deviations were obtained for several different rays, and a curve of dispersion constructed for the prism."

In a first investigation with this apparatus Langley carried his measurements to the limit $\lambda = 2{\cdot}03\mu$. After this work the apparatus was greatly improved in many ways; greater sensitiveness was obtained in the bolometer and galvanometer, and also the prisms and lenses were made of rocksalt, which eliminated the absorption exercised by the glass.

In a later investigation[2] upon the solar and lunar infra-red spectra, Langley found that the limit of the former was practically at $\lambda = 5\mu$, but that he was able to trace it to an

[1] In Langley's paper this is given as $1{\cdot}178\mu$ in error.
[2] *Phil. Mag.*, **26**. 505 (1888); and **29**. 31 (1890).

estimated limit of $\lambda = 18\mu$. It is probable that the heat energy in this part of the sun's spectrum is strongly absorbed by the atmosphere. In the moon's spectra the chief maximum lies between $13 - 14\mu$, and from these and other observations Langley estimates the temperature of the moon in sunshine to be not more than 0°.

In his final work upon the solar spectrum, Langley made use of a new apparatus;[1] the light from a 20-inch siderostat passed through the slit of a horizontal collimator, which possessed a lens of rocksalt 17 cms. clear aperture, and 10 metres focal length. This lens focussed the ray upon a prism or grating; the prism was of rock-salt, and was 18·5 cms. high and 13 cms. deep in the face, and had a refracting angle of 60°. The angular width of the bolometer thread was decreased to 2″ of arc by using a telescope lens of 5 metres focus; the sensitiveness was thereby increased, and by improvements in the galvanometer the apparatus was made capable of detecting a temperature change of 0·000001° C. The whole spectrometer was of the fixed-arm type, and the spectrum was made to pass over the bolometer strip by rotating the prism. An automatic self-registering method was adopted of recording the galvanometer readings. The spot of light reflected from the galvanometer mirror was focussed upon a broad strip of photographically sensitive paper. This paper strip was caused to move slowly in a vertical direction, and in this way a faithful record of the excursions of the light spot was obtained. At the same time the prism was slowly rotated, and, therefore, this record clearly showed all the temperature changes of the bolometer as the spectrum passed over it. Further, the motions of the sensitised paper and the prism were exactly co-ordinated, so that the angular position of the prism corresponding to any portion of the galvanometer record could at once be obtained. In this way, since the dispersion of the prism was already known, the wave-length of any spectrum line shown upon the record could be found, and also, from the length of the throw of the light spot its intensity estimated. The delicacy of this apparatus was sufficient to show the D lines widely separated, with the

[1] *Brit. Ass. Rep.*, 1894, p. 465; and *Nature*, 51. 12 (1894).

nickel line in between; a diagram of a portion of the bolograph record is shown in Fig. 97, which is reproduced with Professor Langley's permission from the *Annals of the Astrophysical Observatory, Washington.* By means of this apparatus Langley mapped the solar spectrum as far as $\lambda = 5{\cdot}5\mu$, and observed 700 lines between A and this limit.

Although for many years Langley was the only worker in this field, yet, before his final results were published, investigations had been begun and carried out by other experimenters, though not in the direction of the determination of the wavelengths of the Fraunhofer lines. One of these was by Carvallo, on the dispersion of fluorite, under the title of *Spectres Calorifiques*, carried out during 1893 and 1894.[1] The chief interest of this paper lies in the improvement he introduces into Mouton's method described above. Mouton's method depended upon the use of the black bands in the spectrum produced, according to Fizeau and Foucault, with two Nicols and a quartz plate in between them; these black bands served the same purpose as the Fraunhofer lines in the visible spectrum, the indices of refraction being measured for the points of minimum intensity of the black bands. Carvallo found fault with the use of these points of minimum intensity, because the change of intensity at these places is very slow, and therefore the setting of the thermopile or bolometer is a matter of some uncertainty. It is preferable to use the regions where the rate of intensity change is the greatest, *i.e.* halfway between the centre of a black band and the centre of a bright band. At these places the difference of phase between the interfering rays is equal to a whole number of waves $\pm \frac{\lambda}{4}$. If now ϕ be the difference of phase, the intensity i of the spectrum can be found from the equation $i = \mathrm{I} \cos^2 \pi\phi$, where I is the intensity of the incident light. If now either the analyser or the polariser be turned through 90°, so that they became crossed instead of parallel, as they were in Mouton's case, then the intensity is complementary to i, and may be found from $i' = \mathrm{I} \sin^2 \pi\phi$. Carvallo bases two methods of experiment upon this; in the

[1] *Ann. Chim. et Phys.* (7), 4. 5 (1895).

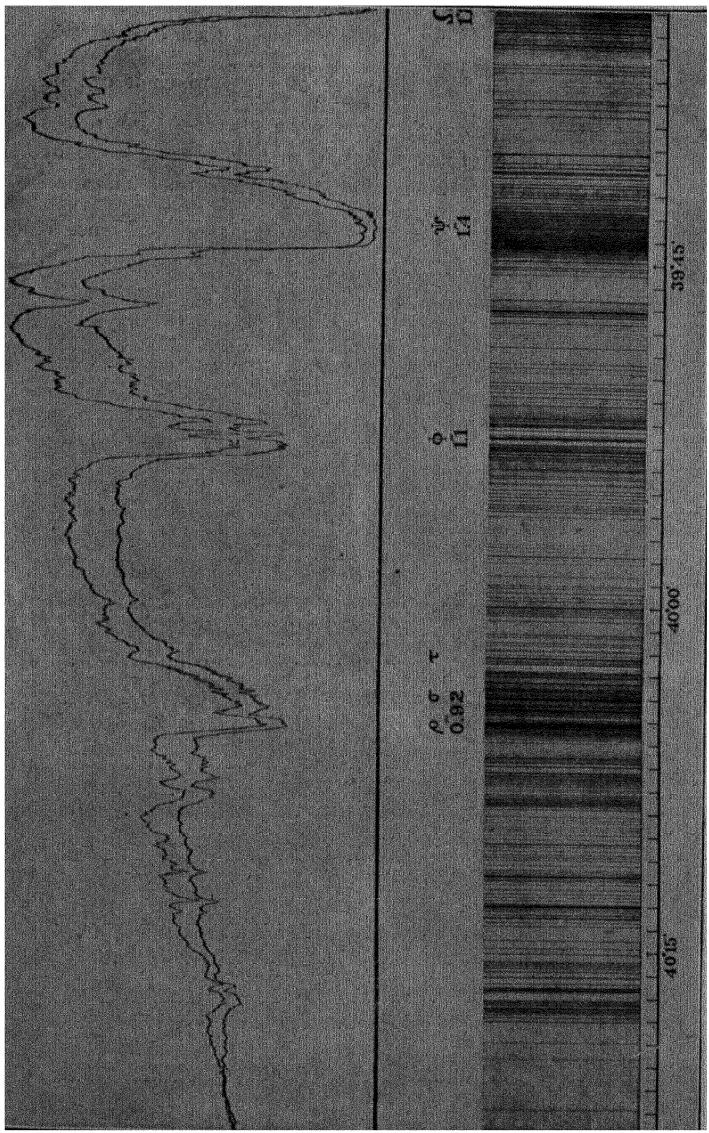


FIG. 97.

first of these he measures by the thermopile both i and i', one with the Nicols parallel, and the other with them crossed, and from these values finds the value of $\frac{i - i'}{i + i'}$, which it can be seen is equal to cos $2\pi\phi$. Now, when $\phi = k + \frac{1}{4}$, where k is the whole number of waves, then, of course, cos $2\pi\phi = 0$; by a series of observations, therefore, the deviation is found corresponding to $\frac{i - i'}{i + i'} = 0$, which is where the phase difference is equal to a whole number of waves $+ \frac{1}{4}$. In the second method the quartz plate and the analyser are set between the prism and the telescope, the analyser being so turned that its double refraction is utilised, and two spectra, one immediately above the other, are seen in the telescope; the intensity of one of the spectra is equal to i, and that of the other to i'. These two spectra are thrown upon the two arms of a differential thermophile, so that $i - i'$ is automatically measured by the galvanometer. As before, the position of the telescope is found corresponding to the condition that $i - i'$, and therefore also cos $2\pi\phi$ is equal to 0. By this method the refractive indices of fluorite were measured between $\lambda = 1{\cdot}849\mu$ and $\lambda = 0{\cdot}39681\mu$ (H line).[1]

A considerable amount of very important work has been carried out by Rubens in the way of measuring the dispersion of various bodies for rays of very long wave-length; the first paper by Rubens was on the dispersion of infra-red rays.[2] In this research the indices of refraction of very many substances were determined with the help of a bolometer, interference bands being employed as landmarks, as in the case of Mouton's method. These were, however, produced in a different way; the light beam from an artificial source was reflected into the spectroscope from the two parallel walls enclosing a thin layer of air, and in this way the interference bands were produced. The determination of the wave-length corresponding to the centres of these bands is rather simpler than it is in the case of the Fizeau and Foucault bands used by Mouton. If m is the order number of a particular band,

[1] See p. 95. [2] *Ann. der Phys.*, **45**. 238 (1892).

d the thickness of the air layer, and α the angle at which the air-plate is set to the incident beam, in this case 45°, then we have—

$$m\lambda_1 = 2d \cos \alpha = K$$

and $$(m + 1)\lambda = 2d \cos \alpha = K, \text{ etc.}$$

By the observation of several bands in the visible spectrum it is possible to determine the values of m and λ for the bands, and also of the constant K. When the order number m is known for any one band, the numbers of all at once become known, as those of two consecutive bands simply differ by unity, and, of course, as one follows the bands towards the red their order numbers decrease. If now n be the order of the last visible band in the red, then the wave-length corresponding to the first band in the infra-red will be equal to $\frac{K}{n-1}$.

The position of the bands was observed by means of a bolometer, two being used, which had a sensitiveness of 5×10^{-6}° and 8×10^{-6}° C., respectively. Rubens measured the dispersion of five crown and five flint glasses, differing in constitution amongst themselves, water, xylene, benzene, carbon bisulphide, quartz, rock-salt, and fluorite, to as far as $\lambda = 3{\cdot}0\mu$, when absorption begins; for the three last-named substances, the measurements reached $\lambda = 3{\cdot}5\mu$. The results of measurements of the dispersion of rock-salt, sylvin, and fluorite were published by Rubens and Snow,[1] in which the same apparatus and method were used but the bolometer was rendered more sensitive, the limit being reduced to 3×10^{-6}° C. Rubens, in his next investigation,[2] on the dispersion of fluorite, altered the experimental method and adopted that of Langley, viz. a grating and prism combined. Two gratings were employed, made of wire wound round a frame; in the one gold wire 0·0331 mm. in diameter, and in the other copper wire 0·0250 mm. was used.[3] These gratings were made in such a way that the space between two consecutive windings was exactly equal to the thickness of the wires, *i.e.* in grating No. 1 the

[1] *Ann. der Phys.*, **46**. 529 (1892). [2] *Ibid.*, **51**. 381 (1894).
[3] *Ibid.*, **49**. 594 (1893).

grating space was 0·0662 mm., and in No. 2 it was 0·0500 mm. Under these circumstances (see Chapter VI., p. 178) the even orders of spectra are absent, and only the odd numbers are present, which are consequently brighter. With the two gratings mentioned, the fifteenth and the thirteenth orders respectively were very good. The bolometer was the same as used in the last research, and the measurements were taken as far as $\lambda = 6{\cdot}48\mu$.

In his next papers[1] Rubens extends his measurements, and shows the applicability of the Ketteler-Helmholtz dispersion formula; but, as the constants obtained in this formula were not the same as those calculated from some later measurements, they need not be more than mentioned in this place.

In order to understand the latest work of Rubens, in which he deals with the dispersion of substances for heat rays of the greatest wave-length, it is necessary to discuss the research in which the existence of these rays and the method of dealing with them were discovered. In 1896 Nichols, in Rubens's laboratory, studied the reflecting power of different substances, especially quartz, and found that metallic reflection exists with the last for rays of about $\lambda = 9\mu$; the following brief description may be given of the apparatus employed. The rays from a Linnemann zircon burner were reflected from a polished plane surface of quartz, and were focussed upon the slit of a spectrometer by a rock-salt lens; a fluorite prism was employed as the dispersing apparatus, and for detection of the rays a radiometer was used. It may be mentioned that Rubens had already measured the dispersion of fluorite so that the wave-lengths of the rays dealt with could be found from the dispersion curve of this substance. The radiometer employed by Nichols in this work was a modified form of the instrument as originally devised by Crookes, in which mica vanes, accurately mounted upon a central spindle in vacuo, rotate when placed in the path of radiant energy. In Nichols's form[2] of this apparatus the mica vanes are suspended by a quartz fibre, and the angle through which they are turned from their position of rest is

[1] *Ann. der Phys.*, **53**. 267 (1894); and **54**. 476 (1895).
[2] *Ibid.*, **60**. 402 (1897).

measured by the excursion of a spot of light reflected, as in the case of a galvanometer, from a very small mirror carried by the vanes. The following is a description of the apparatus which is shown in Fig. 98:—

The outer case consists of a bronze cylinder, A, bored out to within 5 mm. of the bottom; this cylinder is mounted upon a base provided with levelling screws. A glass cover, B, is ground accurately to fit the top of A, and a tube connects the apparatus through the stopcock H to an air-pump. At *g* is a small bridge, from which hangs a quartz fibre carrying the two mica vanes *a*, *a*; at *e* is a small mirror suspended from the vanes by a very narrow glass rod, *s*. The weight of the whole apparatus on the quartz fibre is only 7 milligrammes. There are two openings in A at *c*, *c*, one of which is provided with a brass tube closed with a fluorite plate through which the rays pass to the mica vanes; the other opening is closed with a glass plate, and serves to admit the light to illuminate the mirror at *e*.

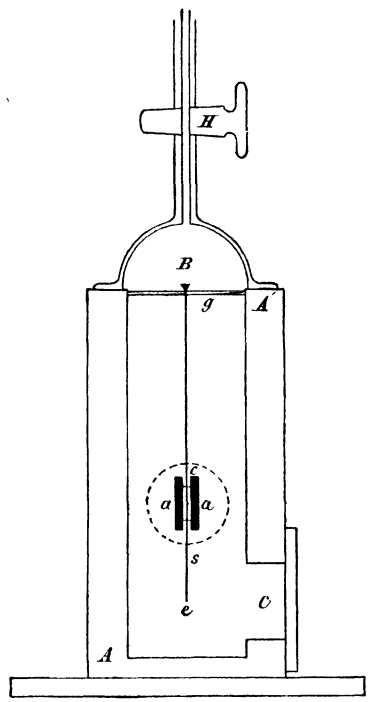


FIG. 98.

The rays were allowed to fall upon one vane only, the other one acting as a compensator; the apparatus was so delicate that the energy from a candle 6 metres distant caused the deflection of the spot of light over sixty divisions on a scale placed $1\frac{1}{3}$ metres away. Nichols claims that the radiometer

has the following advantages over the thermopile and the bolometer. It is quite undisturbed by all magnetic and electrical influences. It can be better compensated against stray radiations, and, finally, it is free from disturbance due to air currents. Against it, however, may be urged that it is not as transportable as the bolometer or thermopile, and, further, all the rays examined must pass through the radiometer window, so that they suffer a certain amount of loss by reflection and absorption.

In Nichols's apparatus an arrangement of mirrors was adopted, so that the telescope need not be moved, the spectrum being caused to pass in front of the slit by simply turning the fluorite prism. The wave-lengths of the rays were found from the deviation, using Paschen's values of the dispersion of fluorite.[1]

With this apparatus it was found that a polished quartz plate had a reflecting power of about 0·33 per cent. at $\lambda = 7{\cdot}4\mu$, and at $\lambda = 8{\cdot}5\mu$ the reflecting power was about 75 per cent., equal to that of polished silver for ultra-violet light. On examining the amount of light transmitted it was found that absolute absorption takes place for rays between $\lambda = 8\mu$ and $\lambda = 9\mu$.

Immediately following this paper is one by Rubens and Nichols,[2] dealing with the metallic reflection occurring with quartz and other substances. The method of experiment was very similar to that used by Nichols, but the rays from the heat source were made to undergo three or four reflections before entering the spectrometer. A grating was employed which was made by winding silver wire round a frame, and, as the wire was 0·1858 mm. thick, and the grating space 0·3716, it follows that the spectra of even orders were absent. A bolometer was used with fine platinum strips 0·5 mm. broad and 0·001 mm. thick; also a radiometer exactly similar to that used by Nichols in all respects, except that the fluor-spar and mica windows were removed, and one 2·5 mm. thick of silver chloride was substituted. This instrument, however, could not be used for the rays of greatest wave-length, owing to their

[1] See Chapter III., p. 95. [2] *Ann. der Phys.*, **60**. 418 (1897).

absorption by this window. The name given by Rubens and Nichols to the rays obtained by metallic reflection is "residual rays" (Reststrahlen), and the properties of these rays were investigated for many substances, of which the most important for our present purpose are quartz and fluorite. In the case of the former metallic reflection was found to take place at three points of the spectrum, viz. $\lambda = 8{\cdot}50\mu$, $\lambda = 9{\cdot}02\mu$, and $\lambda = 20{\cdot}75\mu$, of which the first two correspond to those found by Nichols, and the last one is generally known as the residual ray of quartz. In the case of fluorite the residual rays have a wave-length of $\lambda = 24{\cdot}4\mu$, and, after passing through a silver chloride plate, a wave-length of $\lambda = 23{\cdot}7\mu$, showing that the rays of mean wave-length of $\lambda = 24{\cdot}4\mu$ are not homogeneous. Further, the absorption of these rays by substances, and the indices of refraction of rock-salt and sylvin for these rays were measured, and also their electro-magnetic character was proved. The absorption and refractive indices were examined further, and published in a later communication [1] by Rubens and Trowbridge, and the absorption by Rubens,[2] and by Rubens and Aschkinass.[3] The residual rays of rock-salt and sylvin were investigated by the last two observers [4] with exactly similar apparatus, with the exception that a thermopile was used in place of the bolometer and radiometer which had been previously used. This instrument consisted of twenty elements of iron and the alloy constantan; short wires of these metals were soldered together, and the alternate joints were arranged together so as to form a vertical line about 18 mm. long. This vertical line only was well covered with soot and exposed to the radiations; the resulting potential difference was measured by means of a galvanometer which gave a throw of 1 mm. upon the scale with the current of $1{\cdot}4 \times 10^{-10}$ amperes; and thus the accuracy of the reading of temperature was $1{\cdot}1 \times 10^{-6}$° C. The rays came from an incandescent gas mantle, and were reflected five times from sylvin or rock-salt faces. The wave-lengths of the residual rays were found to be, for rock-salt, $\lambda = 51{\cdot}2\mu$, and for sylvin, $\lambda = 61{\cdot}1\mu$.

[1] *Ann. der Phys.*, **60**. 724 (1897).
[2] *Ibid.*, **64**. 584 (1898).
[3] *Ibid.*, **64**. 602 (1898).
[4] *Ibid.*, **65**. 241 (1898).

Later, Rubens and Aschkinass devised a method of separating the long rays by passing through them a quartz prism of very narrow refracting angle; for, though this substance absorbs rays of shorter wave-length, yet it is very reasonably transparent to these rays—a quartz plate 0·5 mm. thick allows 61 per cent. of the residual rays from rock-salt and 77 per cent. of those from sylvin to pass. A diagram of Rubens's apparatus is

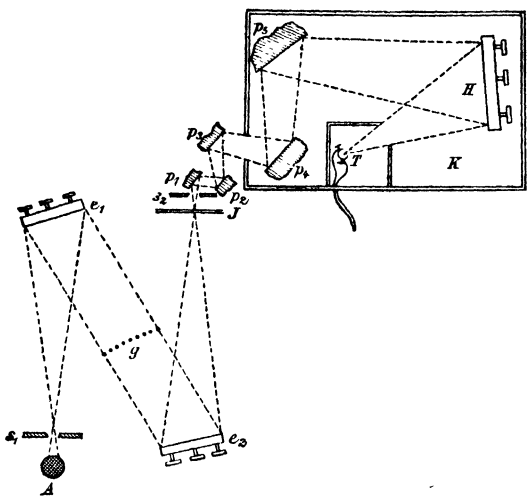


FIG. 99.

shown in Fig. 99; A is the source of light, and s_1 is the first slit; the light then falls upon a concave mirror e_1, whence it falls as a parallel beam on to the grating g and the second concave mirror e_2. This mirror focusses the rays upon the second slit s_2, after leaving which they undergo five reflections from the surfaces p_1, p_2, p_3, p_4, and p_5 of the material under investigation. The rays are finally focussed by the mirror H on to the thermopile T. K is a large chest which encloses the apparatus from stray heat waves, and the thermopile is further protected by being placed within an inner chamber.

In Fig. 100 is shown a plot of the results obtained for rock-

salt, in which the ordinates are the excursions of the galvanometer needle, and abscissæ the deviations produced by the grating. The maximum plotted in the centre of course corresponds to the rays transmitted directly through the grating, while the two side maxima are due to the residual rays when diffracted by the grating on each side of the normal. The

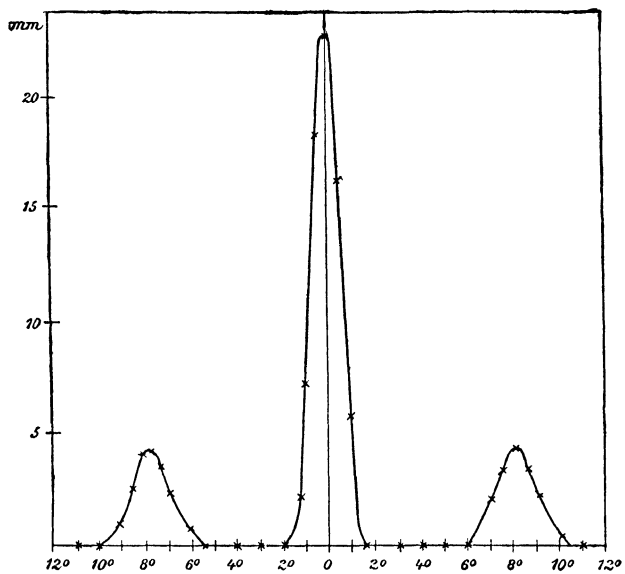


FIG. 100.

actual numerical results of Rubens and his school's work will be found under the heading of prisms in Chapter III., and therefore will not be given again here.

An interesting investigation on the sensitiveness of the thermopile for measuring radiation has been carried out by Johansen,[1] who gives in his paper a theoretical discussion of the best conditions obtainable for the use of this instrument. He finds that a very great improvement is gained by mounting

[1] *Ann der Phys.*, **33**. 517 (1910).

the instrument in vacuo, and shows that the loss of heat due to conduction through the wires of the thermo-junction must be equal to the heat loss due to radiation from the junction, and also that the radii of the thermocouple wires must be so chosen that the ratio of the heat conductivity to the electrical resistance in each is the same. Johansen has tested vacuum thermopiles constructed on these principles, and finds that the sensibility is equal to the product of the square root of the surface exposed into a constant. If the value of this constant for Rubens' apparatus mentioned above is put equal to 1, then the value for the vacuum thermopile iron-constantan is about 4·5, and for iron-bismuth about 9·5, that is to say, in the latter case the sensitiveness is about 9½ times that of Rubens' instrument.

Very valuable work has been carried out by Paschen in the direction of mapping the normal emission spectrum of an absolutely black body. In these investigations Paschen employed both a radiomicrometer and a bolometer for the measurement of the intensity of the radiation. The first-named instrument was a modified form of that invented and used by Boys[1] for the measurement of the heat of the moon and stars, etc. This instrument, as modified by Paschen,[2] may be described as follows: two alloys are prepared, one containing ten parts of bismuth and one part of antimony, and the other equal parts of cadmium and antimony; both of these alloys are cast into very small slabs, 0·3 mm. thick, 0·5 mm. broad, and 4 to 5 mm. long. One of each kind of these strips is soldered to a strip of silver 0·5 mm. broad, 0·03 mm. thick, and several mm. long; this operation is carried out by heating the silver and gently pressing the alloy against it, when a good joint will be obtained. The general arrangement is shown in Fig. 101, where *a* and *b* are the little slabs of the two alloys which are soldered to the silver strip *c*. To the upper ends of these slabs and on the inner sides, the two ends *d*, *e* of a thin silver wire are soldered; this wire is bent round to a hoop as is shown at *c* in Fig. 102. A very thin glass rod, G, is fastened to the silver wire, and carries a mirror, S, the whole being

[1] *Phil. Trans.*, **180.** A, 159 (1889). [2] *Ann. der Phys.*, **48.** 272 (1893).

suspended by a quartz fibre, Q. It is, of course, necessary that the whole hang vertically and swing on its central vertical line. The thermocouple is suspended in the centre of a thick iron block, E, as shown in Fig. 103,[1] and the iron block E in its

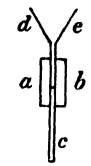


FIG. 101.

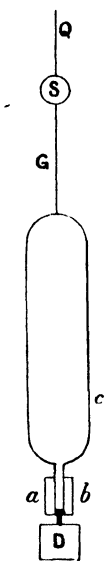


FIG. 102.

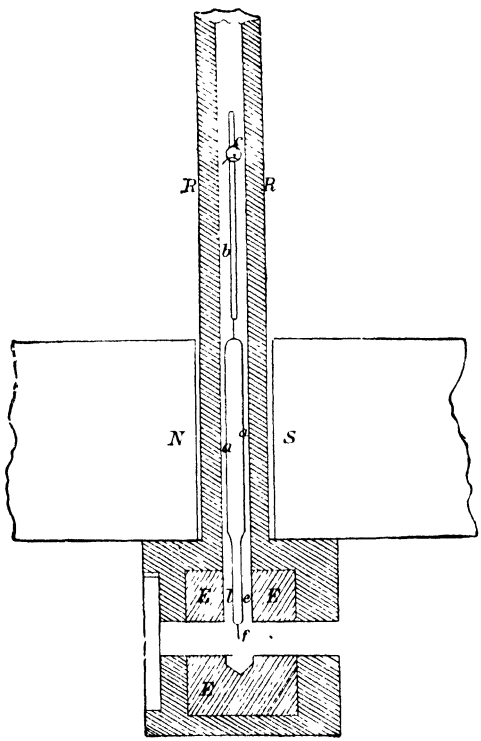


FIG. 103.

turn is set inside a copper block ; a hole is bored, as shown, to admit the radiations; the silver hoop *a* hangs in a copper tube, R, which also has a window for the illumination of the mirror *c*.

[1] Boys, *Phil. Trans.*, **180**. A, 183 (1889).

The poles N, S of a magnet are brought up against the opposite sides of the copper block, and the whole thermopile is made as small as possible, so that it all lies in an equal magnetic field. The portion of the silver strip exposed to the radiations is well covered with soot, in order to absorb them with greater ease. The apparatus thus consists of a very small thermopile, which is formed of a triple junction instead of the usual couple. By the construction it will be seen that only the lower junction can get heated, and by this a small current will be sent round the silver wire, which will cause the rotation of the instrument in the magnetic field. Generally, as Paschen says, the first test of an instrument will show that it is very unsensitive. This is owing to the para or diamagnetic properties of the materials used. For every instrument there will be found a particular strength of magnetic field for which the greatest sensitiveness is obtained. Those which give the smallest oscillation period in strong fields are the best. The alloys may be obtained sufficiently free from iron by repeatedly melting them, and the silver by electrolytic deposition. Less diamagnetic circuits are obtained by using for the hoop silver wire drawn through an iron wire-drawing plate. Paschen never succeeded in making an instrument completely indifferent to a magnet. He made two instruments, which were equally sensitive in the same field, and gave with a candle at 6 metres distance a movement of the spot of light over sixty to seventy divisions with an oscillation period of forty seconds.

Paschen has also employed a bolometer, in which he used the platinum-silver foil according to Lummer and Kurlbaum's method.[1] Three strips, 0·001 mm. thick (platinum, 0·0005 mm. thick), 0·5 mm. broad, and 15 mm. long, were stretched as close to one another as possible, and formed one arm. Only those portions exposed to the radiations were freed from silver, and then they were sooted. The compensation resistance was adjustable by means of mercury contacts actuated by micrometer screws.

The galvanometer[2] used in connection with the bolometer had a degree of sensitiveness such that a movement of the spot of

[1] See below, p. 274. [2] *Zeitschr. für Instrumentenk.*, **13**. 17 (1893).

light 1 mm. upon the scale at 2·7 metres distance corresponded to a current of $1{\cdot}6 \times 10^{-11}$ ampere. The bolometer could carry a current of 0·06 ampere without disturbing the galvanometer needle, but only 0·038 to 0·04 ampere was generally used, and the delicacy was then found to be such that 1 mm. throw on the galvanometer scale was produced by a change of temperature of $\frac{1}{1000000}$° C.

The arrangement of Paschen's apparatus is shown in Fig. 104; it may be pointed out that he was the first to substitute concave mirrors for rock-salt lenses, thereby doing away with, amongst other objections, chromatic aberration. The rays enter the slit *s* and fall on to the concave mirror S_1, by which they are directed as a parallel beam through the fluorite prism P on to the concave mirror S_2, which focusses them on to the bolometer at B. As will be seen, an automatic arrangement is employed for keeping the prism in the position of minimum deviation.

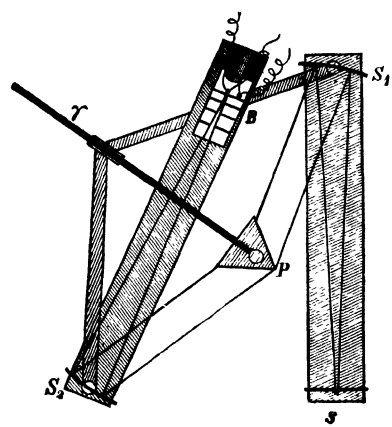


FIG. 104.

It is quite impossible within the scope of this book to follow Paschen through all his work in this domain, and give an account of it which could in any way do justice to it. One section of it only can be mentioned here, namely, the dispersion of fluorite.[1] In this investigation it was necessary to employ a linear bolometer, and not a surface instrument such as was described above; the three platinum strips, used in the latter case, were replaced by a single strip of platinum, sooted on one side, 7 mm. long, 0·25 broad, and 0·0005 mm. thick, with a resistance of 8 ohms. This instrument had about the same

[1] *Ann. der Phys.*, **53**. 301 (1894).

sensitiveness as the former instrument. One of Rowland's gratings was used, which had been specially ruled for Langley. This grating had a ruled surface of 132 mm., with 142·1 lines to the millimetre, and a focus of 1·753 metres. The results of these measurements are given in Chapter III., p. 95.[1]

Certain considerations respecting the construction and use of bolometers have been given by Lummer and Kurlbaum[2] which may prove of use. As a bolometric measurement is nothing more or less than the measurement of a resistance change with a Wheatstone's bridge, therefore the general rule of a Wheatstone's bridge here holds good; namely, that the best relation between the resistances is obtained when the four arms (if four are used) and the galvanometer have the same resistance. In order to obtain the best conditions for a bolometer the following quantities should be made as large as possible :—

1. The chief current through the instrument.
2. The temperature coefficient of the metal strip.
3. The portion of the bolometer resistance exposed to radiations.
4. The resistance of the instrument.
5. The absorption coefficient of the exposed surface.
6. The irradiated surface.

On the other hand, the following should be as small as possible :—

7. The emission coefficient of the surface exposed.

[1] The following is a list of Paschen's papers upon his work in the infra-red :—"Bolometrische Untersuchungen im Gitterspectrum," *Ann. der Phys.*, **48**. 272 (1893); "Die Gesammtemission gluhenden Platins," *Ann. der Phys.*, **49**. 50 (1893); "Die Emission der Gase," *Ann. der Phys.*, **50**. 409 (1893); **51**. 1 (1894); and **52**. 209 (1894); "Die Dispersion des Fluorits im Ultraroth," *Ann. der Phys.*, **55**. 301 and 812 (1894); **58**. 762 (1895); "Die Dispersion des Steinsalzes im Ultraroth," *Ann. der Phys.*, **55**. 337 (1894); "Gesetzmässigkeiten in der Spectren festen Körper," *Ann. der Phys.*, **58**. 455 (1896); **60**. 662 (1897); "Die Vertheilung der Energie im Spectrum des schwarzen Körpers," *Berl. Ber.*, 1899, pp. 405 and 959. Certain later work by Paschen on infra-red emission spectra is dealt with below (see p. 287).

[2] *Ann. der Phys.*, **45**. 204 (1862).

8. The heat capacity; in order to ensure this, the thickness of the metal strip should be as small as possible.

In practice, unless precautions are taken to the contrary, it will be found that troublesome movements of the galvanometer needle take place, either in the shape of a steady motion in one direction or of unsteady oscillations. The first of these motions is due to the heating of the bolometer filament by the current flowing through it, while the second is due to air currents within the instrument, caused by the heating of the filaments. Concerning the first trouble—namely, the steady motion of the spot of light, which often lasts a quarter of an hour after the current has been started—it is clear that, if all four arms of the bolometer had exactly the same resistance, cross-section, surface, etc., then no change in the spot of light would be obtained, as the changes would be the same in all; this is also true, of course, if there be only two arms instead of the four.

We have thus another condition for good working—

9. That the resistance of the bolometer arms must be equal.

10. To meet the second trouble—the irregular oscillations of the spot of light—it is necessary to arrange that the air currents be as regularly distributed as possible. This is a tenth condition for efficiency. As the air currents arise from the heat produced by the current, and as the heat depends upon the current density and the resistance, one might suppose it possible to choose such a resistance that the air currents would be reduced to a minimum; but Lummer and Kurlbaum show that changing the specific resistance and the thickness of the filaments has no effect upon the air currents, as $\frac{c}{\sqrt{R}}$ is a constant where c is the current and R the resistance.

By changing the length of the filament, so that the resistance is n times as great, the throw of the galvanometer mirror is $\sqrt{n}$ times as great. If n filaments are used in parallel or one filament n times as broad, and the current n times as great, this being necessary for equal galvanometer throw, then the same relation is also true, that the throw is proportional to $\sqrt{n}$.

In the first case we have a weaker current flowing through a high resistance, and in the second a stronger current through a low resistance. From a practical point of view the first condition is far more convenient, and thus we have another condition for efficiency—

11. That the bolometer consist of a very long and narrow filament.

Lummer and Kurlbaum describe the method of construction of a surface bolometer—that is to say, an instrument for measuring the total radiation from a body; as in the case of a linear bolometer the details are very similar, they may be quoted here at length. The chief difficulty lies, as can readily be imagined, in the preparation of the filament, so that all four arms of the bolometer can be exactly the same in every way as prescribed by condition 9 above. None of the commercially prepared wires are anything like sufficiently accurate, nor is gold leaf, tin foil, or the like of any use. The difficulty of preparing a good filament is perhaps evidenced best by the fact that Julius[1] made use of the nickel plating of his teapot, which he dissolved off with acid. A suitable filament can, however, be prepared in the following way. A piece of platinum foil is welded together with a piece of silver foil about ten times as thick, and the whole rolled out. It is necessary, of course, continually to soften the metal during the process by heating to redness in a charcoal fire, and then plunging into cold water. When the double foil has become very thin, it may be enclosed between two pieces of copper foil, and the whole again rolled. The thickness of the platinum can at any moment be estimated by noting its area. The platinum-silver foil can easily be separated from the copper pieces as long as its thickness is greater than 0·0005 mm. With thinner pieces the silver becomes so pressed into the copper that they cannot be separated. When a sufficiently thin piece of foil has been prepared it is mounted upon a glass plate with Canada balsam, and cut to the required size by means of a dividing engine. For the surface bolometer

[1] *Arch. Néer.*, **22**. 310 (1888).

described by Lummer and Kurlbaum, it is cut into the shape shown in Fig. 105, with twelve parallel strips 32 × 1 mm. and 1·5 mm. apart. It is then dissolved off with chloroform, and mounted upon a slate frame with a solution of colophony in ether, which allows the strip to be accurately adjusted, as it dries very slowly. The appearance when mounted is shown in Fig. 106.

The two ends *a* and *b* are soldered to two pieces of copper foil; these joints and the ends of the filament *m* and *m'* are covered with lacquer. The appearance of the mounted filament from the back is shown in Fig. 107. The whole frame is then placed in dilute nitric acid to dissolve off the silver from

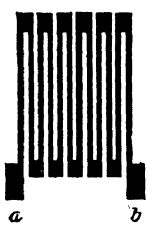


FIG. 105.

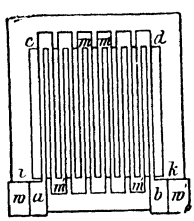


FIG. 106.

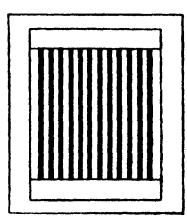


FIG. 107.

the platinum; very great care must be taken not to break the filament in doing so. Special precautions are necessary when washing with water after treatment with acid, as otherwise the surface tension between the acid and water will inevitably break the filament. Paschen, in the description of his linear bolometer, gives a method of doing this. A narrow glass tube sealed at one end is filled with dilute nitric acid so full that a convex meniscus of acid stands above the level of the end of the tube. With this meniscus the etching is done, and then similar menisci of weaker and weaker acid are used, until water is finally employed. The filament is then allowed to dry.

The next point is the covering with soot. Lummer and Kurlbaum recommend a small paraffin lamp, *e.g.* a wick

placed in a 4-mm. brass tube. A chimney is put round this and on the top is a copper disc about 12 cms. in diameter with a 4-mm. hole in the centre. The bolometer filament is moved about in the soot coming through this hole until it is well covered; only one side of the filament is sooted, the other being protected during the process by a metal plate.

In the four-arm bolometer four such filaments are prepared, all of exactly the same size; the method of connecting them together is shown diagrammatically in Fig. 108.

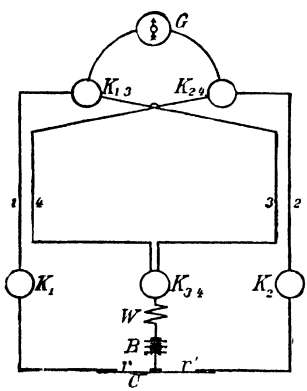


FIG. 108.

The arms of the bolometer are placed at 1, 2, 3, 4; G is the galvanometer, and K_1, K_2, etc., are simply plug keys, the numbers signifying the arms they connect together; B is the battery, W a regulating resistance, and r, r' two mercury contacts. Either 1 and 4 or 2 and 3 are exposed to the radiation; each arm consists of a filament prepared as described above, and the two together are mounted one behind the other, so that one set of strips is visible between the other set. This can easily be managed, as the strips are 1 mm. wide, while the distances between them are 1·4 mm.

One instrument prepared according to these directions gave, with an electric lamp of 3 candle-power placed at 1 metre distance, a throw of 414·8 mm. As regards the galvanometer, needless to say, a very sensitive instrument must be employed Paschen describes the making of one, on the model of Thomson's astatic instrument, to which, however, reference can only be made.[1] The degree of sensitiveness of this instrument was about $3{\cdot}3 \times 10^{-12}$ amp.

A very extended and accurate investigation has been

[1] *Zeitschr. für Instrumentenk*, **18.** 13 (1893).

carried out by Coblentz [1] into the infra-red reflection and transmission spectra of a great number of minerals, with the view of determining, if possible, the relation between their constitution and the absorption which they exert. The apparatus consisted of a mirror spectrometer, a rock-salt prism, and a Nichol's radiometer. The rock-salt prism had faces 9·9 cms. square, and the radiometer required about twenty seconds to reach its maximum deflection. The source of energy employed was a 110 volt Nernst lamp fed from an 80 volt storage battery. The radiometer only differed from the one described above by being covered with a heavy piece of brass tubing, within which was a layer of coarse felt. The sensitiveness of the instrument was about 10 cms. deflection per square millimetre of exposed surface with scale and candle at one metre distance. The accuracy, judging by repeated series of measurements at various times, was about 0·02μ.

The absorption and reflection spectra of at least 125 elements and substances have been examined, many of them to as far as 15μ. The principal object of this investigation was to gain information with regard to the molecular structure of minerals containing oxygen and hydrogen. A detailed account of Coblentz's results would take far too much space, but there is no question of any doubt that very valuable knowledge has been gained of the vexed problem of the constitution of minerals.

The organic chemist by his own particular methods is able to study the constitution of the compounds with which he has to deal, but the mineralogist is unable to do this. The relation between absorption and constitution in the case of organic compounds has carried us far towards a comprehension of what is the real meaning of chemical reactivity and chemical combination. Owing to our entire ignorance of anything more than the empirical formulæ and crystalline structure of minerals, it is not surprising that the tentative rules for classifying minerals break down in certain cases. It is therefore to such investigations as that of Coblentz that the mineralogist must look for a solution of his problems.

[1] Investigations of Infra-Red spectra, Publications of the Carnegie Institution, Washington, 1905 and 1906.

A very interesting investigation has been carried out by Coblentz dealing with the relative values of the four instruments, Radiomicrometer, Thermopile, Radiometer and Bolometer. It may be said at once that although the radiomicrometer, such as is used by Paschen, may be much improved by placing it in a vacuum it is not nearly so sensitive as the most modern forms of the other instruments.

It has been pointed out by Warburg, Leithäuser and Johansen[1] that considerable advantage is gained by mounting the bolometer in vacuo. The authors give a theoretical investigation of the loss of heat by conduction and radiation, and they find both theoretically and experimentally that there is a considerable advantage gained as regards sensibility in the vacuum instrument, especially when the bolometer strip is narrow.

Recently a new method for the investigation of the long wave radiation has been devised by Wood,[2] who has succeeded in ruling a grating which partakes of the type of a reflecting echelon grating. For a description of this instrument see page 200. Trowbridge and Wood[3] have found that on applying this grating to the study of infra-red region a higher resolving power is obtained than has ever yet been applied to the infra-red region. These investigators find that the residual rays of quartz show two maxima of which the longer wave-length one is considerably higher than the shorter wave-length one with a shallow minimum between them. The Echelette grating shows that the maxima are nearly the same height, and the minimum between them is very much deeper than was previously supposed, its intensity being only one-third that of the maxima. The wave-lengths of the two maxima are found to be $8{\cdot}41\mu$ and $8{\cdot}30\mu$. Similarly with regard to the radiation from the carbon di-oxide in a bunsen burner, the Echelette grating resolves a strong band at $4{\cdot}3\mu$ into two, the wave-lengths of which are $4{\cdot}32\mu$ and $4{\cdot}43\mu$.

Rubens and Hollnagel[4] have adopted the interference

[1] *Ann. der Phys.*, **24.** 25 (1907).
[2] *Phil. Mag.*, **20.** 770 and 886 (1910).
[3] *Ibid.*, **20.** 898 (1910).
[4] *Berl. Ber.* (1910), **26**; and *Phil. Mag.*, **19.** 761 (1910).

method for the investigation of radiations of long wave-length. The interferometer they used was similar to that employed by Michelson for obtaining his "visibility" curves (see page 314), the only difference being that very thin quartz plates were used in place of the glass ones used by Michelson, in order to reduce the absorption of the rays to a minimum. In one case a plane parallel pair was used, each being 0·6 mm. thick, and in the other case a wedge-shaped pair tapering from 0·8 to 0·4 mm. thick was used. The pitch of the micrometer screw was 0·5228 mm., and as the drum actuating this screw was divided into 100 parts, a rotation of one division corresponds to a displacement of $5{\cdot}228\mu$.

The arrangement of the apparatus was very similar to that already described under Rubens' work, with the addition that the rays from the source pass through the interferometer before they fall on the reflecting surfaces of the substances to be investigated. The source of energy was a Welsbach burner, the rays from which were focussed by a concave mirror on to the air space between the interferometer plates. After emerging from the interferometer the rays were reflected four times from the polished surfaces of either sylvin, potassium bromide, or potassium iodide, and were then focussed by a second concave mirror upon the thermo-junction of a very delicate radiomicrometer. By altering the distance between the interferometer plates, and measuring the energy received by the radiomicrometer, it will be seen that a "visibility" curve can be constructed in which the ordinates represent "intensities of radiation" and the abscissæ the distances between the interferometer plates. The distribution of energy in the radiation from the source was calculated in a very similar way to that used by Michelson in his experiments. The reflecting plates of sylvin were obtained simply enough by cutting a block of this material obtained from Stassfurth. In the case of the potassium bromide and iodide the following method was employed. A quantity of the salt was melted in a nickel crucible and the molten mass poured into a brass vessel 10 cms. square and 1·5 cms. deep and then allowed to cool. Such blocks were rendered plane by turning in a lathe. No difficulty was

experienced in grinding and polishing the potassium bromide, but considerable difficulty was found in dealing with the iodide. In this case good surfaces were ultimately obtained by grinding against one another, until they were dry, two surfaces previously moistened with water. Such surfaces, when carefully ground, were polished with the palm of the hand, using diamantine powder and paraffin oil. It was found that these mirrors preserved their polish for several days. The wave-lengths of the residual rays were as follows:—

	μ	μ	λ_0	mw
Rock-salt	53·6	46·9	51·7μ	58·5
Sylvin	62·0	70·3	63·4μ	74·6
Potassium bromide . .	86·5	75·6	82·3μ	119
Potassium iodide . . .	96·4		96·4μ	166

It will be seen from the above table that potassium iodide only gives one radiation, while the other three substances give two. In the third column of the table headed λ_0 are given the means of the wave-lengths, and in the last column the molecular weights of the compounds. It will be seen that the mean wave-length increases more rapidly than the square root of the molecular weight and less rapidly than the molecular weight itself.

A still further improvement in the method of isolating the very long heat waves has been made by Rubens and Wood.[1] The method is based on the selective refraction by quartz lenses, for which material the refractive index for the light and the short heat waves lies between 1·43 and 1·55, while for the very long heat waves the refractive index approximates to 2·14, which is the square root of the dielectric constant for slow oscillations. The arrangement of lenses is shown in Fig. 109, which is taken from Rubens and Wood's paper. The two lenses L_1 and L_2 have a diameter of 7·3 cms. and a thickness of 0·8 cm. in the middle and 0·3 cm. at the edge. Their focus for the mean light rays is 27·3 cms. The radiation from a

[1] *Phil. Mag.*, **21**. 249 (1911).

Welsbach burner A passes through a circular aperture 15 mm. in diameter B in a screen made of two large sheets of tin plate, and then through the quartz lens L_1, a second aperture F and the quartz lens L_2, which focusses them on the thermo-couple of the radiomicrometer M. The central zones of the two lenses are covered by circular discs of black paper α_1 and α_2, 25 mm. in diameter. A movable shutter D is used to cut off the radiation at will. The distance of the lenses from the circular aperture are so arranged that a sharp image of the circular source B is focussed upon F only for radiation, for which the refractive index for quartz is 2·14. The path of these very long waves is shown in the diagram by the coarse

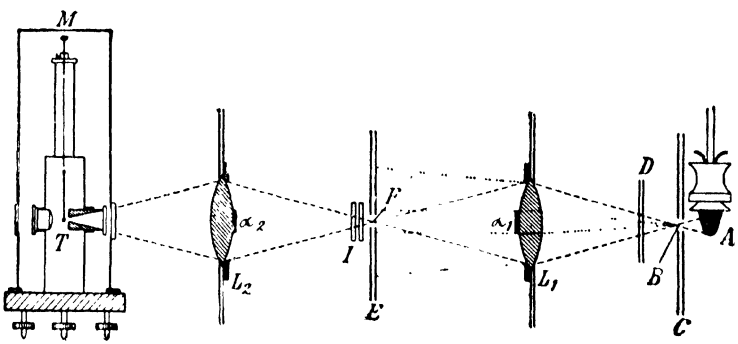


FIG. 109.

dotted lines. Owing to the very much smaller indices of refraction for the light waves and short heat waves it is evident that these, after emerging from the lens L, will form a divergent cone shown by the fine dotted lines in the diagram. The central portion of this cone, such as would otherwise fall on the aperture F, is intercepted by the small black screen α_1. As a result of this only the very long heat waves can pass through the aperture F. The second quartz lens L_2 acts in exactly the same way, and still further purifies the radiation.

The great advantage of this method of focal isolation is that large angular apertures can be used, and the radiation is

weakened only by reflection and absorption by the two quartz lenses. Its only disadvantage is that all radiations for which the refractive index approximates to 2·14 passes through the apertures. For $\lambda = 63\mu$ the refractive index of quartz is 2·19, decreasing to 2·14 as the limiting value. The very powerful absorption of quartz for rays between 60μ and 80μ prevents the shorter waves from getting through the system. Beyond 80μ the quartz begins to show stronger transparency, 17 per cent. of the residual rays from potassium iodide passing through a quartz plate 18 cms. thick, which is about the amount of quartz present in the path of the rays. The result of this is that the energy curve of the transmitted radiation is very steep on the shorter wave-length side, while on the other side it slopes gradually at a rate determined by the energy curve of the light source, which decreases as the fourth power of the wave-length and the increase in transparency of the quartz with the increasing wave-length.

Rubens and Wood describe in their paper the result of some investigations with this apparatus. In order to determine the wave-length of the radiations they made use of the quartz interferometer of Rubens and Hollnagel as described above. The only difference in the instrument was that the quartz plates were rather thicker, two pairs being used, one 1·2 mm. and the other 7·3 mm. thick. In Fig. 110 is shown one of the "visibility" curves obtained, in which the ordinates represent the radiomicrometer deflections in millimetres and the abscissæ represent the thicknesses of the air film expressed in sodium wave-lengths. This curve shows a minimum at $46\lambda_D$ and a maximum at $85\lambda_D$ and a second minimum at $122\lambda_D$. The mean wave-length of the radiation complex is found from this curve to be $108{\cdot}2\mu$, 100μ, and $96{\cdot}3\mu$ according to whether the first minimum or the maximum or the second minimum is used in the calculation. The explanation of this difference lies, of course, in the unsymmetrical character of the energy curve. The first minimum gives the value of the wave-length corresponding to the centre of gravity of the wave-curve, while the following maximum and minimum approach more and more nearly to the wave-length of the maximum in the energy curve.

By the process of trial by error the authors have constructed an energy curve which would give the same "visibility" as that shown in Fig. 110. This curve shows very conclusively that the maximum radiation is about 96μ, and that there are present in the radiation from a Welsbach burner rays certainly as long as 150μ, and probably as long at 200μ.

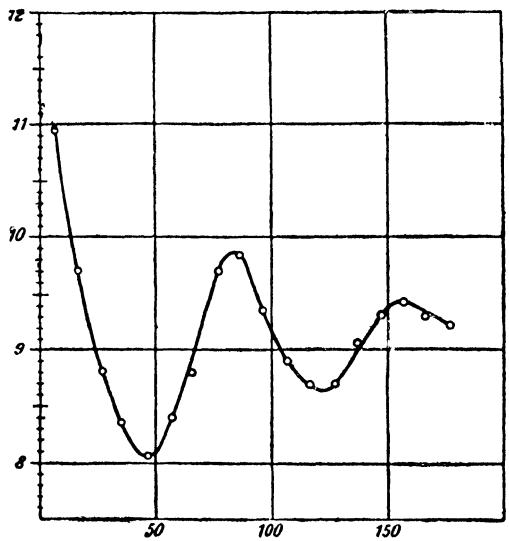


FIG. 110.

It has been shown possible to combine the method of residual rays with the method of focal isolation as described above, for Rubens [1] has isolated the residual rays of calcite by passing through the quartz lens apparatus the rays successively reflected from two calcite mirrors. The result was a pure and bright pencil of residual rays. It was evident, on a comparison between the radiomicrometer deflection obtained with the apparatus with and without the calcite mirrors, that a

1 *Verh. der Deutsch. Phys. Gesell.*, 13. 102 (1911).

considerable selective weakening was sustained by the radiation on reflection at the two calcite surfaces, and also that the reflection made the radiation more homogeneous. The wave-lengths of the residual rays were determined by means of the interferometer, as already described, and from an analysis of the "visibility curve" it is found that they consist of a strong band at 93μ and a weaker band at $116{\cdot}1\mu$. The mean wave-length, *i.e.* the optical centre of gravity, is calculated to be $98{\cdot}7\mu$.

The application of the focal isolation method has enabled Rubens and von Baeyer[1] to discover the existence of waves of exceedingly long wave-length in the emission spectrum of quartz mercury lamps. They investigated the radiation from a large number of sources, including sparks between various metal electrodes and the arc between carbon electrodes. It was at once found on trying with a quartz mercury lamp that there is present a very strong long-waved radiation, and it was soon discovered that this radiation must possess an essentially different composition from that of the Welsbach mantle, the mean wave-length of which is 108μ. For instance, a layer of quartz 14·6 mm. thick transmits 46·6 per cent. of the mercury lamp radiation and only 20 per cent. of the Welsbach mantle radiation. A number of experiments were carried out to test the transmitting power of various substances for these rays and for the rays from the Welsbach mantle. About seventeen different substances were experimented with, and in every single case the percentage transmission for the mercury lamp radiation was greater than for the Welsbach mantle radiation. Further, it was found that the percentage transmission was increased very materially if these radiations were previously passed through a 2 mm. layer of fused silica. It is evident, therefore, that the fused silica acts as a filter and cuts off some of the shorter wave-length radiation. Therefore, the percentage of transmission given by the same set of substances with the Welsbach radiation is very much smaller. Further experiments showed that the most effective ray filter is black card-

[1] *Phil. Mag.*, **21**. 689 (1911).

board, and the authors finally substituted for the silica a filter of black cardboard 0·38 mm. thick. In order to determine the average wave-length of these radiations attempts were made to measure them by the quartz interferometer, as already described. The interferometer curves obtained with the quartz mercury lamp without any filter showed a very irregular character. Nevertheless, it was evident that the main element of the radiation was about the same mean wave-length as that already dealt with from the Welsbach mantle. As soon as a 15 mm. layer of quartz was inserted a very considerable difference in the curve was noticed, for the first minimum which previously was observed at a thickness of the air film of about 26μ now did not appear until the air layer was 42μ thick. If the thickness of the quartz filter was increased to 42 mm. the first minimum was not observed until the air layer of the interferometer was 68μ thick. At the same time the interferometer curve became more regular, and the faintly-marked maximum began to make its appearance. With a filter of black cardboard 0·4 mm. thick the periodic nature of the curve becomes more distinct. Here the minimum lies at a thickness of 78·4μ, and a strong maximum at 156·9μ, but even in this case an accurate determination is still very difficult. It is evident, as is previously deduced from experiments on transmission, that the radiation after filtration through black cardboard contains a greater amount of the long wave radiation. It is still doubtful whether the long wave radiation consist of rays of different wave-length such as would be expected if they arose from the luminiferous radiation of mercury vapour, or whether it is simply a continuous thermal radiation. It is, however, safe to deduce from the observations that a large portion of this radiation possesses a mean wave-length of 314μ, or very nearly one-third of a millimetre. It may be added that Rubens and von Baeyer have satisfied themselves that the radiation in question has its origin in the mercury vapour itself and not in the hot quartz walls of the lamp. This is the longest wave-length that has been reached in an emission spectrum.

Since the time Rubens discovered the existence of the residual rays and first measured the wave-lengths of those

arising from calcite, fluorite, sylvin and quartz, the residual rays from many other substances have been observed by various experimenters. In the following table are given the values obtained by Porter :—[1]

Marble	6·77μ	Ammonium Chloride .	3·44μ
Potassium Bichromate.	10·31μ	Potassium Sulphate . .	8·42μ
Copper Sulphate . .	2·30μ	Potassium Bisulphite .	8·21μ
Tartaric Acid . . .	4·72μ	Potassium Ferrocyanide	4·84μ

Nichols and Day [2] obtain the following values :—

Rock Salt	52·3μ	Witherite	46·0μ
Ammonium Chloride .	51·4μ	Strontianite.	43·2μ

Nichols and Day pointed out how the wave-length of the residual rays follow the atomic weight of the metallic radicle in the salt; for example, in the chlorides of sodium, potassium and ammonium, in which the atomic weight relations are 39, 23 and 18, the wave-lengths of the residual rays are in the same order, 61·1μ, 53·3μ and 51·4μ. Similarly, in the case of barium and strontium, of which the atomic weights are 137 and 88, the wave-lengths of the residual rays are 46μ and 43·2μ.

It has already been pointed out that the residual rays are due to what is known as metallic reflection of those rays for which the substance in question possesses powerful absorption. It is evident that if the phenomenon is really one of metallic reflection that the rays reflected must be elliptically polarised. The existence of this elliptical polarisation of the infra-red rays was proved by Pfund,[3] who used a polariser and analyser made of selenium plates set at the polarising angle. He found that the reflecting power of selenium between 2μ and 13μ is extraordinarily constant, and the first question taken up was

[1] *Astrophys. Journ.*, **22**. 229 (1905).
[2] *Phys. Rev.*, **27**. 225 (1908).
[3] *Astrophys. Journ.*, **24**. 19 (1906).

whether these reflected infra-red rays are polarised by the selenium. This was proved by the ordinary method of adjusting the mirrors till maximum polarisation is obtained and then crossing them. The radiometer readings now showed a ratio of 1000 : 1, showing that the radiation is plane-polarised to a very high degree. Deflections of the radiometer were observed as far as 13μ, so that it is clear that the infra-red rays are capable of being polarised as far as this wave-length, which is as far as the apparatus allows.

In order to determine whether a non-metallic substance such as calcite in its region of metallic reflection behaves as a metal towards plane-polarised light, a polished plate of calcite was set up between the analyser and the polariser so as to reflect the plane-polarised light reflected from the first selenium mirror. The readings of the radiometer were then observed corresponding to the two positions of the analyser giving maximum and minimum energy. When $\lambda = 4\mu$, where the calcite only reflects vitreously, these readings were in the ratio 500 : 0, but when $\lambda = 6{\cdot}7\mu$ where the calcite reflects metallically, the radiometer readings were in the ratio 90 : 50. This shows conclusively that calcite transforms plane-polarised waves into elliptically-polarised waves within the region of metallic reflection.

In addition to the great number of researches which have been made into the domain of residual rays, very valuable work has been done by Paschen[1] and others on the selective emission spectra of elements in the infra-red region. This work is especially important in connection with the problem of series of lines in spectra, and an account of the values obtained by these authors will be found in Chapter XVII. A few words, however, may be said here as regards the apparatus and method employed by Paschen. He used in his experiments either a bolometer or a very sensitive thermopile. This latter instrument was of the Rubens pattern, but was much

[1] *Ann. der Phys.*, **27.** 537 (1908), **29.** 625 (1909), **33.** 717 (1910). Randall, *Ann. der Phys.*, **33.** 739 (1910). Moll, *Konink. Akad. Wetensch. Amsterdam. Versl.*, **15.** 469 (1907).

improved in sensibility. The thermocouple was made of iron and constantan. The measurements in the case of thallium and the alkali metals extended as far as 5·4μ.

The Extreme Ultra-Violet Region.—It was described in the introduction how the discovery of the ultra-violet region was made first by Ritter and by Wollaston. This region was first photographed by E. Becquerel by projecting it upon paper coated with silver chloride, when he observed the continuance of the Fraunhofer lines as far as he was able to reach in this region. Investigations were carried out in this region by Stokes,[1] who made use of a quartz prism apparatus, and observed the spectrum visually by projecting it upon a fluorescent screen. He observed in this way the solar spectrum to about $\lambda = 3000$, which is the limit set by the absorption of the rays by the atmosphere. The spectrum of the electric spark, however, he traced much further, and found that aluminium in the spark emitted rays of the smallest wavelength he was able to reach—in fact, he observed the pair at $\lambda = 1860$ and $\lambda = 1850\mu$. Mascart was the first to make measurements in this region by means of photography, which he succeeded in doing with the help of gratings. These gratings he placed always in the position of minimum deviation (see p. 204), and by means of an ordinary spectrometer, with a small camera put in place of the eyepiece, he took photographs of very small regions of the spectrum. The cross wires were not removed from the eyepiece, and they therefore cast a shadow upon the plate at the point corresponding to the reading of the telescope upon the divided circle of the instrument. From this he was able to measure the angular deviations of the various lines, and thus obtain their wavelengths. The actual determinations were not particularly accurate. Attention may, however, be drawn to the fact that Mascart and also Soret fixed upon certain lines in the spectra of cadmium and other elements, and numbered them as standards of reference. These lines, especially those in the ultra-violet, are often referred to by their numbers, so they

[1] *Phil. Trans.*, **142.** 463 (1852), and **152.** 599 (1862).

may be given here with their wave-lengths; the latter, however, are the most recent determinations.

No.	Wave-length.	Observer.	No.	Wave-length	Observer.
Cd 1	6438·71	P.	Cd 15	2980·75	K. & R.
Cd 2	5378·4	P.	Cd 16	2837·01	K. & R.
Cd 3	5339·7	P.	Cd 17	2748·68	K. & R.
Cd 4	5086·06	K. & R.	Cd 18	2573·12	K. & R.
Cd 5	4800·09	K. & R.	Cd 19	2499·90	K. & R.
Cd 6	4678·37	K. & R.	Cd 20	2470 0	E. & V.
Cd 7	4415·9	E. & V.	Cd 21	2418·2	E. & V.
Cd 8	3988·4	E. & V.	Cd 22	2321·23	K. & R.
	3984·7	E. & V.	Cd 23	2312·95	K. & R.
Cd 9	3613·04	K. & R.	Cd 24	2261·13	K. & R.
	3610·66	K. & R.	Cd 25	2194·67	K. & R.
Cd 10	3467·76	K. & R.	Cd 26	2144·45	K. & R.
	3466·33	K. & R.	Zn 27	2098·8	
Cd 11	3403·74	K. & R.	Zn 28	2061·0	Double (Cornu)
Cd 12	3285·8	E. & V.	Zn 29	2024·3	
	3283·6	E. & V.	Al 30	1988·1	
Cd 13	3133·29	K. & R.	Al 31	1933·5	Double (Cornu)
Cd 14	3085·4	E. & V.	Al 32	1852·2	Double (Cornu)
	3081·0	E. & V.			

P = Paschen; K. & R. = Kayser and Runge; E. & V. = Eder and Valenta.

Somewhat similar methods were used by Cornu, Liveing and Dewar, and later by Hartley and Adeney, in their work on wave-length determination in the same region; the actual details of the work do not require more than this brief mention, because they can hardly be considered as of more than historical interest, since the modern method, with a concave grating, is far more accurate.

At the present time experimental work in the ultra-violet is perfectly simple, owing to the fact that the ordinary photographic plates are sensitive to these rays, so that it is an easy matter to work in this region, either with quartz prism apparatus or with the concave grating. In the first case, of course, for wave-length determinations, it is necessary to use

a comparison spectrum whose lines have previously been measured.

It is necessary that all lenses and prisms used in an apparatus for the ultra-violet should be made of quartz or, better still, of fluorite, on account of the absorption exerted upon these rays by glass or calcite. The first-named can now be obtained transparent to $\lambda = 2480$, but not further, while calcite possesses an absorption band beginning at $\lambda = 2150$, so that it cannot be used for rays of very short wave-length. It is generally stated that quartz is transparent to rays of as short a wave-length as $\lambda = 1850$, but this depends very much upon the thickness of the quartz traversed by the rays.

When it is desired to photograph the rays of very short wave-length, like Al Nos. 30, 31, and 32, several absorbing actions must be diminished as far as possible; these are exerted by the prism and lenses, by the air, and by the gelatine of the photographic plate. The first two may be remedied by using an apparatus with small dispersion so as to lessen the amount of material, and lenses of short focal length so as to lessen the thickness of the air traversed by the rays.

The absorptive power of quartz has been investigated by Schumann with the following results.[1] He made use of an apparatus with a single quartz prism of 60° refracting angle, and plano-convex lenses of 150 mm. focal length; the mean thickness of quartz traversed by the rays was 21 mm. With this apparatus the aluminium lines, Nos. 30, 31, and 32, were readily obtained upon a sensitive photographic plate. Exposures were then made of the spectrum of the spark between aluminium electrodes with quartz plates of different thicknesses placed in front of the slit, in order to obtain the comparative effect. The first plate was 3 mm. thick, and in this case a distinct weakening of the lines was noticed upon comparing photographs with and without the plate; this was especially the case with the line No. 32. The second quartz plate was 20 mm. thick, and again comparison photographs with and without the plate were taken. In this case complete absorption took place of all three lines, even with five minutes'

[1] *Wien. Ber.*, **102.** IIa, 415 (1893).

exposure, while without the plate five seconds were amply sufficient; the same was true, of course, for a 50·mm. plate. From these experiments it is possible to gain some idea of the absorptive power of quartz; they show clearly how necessary it is to use apparatus with small amount of material and short focal length in order to photograph the lines of aluminium Nos. 30, 31, and 32.

The actual absorption exerted by the air is not accurately known, those estimations of Cornu[1] being clearly too high, in which he said that 10 metres of air were sufficient to absorb rays of the wave-length $\lambda = 2118{\cdot}4$. Schumann succeeded in photographing Zinc 29 ($\lambda = 2024$) through 17 metres of air, and, after forty-five minutes' exposure with a slit 1·5 mm. wide, in just reaching aluminium No. 31 through 2 metres; this latter only proves the opacity of this thickness of air to such short waves. More important is the fact that Kayser and Runge with an air layer of 14 metres succeeded in measuring rays in the arc spectrum of arsenic with a wave-length of 2009 tenth metres.[2]

These observations, although not quantitative, are sufficient to prove the point emphasised above, that, in order to reach Al 32, it is necessary to use short layers of air.

Now, Al 32 represents the practical limit of the spectrum, as it is the utmost limit to which the ordinary spectrograph will reach.

We are, however, indebted to Schumann and to Lyman for the extension of our knowledge to a limit of $\lambda = 1030$. Schumann was the first to prove the existence of this short wave region, but he was unable to measure the wave-lengths of the lines owing to his using a prismatic apparatus and to his ignorance of the dispersion of any substance for these very short wave-lengths.

In order to extend beyond the limits of Al 32, it is necessary entirely to eliminate the three absorptive influences mentioned above. The first and simplest is to replace the quartz in the

[1] *Comptes Rendus*, **88**. 1885 (1879).
[2] *Abh. Berl. Akad.*, 1893.

apparatus throughout by fluorite, which has been found to be perfectly transparent to the rays as far as $\lambda = 1200$ A.U. It is hardly necessary to point out that this substance must be absolutely clear and faultless—at the present time it is of very great rarity. The absorptive action of the air is eliminated by working in a high vacuum, that is to say, the whole apparatus is exhausted as far as possible by a mercury pump, so as to enable the rays to pass from source to photographic plate without passing through any air at all. It is needless to point out how carefully such an apparatus must be made. Schumann describes two instruments, the second one being a perfected form of the first. It would take far too much space to describe the apparatus in its entirety, but a brief description of the essential parts will not be out of place.[1]

Schumann points out that the whole apparatus must be exhausted, and that the following adjustments must be so arranged as to be controllable from outside the apparatus, without disturbing the vacuum: (1) rotation of the slit round the collimator axis; (2) the width of the slit; (3) the length of the slit; (4) the position of the effective slit aperture (this adjustment being for the purpose of taking adjacent spectra upon the plate for wave-length determination; (5) focussing of both collimator and camera lenses; (6) adjustment for minimum deviation; (7) adjustment of the angle between camera and collimator, so as to enable different regions of the spectrum to be photographed; (8) adjustment of the tilt of plate in the camera; and (9) movement of the plate in a vertical plane. All these adjustments Schumann has arranged for in his instrument, which may be briefly described as follows:—

Fig. 111 is a diagram of the principal part of the system, namely, the central bearing, in sectional deviation; *a* is the central cone, which is firmly screwed to the centre of a strong tripod stand, *d*, a lock nut being shown at *e*. This cone is bored out in the centre, and forms the prism chamber; it has a cover, *c*, accurately fitted upon the top. Over the outside of the cone *a* is fitted the hollow cone *b*, which is accurately ground upon *a*, so that a perfect fit is obtained all over the

[1] *Wien. Ber.*, **202.** IIA, 625 (1893).

surface. The collimator tube is fastened to the inner cone *a*, while the camera tube is fastened to the outer cone *b*; this

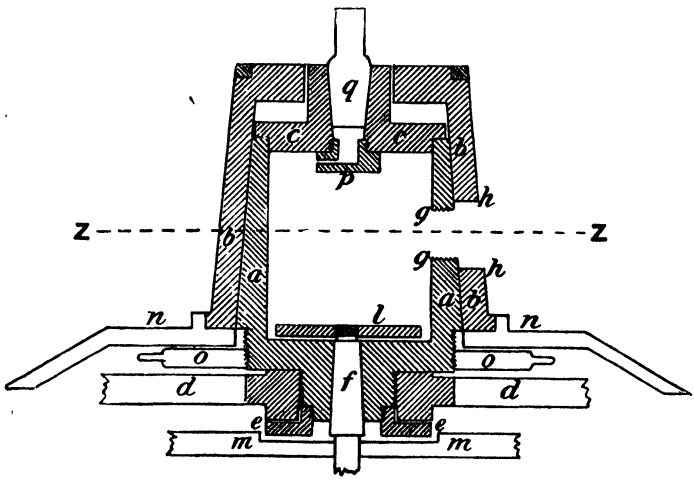


FIG. 111.

allows the latter to be rotated round the central vertical axis of the instrument. The method of attachment of the collimator and camera tube is shown in Fig. 112, which is a diagram of a horizontal section cut along the dotted line ZZ of Fig. 111.

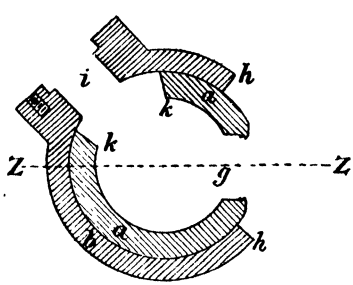


FIG. 112.

The collimator is screwed into the inner cone *a* at *g*, and the outer cone *b* is slotted from *h* to *h* to permit of its rotation within the necessary limits; the telescope is screwed on to the outer cone *b* at *i*, while the inner cone is slotted from *k* to *k*, to allow the passage of the rays from the prism.

As will be seen in Fig. 111, the bottom of the inner cone *a* is conically bored, and into this is fitted the plug *f*, which is

screwed into the disc *l*; the plug *f* is held in position by lock-nuts to prevent its falling out when the apparatus is not exhausted. The disc *l* is the platform upon which the prism table rests; this may be rotated by turning the plug *f*, which may readily be done by means of a large milled head upon its lower end. The two arms *m*, *m* are fixed to *f*, and are fitted with verniers reading upon a divided circle, so as to enable the position of the prism to be read at any time. A similar purpose is served by the arms *n*, *n*, which are provided with verniers reading upon the same divided circle; these give the rotation

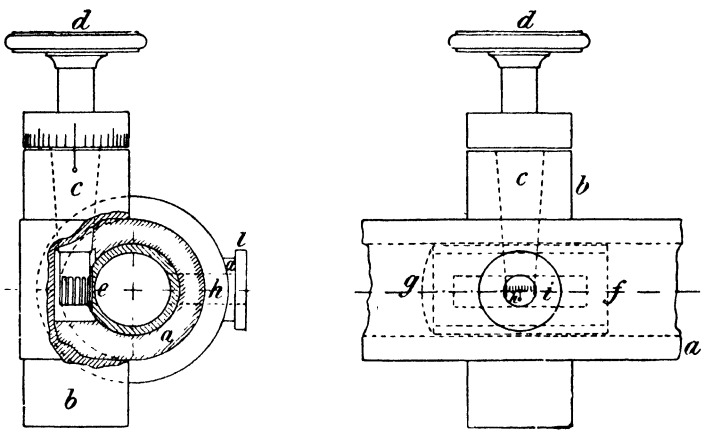


FIG. 113.

of the camera tube, and hence the angle of deviation. Attention may be drawn to the ring *o*, which is screwed on to the inner cone *a*, and is provided with lugs; by screwing up the ring *o* one is enabled to raise the outer cone off the inner one, if by any chance it has become fixed by remaining in one position too long.

The upper lid *c* is conically bored in the centre, and the glass tube *q* is ground therein; this tube connects directly with a mercury pump; a plug is screwed in at *p* to restrain the flow of air when the apparatus is suddenly exhausted or opened when vacuous to the atmosphere.

A diagram of the arrangement for focussing is shown in Fig. 113, in plan and end elevation. *a* is a portion of the collimator or camera tube, and *b* is a round metal block soldered to the side. The plug *c* is ground into a conical hole drilled in *b*, and carries a pinion wheel, *e*, which engages in a rack, screwed to the inner tube *f*, which carries the lens at *g*; the plug *c* is fitted with a milled head, *d*, whereby it may be turned. In order to know the position of the inner sliding tube *f*, on

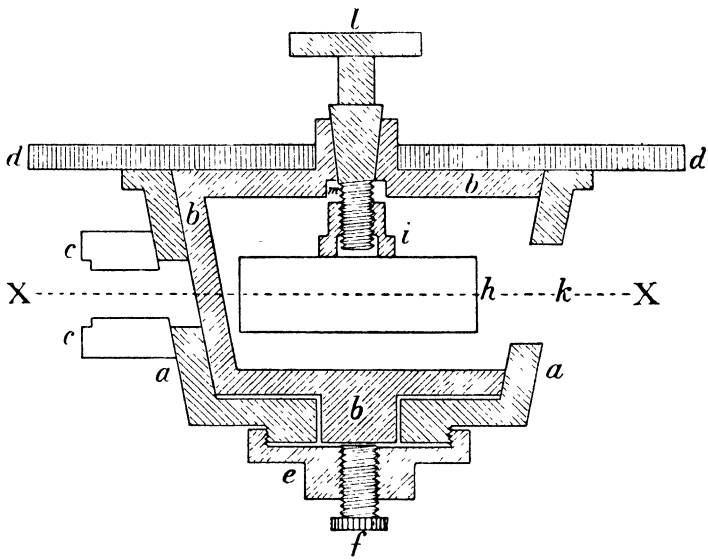


FIG. 114.

the opposite side of the tube *a* is a hole cut at *h*; and this is hermetically sealed with a glass plate *i*; the sliding tube is ruled in millimetres, and its position may be read off against a zero mark upon the tube *a*.

The camera itself very much resembles a stop-cock placed in a vertical position. Fig. 114 represents the camera in sectional elevation, and Fig. 115 a horizontal section through the axis of the telescope tube, *i.e.* through the line XX. The outer barrel of the apparatus is shown at *a*, and the inner

conical fitting at *b*, the two cones being very accurately ground together. The inner part of *b* is cut away, as shown in the two diagrams, while the camera tube is securely fastened on to the barrel *a* at *c*. Two lugs, *d*, *d*, are screwed on to the top of *b*, and serve as handles for the rotation of *b*. The top of *a* is divided for a short distance in degrees to enable the rotation of *b* to be measured. On to a projection under *a* is screwed a nut *e*, into which again *f* is screwed; this, as before described for the main conical bearing, is for the purpose of loosening the cone *b* if it has got jammed in *a*.

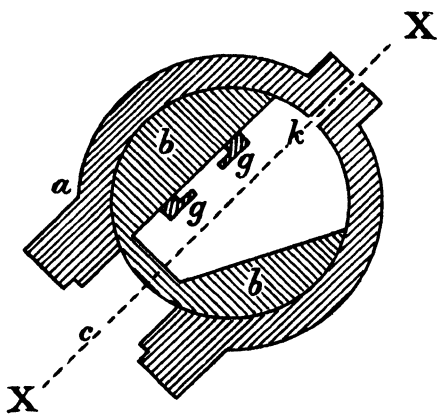


FIG. 115.

For the vertical motion of the plate the following device is adopted: On the back of the opening in *b* is a long vertical slide running from top to bottom—this is not shown in Schumann's diagram, but may be represented by the slotted pieces *g*, *g* (see Fig. 115). The sliding piece in these two ways is fastened to a frame, *h* (Fig. 114), into which slides the plate-carrier. This sliding piece is also fastened to the nut *i*, in which works the screw *m*, which forms part of the plug *l*. This plug *l* is ground in to a conical hole bored in the top of the inner cone *b*. Thus, by simply rotating this plug, the plate can be raised or lowered as required; the amount it is raised or lowered can be directly read off upon a scale by means of a divided drum, not

shown in the diagram. The slot *k* cut in the outer cone *a* is for the purpose of putting in or taking out the plate carrier, which is done by means of a key. In the diagrams the inner cone *b* is so turned that the plate may be put in; when this has been done, *b* is turned round so as to bring the opening opposite to the camera-tube end, and set the plate at the proper angle to the axis of the camera lens. The plate carrier has no cover, and therefore the changing of a plate must be done in the dark or ruby light. The size of plates actually used by Schumann is 37 × 12·5 mm., and the amount of possible vertical shift that can be given to the plate is 9 mm.

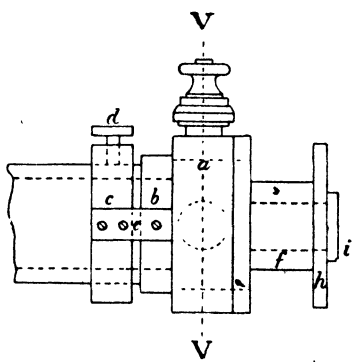


FIG. 116.

The slit is a very complex mechanism, and is shown in Figs. 116 and 117; the former is a diagram of the apparatus in elevation, and the latter a view of the slit mechanism obtained by cutting a section through the line VV. In Fig. 117 only the essential parts are shown, as Schumann's drawing is very complicated, and hardly suited for reproduction. The main chamber containing the slit mechanism is shown at *a*; the plate *b*, which is securely screwed to *a*, is ground flat on the outer face, and this is held up against the similarly ground end of the collimator tube; a small quantity of grease makes a perfectly airtight joint. The slit is centred and held in position by the collar *c* and the set-screw *d*, the former being fastened to the plate *b* by two straps, one of which is shown at *e*. The slit cover consists of a tube, *f*, which also has a ground end, and is thus held by the atmospheric pressure against the slit chamber *a*. The plate *h* is screwed to the end of the tube *f*, and *i* is a fluorite plate cemented on to *h*. The reason for these fittings will be given below. The slit mechanism proper is shown in Fig. 117, and consists of a vertical and horizontal

slit; the vertical slit, or slit proper, consists of one fixed jaw and one jaw movable by a micrometer screw; the horizontal slit also consists of one fixed and one movable jaw, but there is an additional arrangement by which the whole of this slit can be bodily moved without altering its width. The two slits are immediately behind one another, there being about

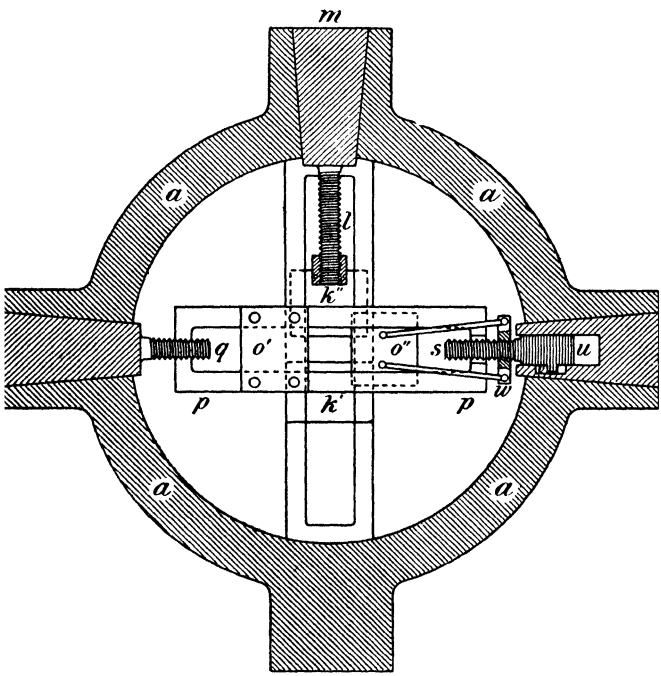


FIG. 117.

0·01 mm. clearance between the two sets of jaws. Inside the frame *a* is a strong back plate, on which the jaws are mounted, but this plate is not shown in the diagrams; the jaws of the vertical slit are shown at *k'k''*, and these are fitted in grooves mounted on the back plate. When the apparatus is mounted, it is so placed that the edges of the jaws *k'k''* are parallel to the refracting edge of prism. One of the jaws, *k'*,

is screwed to the back plate, while the other is moved by the micrometer screw *l* with a pitch of 0·2 mm., which projects from the taper plug *m*; this plug, like all the others, is carefully ground into a conical hole bored in *a*, and is provided with the usual apparatus for measuring its rotation.

The jaws of the horizontal slit are shown at *o'* and *o''*, and are fitted to grooves on the frame *p*, which works in grooves on the back plate; the micrometer screw *q*, of 0·5 mm. pitch, works in a nut fastened to *p*, so that by turning the taper plug *r* the frame *p* carrying the whole horizontal slit can be moved to and fro. The micrometer screw *s*, of 0·2 mm. pitch, also engages in a nut on the frame *p*, but does not form part of the taper plug *t*; this plug *t* is centrally bored for some distance, and in this hole fits the cylinder *u*, which is an extension of the micrometer screw *s*. On the side of *u* is a small pin, *v*, which slides in a groove cut in the inside of the plug *t*. It thus follows that when *t* is turned the screw *s* is made to revolve; but when by means of the plug *r* the frame *p* is made to travel backwards or forwards, the cylinder *u* simply slides in or out of the boring in the plug *t*. There is a small ring, *w*, fitted to the spindle *su*, which is connected by a light framework to the movable jaw *o''*; the ring *w* does not rotate with the screw *s*, and is held in position by a collar on each side, so that when *s* is screwed in or out of its nut on the frame *p*, the jaw *o''* is moved in or out. Each of the plugs is fitted with an apparatus for measuring the rotation, and in this way the travel of the slit jaws can be found at any time; further, on the plug *m* there is a stop fixed so that the jaws cannot be brought into contact; this stop, in Schumann's apparatus, limits the width of the slit to 0·007–·02 mm., which is quite sufficient for ordinary work, but if required the stop may be removed and wider slit breadths obtained. These two diagrams of the slit give all the essential points of Schumann's arrangement, but of course certain details are omitted, such as the springs to obviate the backlash of the screws, the slit grooves, etc. For more complete designs the original memoir must be consulted.

Only one detail of construction now remains to be

described, namely, the arrangement by means of which the rotation of the various taper plugs controlling the different adjustments is measured. These are shown in sectional and ordinary elevation in Figs. 118 and 119 respectively. The taper plug is shown at *a*, and the divided drumhead at *b*; this is accurately fitted to the plug *a*, and is fastened thereon by the nut *c*. Fitting accurately upon the outer cylinder *e* is a double-walled ring-piece, *d*, upon which a screw-thread is cut which engages, as shown, into a similar thread cut upon the inner side of the drum *b*. The ring-piece *d* is not permitted to rotate upon *e*, but is prevented by means of a pin working in a slot.

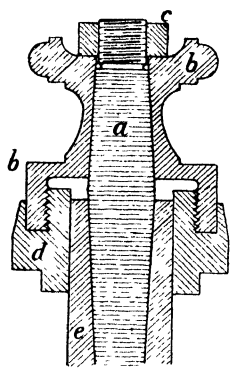


FIG. 118.

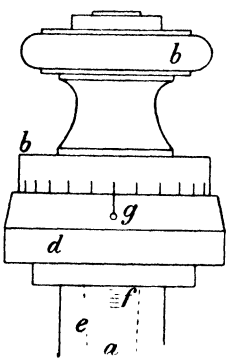


FIG. 119.

It follows that, as the taper plug *a* is turned, the ring-piece *d* is caused to move up or down, and its travel may be measured upon a scale at *f* (Fig. 119). This scale is so arranged that one division corresponds exactly to one whole revolution of *a*, the fractions of a turn being read off the divided drumhead at *g* (Fig. 119). This arrangement is common to all the adjusting plugs in Schumann's apparatus.

In carrying out work on the extreme limit of the ultra-violet spectra, it is necessary that the air layer between the source and the cover-plate of the slit of the vacuum spectrograph should be as small as possible. In the case of the spark discharge Schumann succeeded in bringing the electrodes

within 1 mm. of the cover-plate; this distance was, therefore, the total amount of air traversed by the rays. A series of photographs of the spectra of various metals has in this way been obtained; it has, unfortunately, not been found possible to remove this air layer entirely. The spectrum of the discharge through vacuum tubes, however, can more easily be dealt with, because an ordinary "end-on"[1] tube may be used; such a tube has no transparent plate of its own sealed to the end, but is directly fitted on to the fluorite cover-plate of the slit. The end of the tube is greased and put in position on the fluorite plate, so that when exhausted it holds itself quite securely without any further support. In this way Schumann succeeded in photographing the spectrum of hydrogen down to an estimated wave-length of $\lambda = 1200$ A.U. It may again be pointed out that it is quite impossible to measure wave-lengths by the prism in this new region, where nothing is known at present about the dispersion of fluorite; the estimated limit of $\lambda = 1200$ A.U. was arrived at by assuming the applicability of the known dispersion formula for fluorite.[2]

The following may be quoted from Schumann's paper as a report of the results he has achieved. Of all the substances yet examined hydrogen alone gave a spectrum reaching the furthest limit; next follow the metals aluminum, cadmium, cobalt, copper, magnesium, lead, thallium, and tungsten, all of whose spectra end somewhere about $\lambda = 1700$; this, however, is undoubtedly due to the layer of air unavoidably present in the path of the rays. The atmospheric air absorbs these rays with great ease, as it has been found that a layer 1 mm. thick at 760 mm. pressure entirely absorbs all the rays below $\lambda = 1700$ A.U.

In the experiments upon the spectrum of hydrogen the vacuum tube was in connection with the whole of the apparatus, so that this became filled with hydrogen as well as the vacuum tube itself. The rays on their journey to the plate had to pass through an atmosphere of hydrogen under reduced pressure, and it was found that this hydrogen exerted no absorptive

[1] See p. 423. [2] See p. 95.

power upon the less refrangible of the new rays, and probably none on those most refrangible. The new spectrum of hydrogen is one of considerable extent, consisting of fifteen groups of lines which are equally distributed; there may be as many as a hundred lines. The maximum brightness lies about $\lambda = 1620$, so that for this region a few minutes' exposure was sufficient, while as many hours were required for the most refrangible rays.

It was mentioned above that the gelatine of the photographic plate exercises a very great absorption upon these rays of short wave-length; Schumann has investigated the amount of this absorption, and has devised special methods for the manufacture of plates suitable for this region, in which the gelatine is either reduced to a minimum or done away with altogether; in the latter case a deposit of pure silver salt is employed. In his investigations on the absorptive power of gelatine, Schumann employed films of this material of different thicknesses, from 0·13 mm. to 0·00004 mm., which he prepared by allowing a definite quantity of gelatine solution of known strength to dry upon a glass plate.

It was found that a film of 0·13 mm. thickness possesses an absorptive power which extends over the whole ultra-violet region, and reaches even into the visible spectrum; the absorption is practically complete beyond $\lambda = 2470$. A film of 0·01 mm. gave total absorption beyond $\lambda = 2266$; while the extreme case of 0·00004 mm. gave a distinct weakening of the extreme ultra-violet rays, which was even noticeable in the case of the lines $\lambda = 2061$ and 2024. These experiments prove conclusively that a gelatine emulsion plate is of absolutely no use for work on the extreme rays; Schumann also found that egg albumen and collodion were just as useless. The special methods employed by Schumann for making his plates will be given in the chapter on the photography of the spectrum (p. 375).

Recently Lyman has carried out an investigation into the wave-lengths of the lines in this extreme ultra-violet region.[1] He modified Schumann's apparatus somewhat, and substituted

[1] *Astrophys Journ.*, **19.** 263 (1904); **23.** 181 (1906).

a grating for the fluorite prism. The particular grating used was especially ruled so as to concentrate the light as much as possible in one order and as a matter of fact his grating gave a first order spectrum of exceptional brilliancy. Lyman turned his attention to the measurement of the lines of hydrogen in this region. In Schumann's apparatus the optical parts were made of fluorite, and as Lyman has found that even the best quality of this material absorbs all light beyond the limit $\lambda = 1200$, it follows that Schumann's spectra could not have extended beyond this. As a result of his measurements Lyman has been able to attach a wave-length scale to Schumann's spectra and has found that the most refrangible line contained therein has a wave-length of $\lambda = 1267$. Lyman has been able to carry his measurements to as far as $\lambda = 1030$, which establishes a considerable extension beyond Schumann's limit. It is very interesting to note in passing that the speculum metal on which the grating was ruled still possesses reflecting power for rays of such short wave-length. Lyman has succeeded in the measurement of the wave-lengths of about 300 hydrogen lines with an accuracy of not less than 0·3 Ångström, and he has, moreover, found that the secondary spectrum does not extend beyond the limit of $\lambda = 2000$. Lyman in a later paper dealt with the absorption of air for very short wave-lengths and showed that the absorption is in reality due to the oxygen which exhibits a strong absorption band between the limits $\lambda = 1760$ and $\lambda = 1270$ for a column of the gas 0·91 cms. thick and at atmospheric pressure.[1] Recently Lyman[2] has published some results on the emission spectra of certain other gases, more particularly nitrogen and argon, in this extreme ultra-violet region.

He gives the wave-lengths of lines in the blue argon spectrum, *i.e.* the spectrum obtained with a Leyden jar, and the spectrum of nitrogen. In the case of the argon spectrum 39 lines were measured between the limits of $\lambda = 1886{\cdot}1$ and $\lambda = 1333{\cdot}7$. In the case of nitrogen both the band spectrum and line spectrum were observed in this region. One

[1] *Astrophys. Journ.*, **27**. 87 (1908).
[2] *Ibid.*, **33**. 98 (1911).

consists of faint bands degraded towards the red, the other consisting of two pairs of sharp lines. The first spectrum is produced when no condenser is used and while the second is faintly visible under the same conditions it is very much enhanced by the introduction of capacity.

Some measurements have also been made by Morris-Airey[1] of lines in the extreme ultra-violet region in the spectrum of aluminium. A vacuum spectrograph was employed with a transmission grating of 500 lines to the millimetre, ruled on a fluorite plate. The wave-lengths determined were :—$\lambda\lambda$ = 1785, 1741, 1709 and 1693.

[1] *Manchester Lit. and Phil. Soc.*, **49. 3. 1.** (1905).

CHAPTER IX

THE APPLICATION OF INTERFERENCE METHODS TO SPECTROSCOPY

By an interference spectroscope, or interferometer, is meant an apparatus in which a beam of light, coming from a single source, is divided into two portions, which by some means or other are caused to suffer a different amount of retardation, so that, when they are reunited, interference is produced. Michelson was the first to make use of such an apparatus in spectroscopic work, and he was thereby able to bring a much greater resolving power into play than had been possible before. By means of his apparatus, which is known as a refractometer or interferometer, Michelson has studied the structure of radiations or spectrum "lines," which are so far homogeneous as to be beyond the resolving power of the largest gratings, and he has also determined the wave-lengths of certain radiations in the spectrum of cadmium in terms of the standard metre. These wave-lengths were measured with an extraordinary degree of accuracy, and serve as the standards of all interference measurements; as we shall see in the sequel, Fabry and Perot have succeeded in the determination of the wave-lengths of certain lines in the solar spectrum and in the spectra of certain metals by a method of comparison of these with Michelson's cadmium values. There are certain differences between the values of these constants and those which were obtained by Rowland, and, therefore, on account of the greater inherent accuracy of interference methods the former have been adopted as the reference standards for all spectroscopic work.[1]

[1] See Chapter II., p. 47.

A diagram of Michelson's interferometer is shown in Fig. 120.[1]

The rays from the source V pass through one or more prisms, in order to separate the various radiations from one another, and are focussed upon the slit S; in this way any particular radiation can be separately examined. The light passing through the slit is rendered parallel by the collimating

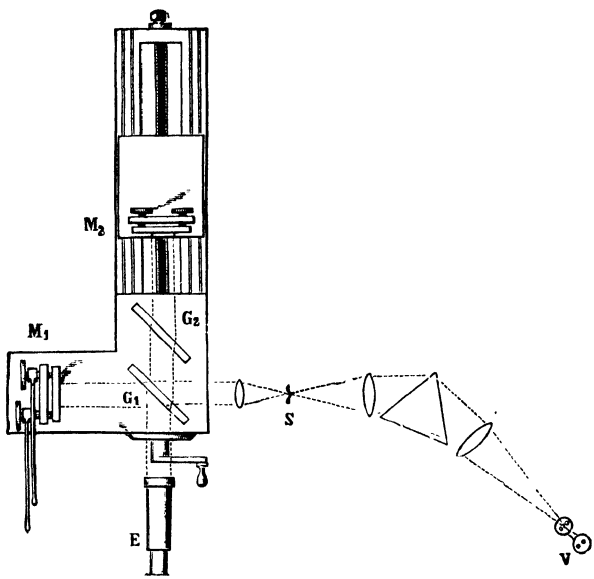


FIG. 120.

lens, and falls upon the plane parallel plate G_1, which is set at an angle of 45° to the path of the light beam. The front surface of this plate is half silvered, so that a portion of the incident ray is reflected, while the remainder passes through the plate. The first portion travels to the movable plane mirror M_2, and the second to the fixed mirror M_1. These mirrors return the light to the silvered surface of G_1, where the first portion is transmitted and the second reflected, so that

[1] *Phil. Mag.* (5), 34. 200 (1892).

both portions coincide and enter the telescope E. As regards the thickness of the silver layer on G_1, Michelson remarks "that the light entering the telescope is a maximum, when the thickness of the silver film is such that the intensity of the transmitted light is equal to that of the reflected light. The silvering has another important advantage, in diminishing the relative intensity of the light reflected from the other surface. Indeed, for this purpose it is advisable to make the film heavier, even so thick that the reflected light is twice as bright as the transmitted. This does not affect the ultimate ratio of intensities of the interfering pencils, for what is lost by transmission on entering the plate G_1 is made up by reflection on leaving it, the effect being simply to diminish somewhat the whole intensity. Another advantage of the thicker film is that it can be made uniform with far less difficulty than the thin film."

The two mirrors are provided with screws for purposes of adjustment, and M_2 is mounted on a sliding carriage, which is moved by a micrometer screw of 1 mm. pitch. The pencil of rays, which is in the first place transmitted by the silver layer on G_1, as will be seen, passes three times through the plate G_1; an exactly similar plate, G_2, is placed at an angle of 45° in the path of the other pencil in order to compensate for the retardation thus caused.

Now, if there be no difference in path travelled by the two pencils, *i.e.* if the distances from the silver layer to the two mirrors be equal, there will be no interference. If, however, a small difference be introduced by the moving of M_2, then interference fringes will be seen in the telescope as a series of concentric circles. These fringes are produced in exactly the same way as by a film or plate of air between two plane surfaces; in other words, they are the same phenomenon as Newton's rings.

Michelson gave the theory of these interference bands,[1] and showed that the position of maximum distinctness is given by the formula—

$$P = \frac{t_0}{\tan \phi} \tan i \cos^2 \theta,$$

[1] *Phil. Mag.* (5), 13. 236 (1882).

where P is the distance of the plane of maximum distinctness from the mirrors, t_0 the thickness of the equivalent air plate where it is cut by the axis of the telescope, ϕ the inclination of the two surfaces, and θ and i the components of the angle of incidence parallel and perpendicular to the intersection of the surfaces.

If, now, θ be small, the variation of P with θ may be neglected, and therefore—

$$P = \frac{t_0}{\tan \phi} \tan i,$$

or, with sufficient accuracy—

$$P = \frac{t_0}{\phi} i.$$

The focal plane, therefore, varies very rapidly with i, so that, unless $\phi = 0$, it is impossible to see all parts of the interference bands with equal distinctness.

Putting $\phi = 0$, that is, making the surfaces truly parallel, then $P = \infty$, so that if the bands be observed with a telescope focussed for infinity the interference fringes will be equally distinct in all parts; they will thus be concentric circles whose angular diameter is given by—

$$\cos \theta = \frac{\Delta}{2t_0},$$

where Δ is the difference in path between the two pencils. If instead of Δ we put $2t_0 - n\lambda$, and for $\cos \theta$ its approximate value $1 - \frac{\theta^2}{2}$

then

$$\theta_n = \sqrt{\frac{n\lambda}{t_0}}.$$

If in the above apparatus the mirror be so set that there is no difference in path between the two pencils, the illumination obtained in the telescope will of course be a maximum; if now the mirror M_2 be moved away 1 mm., a difference of path will be set up of 2 mm., and a series of fringes will be seen. Michelson[1] estimates the "visibility" of these fringes,

[1] *Phil. Mag.* (5), **34**, 280 (1892).

the visibility being found from the expression $V = \frac{I_1 - I_2}{I_1 + I_2}$, where I_1 is the intensity at the centre of a bright band and I_2 the intensity at the centre of the adjoining dark band. This visibility is determined for each successive shift of the mirror M_2 1 mm. outwards, and the values thus obtained are plotted on a curve, the ordinates expressing visibility and the abscissæ differences of path. This visibility curve has various forms depending upon the distribution of light in the radiation examined, and the actual structure of the spectrum "line" can be elucidated by studying the curve obtained.

Before, however, proceeding to discuss the shapes of the visibility curves, it may be pointed out that Michelson drew up a table of corrections to be applied to the visually estimated values, in order to reduce them to the true values, *i.e.* a table of corrections for personal error. This was done in the following way: An apparatus was set up in which interference bands were produced, and in which the two values I_1 and I_2 could be obtained from the constants of the apparatus. The values were also observed and estimated; by comparing the values obtained for the visibility by the two methods, the personal error could be determined.

Two quartz lenses, one concave and the other convex, but of equal curvatures, were mounted with their crystalline axes at right angles to each other between two Nicols. Under these conditions a series of concentric interference rings appeared. If α be the angle between the principal section of the polariser and the axis of the first quartz, and ω the angle between the axis of the second quartz and the analyser, the intensity of the light transmitted will be—

$$I = \cos^2(\omega - \alpha) - \sin 2\alpha \sin 2\omega \sin^2 \pi \frac{k(t_1 - t_2)}{\lambda},$$

where t_1 is the thickness through the first quartz, and t_2 that through the second. If the analyser and polariser are parallel, then $\omega = \alpha$,

and $$I = 1 - \sin^2 2\alpha \sin^2 \pi \frac{k(t_1 - t_2)}{\lambda},$$;

whence $I_1 = 1$, and $I_2 = 1 - \sin^2 2\alpha$,

and $$V = \frac{I_1 - I_2}{I_1 + I_2} = \frac{1 - \cos^2 2\alpha}{1 + \cos^2 2\alpha}.$$

The visibility of the fringes in this apparatus was observed and estimated for all values of α, and was also calculated from the expression $\frac{1 - \cos^2 2\alpha}{1 + \cos^2 2\alpha}$; both sets of values were plotted against the values of α. The two curves differed in shape slightly, and a table of corrections was drawn up which was to be applied to all estimations of visibility, in order to correct the personal error in assessment of the intensities and to reduce them to the true values. These corrected values were used for the visibility curves.

The interpretation of these visibility curves is based on the following.[1]

Michelson first showed that the visibility is given by—

$$V^2 = \frac{S^2 + C}{P^2},$$

where $P = \int \phi(x)dx$,

$C = \int \phi(x) \cos 2\pi D x dx$,

and $S = \int \phi(x) \sin 2\pi D x dx$.

In these expressions D is the difference in path between the two pencils, and $\phi(x)$ is the distribution of intensity in the source, that is to say, in the radiation examined. By $\phi(x)$ is meant the curve of intensity in the spectrum line with abscissa x in oscillation frequencies and ordinate some function of x. In Fig. 121 is shown such an intensity curve of a spectrum line; the abscissæ x are expressed in oscillation frequencies, and it will be noticed that they are measured from the centre of the line. The function of x expressed upon the ordinates is $e^{-0{\cdot}013x^2}$, where e is the base of natural logarithms. Now, Michelson introduced various values of $\phi(x)$ into the above expressions, and calculated the value of the visibility. As, however, the actual experimental observations only agreed with the distribution of intensity as given by Maxwell's law,

[1] *Phil. Mag.* (5), **31**. 338 (1891).

we will only discuss this particular case. The distribution of intensity is given by this law to be $\phi(x) = e^{-\beta\frac{x^2}{a^2}}$, which is expressed graphically in Fig. 121.

It must be remembered that in the expressions for P, C, and S given above the limits of integration are of course the limits of the illumination; if, now, the illumination be perfectly symmetrical, as shown in Fig. 121, then clearly S vanishes, and we have therefore—

$$V = \frac{C}{P}.$$

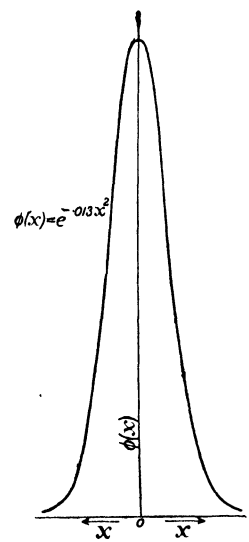


FIG. 121.

Now, Michelson at first assumed the symmetrical distribution of intensity, and afterwards found that this was justified.

If, now, Δ be the extreme difference in wave-length of the radiations in question, and Δ_0 the smallest difference that can be resolved by a grating having as many lines, N, as there are wave-lengths in the difference of path,

then $$\Delta = \lambda_1 - \lambda_2,$$

where λ_1 and λ_2 are the wave-lengths of the extreme rays. If we put the difference in frequency between these rays $= a$, then we have—

$$a = \frac{1}{\lambda_2} - \frac{1}{\lambda_1} = \frac{\lambda_1 - \lambda_2}{\lambda^2},$$

if λ = the mean of λ_1 and λ_2.[1]

Therefore $$\Delta = \lambda_1 - \lambda_2 = a\lambda^2.$$

Again $$\frac{\lambda}{\Delta_0} = N, \text{ and thus } \Delta_0 = \frac{\lambda}{N},$$

[1] Strictly speaking, the geometric mean.

therefore $$\frac{\Delta}{\Delta_0} = \frac{a\lambda^2}{\frac{\lambda}{N}} = aD,$$

where D, as above, = Nλ = the difference in path. The ratio $\frac{\Delta}{\Delta_0}$ is denoted in the following by the letter n.

Amongst the several values used by Michelson for $\phi(x)$ in the calculation of the visibility curves, the most important is —

$$\phi(x) = e^{-p\frac{x^2}{a^2}},$$

which is the distribution resulting from Maxwell's law. The visibility curve is then given by—

$$V = e^{-\frac{\pi^2 n^2}{p}},$$

which is not periodic.

If there are two sources, then Michelson shows that the visibility is given by—

$$V_2^2 = \frac{1 + r^2 + 2r\cos 2\pi\frac{X}{D}}{1 + 2r + r^2} V^2,$$

where r is the ratio of intensities in the two sources, X is the abscissa of the visibility curve, that is to say, the difference in path, and D the period of the curve, which is inversely proportional to the distance between the components.

If now, as before,

$$\phi(x) = e^{-p\frac{x^2}{a^2}},$$

then we have $$V_2 = e^{-\frac{\pi^2 n^2}{p}} \sqrt{\frac{1 + r^2 + 2r\cos 2\pi\frac{X}{D}}{1 + 2r + r^2}}.$$

Michelson now considers the "half-width" of the spectrum line; by the "half-width" is meant the value of x when $\phi(x) = \frac{1}{2}$. It must be remembered that $\phi(x)$ represents the curve of distribution of intensity in the line obtained by putting the values of the oscillation frequency on the abscissæ and

those of $\phi(x)$ on the ordinates. The values of x are measured from the centre of the line, and therefore the true practical width of the line is about four times the "half-width." If we put δ equal to the half-width we then have—

$$\delta = x \text{ when } \phi(x) = \tfrac{1}{2}, \text{ that is to say, when } e^{-p\frac{\delta^2}{a^2}} = \tfrac{1}{2}.$$

Now,
$$e^{-p\frac{x^2}{a^2}} = e^{-p\frac{\delta^2}{a^2}\times\frac{x^2}{\delta^2}}$$
$$= \left(e^{-p\frac{\delta^2}{a^2}}\right)^{\frac{x^2}{\delta^2}}$$
$$= \left(\tfrac{1}{2}\right)^{\frac{x^2}{\delta^2}},$$

or
$$\phi(x) = 2^{-\frac{x^2}{\delta^2}}.$$

We have already seen that $V = e^{-\frac{\pi^2 n^2}{p}}$,

but
$$n = aX,$$

therefore
$$V = e^{-\frac{\pi^2 a^2 X^2}{p}}.$$

Now, as above,
$$e^{-\frac{p\delta^2}{a^2}} = \tfrac{1}{2},$$

therefore
$$\frac{p\delta^2}{a^2} = \log_e 2,$$

and
$$\frac{a^2}{p} = \frac{\delta^2}{\log_e 2}.$$

Substituting this in the expression for V, we have—

$$V = e^{-\frac{\pi^2\delta^2 X^2}{\log_e 2}}.$$

Again, if we put Δ for X when $V = \frac{1}{2}$, that is, let Δ be the value of the abscissa of the visibility curve when $V = \frac{1}{2}$—

then
$$e^{-\frac{\pi^2\Delta^2\delta^2}{\log_e 2}} = \tfrac{1}{2},$$

and
$$-\log_e 2 = -\frac{\pi^2\Delta^2\delta^2}{\log_e 2}.$$

Thus
$$\log_e 2 = \pi\Delta\delta,$$

and $$\delta = \frac{\log_e 2}{\pi\Delta}$$

$$= \frac{0{\cdot}22}{\Delta} \text{ very nearly.}$$

This expression gives the value of the half-width in terms of oscillation frequencies; in order to convert into wave-lengths δ must be multiplied by λ^2.[1]

Substituting $\frac{\log_e 2}{\pi\Delta}$ for δ in the equation—

$$V = e^{-\frac{\pi^2 X^2 \delta^2}{\log_e 2}},$$

we have $$V = e^{-\frac{X^2 \log_e 2}{\Delta^2}}$$

$$= \left(2^{\frac{1}{\log_e 2}}\right)^{-\frac{X^2 \log_e 2}{\Delta^2}}$$

$$= 2^{-\frac{X^2}{\Delta^2}}.$$

Therefore the equation for two sources in which the intensity is distributed according to Maxwell's law is given by—

$$V_2 = 2^{-\frac{X^2}{\Delta^2}} \cos \frac{r}{D},$$

where the symbol $\cos \frac{r}{D}$ is put for the expression—

$$\sqrt{\frac{1 + r^2 + 2r \cos 2\pi \frac{X}{D}}{1 + r^2 + 2r}}$$

Michelson then applied these theoretical considerations to actual observations. He plotted the visibility curves for the radiations from different elements, most of which were excited by electric discharge in vacuo. In the case of the metals a

[1] If the width of a line in oscillation frequencies $= \frac{1}{\lambda_1} - \frac{1}{\lambda_2} = \frac{\lambda_2 - \lambda_1}{\lambda^2}$, while the width of the same line in wave-lengths $= \lambda_2 - \lambda_1$, therefore to convert the former into the latter it must be multiplied by λ^2. This is not strictly true; λ is really the geometric mean of λ_1 and λ_2.

vacuum tube containing some of the substance was placed in a box which was heated just sufficiently for the electric discharge to pass freely and to give a steady light, when the temperature was kept as steady as possible. The visual observations of the visibility were corrected for personal error from the curve of errors previously described, and when the visibility curve was drawn, a formula was found to express it as closely as possible, from which the distribution of intensity in the radiation was obtained.

The visibility curve of the red-hydrogen line is shown in the full curve in Fig. 122 (*b*); the dotted curve represents—

$$V = 2^{-\frac{X^2}{19^2}} \cos \frac{0{\cdot}7}{30}.$$

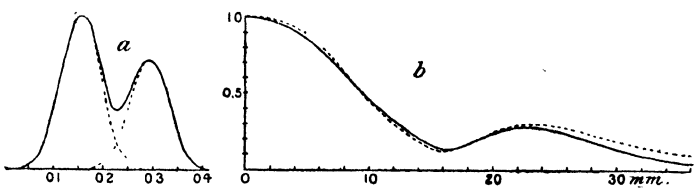


FIG. 122.

The visibility curve is therefore practically the same as that calculated for a double source whose ratio of brightness is equal to 0·7.

Now, D in the formula for V, or the period of the curve, is inversely proportional to the distance between the components of the pair of lines, this distance being measured as hitherto in oscillation frequencies. We may therefore put the distance between the wave-lengths of the two lines equal to $\frac{\lambda^2}{D}$. The formula for the hydrogen red line gives D = 30, and as $\lambda = 6{\cdot}56 \times 10^{-4}$ mm., we have for the separation of the two components—

$$\frac{(6{\cdot}56 \times 10^{-4})^2}{30} = 0{\cdot}14 \text{ A.U.}$$

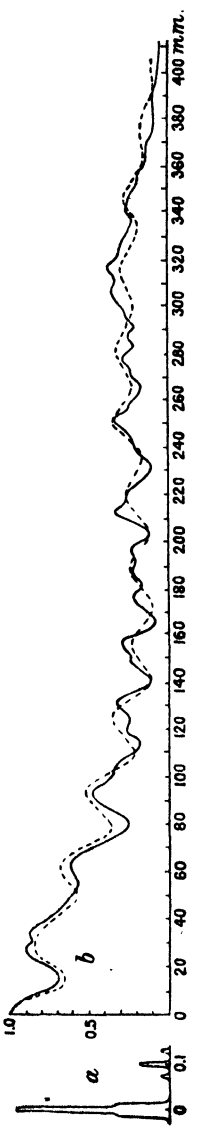


FIG 123.

Again, the formula gives $\Delta = 19$, whence we find that—

$\delta = 0{\cdot}0115$, or $0{\cdot}049$ in Ångström units. Therefore the half-width of each component is 0·049 A.U. From these data the curves in Fig. 122 (*a*) were drawn, the full curve showing the distribution of the intensity.

Similarly for the blue hydrogen line the equation of the visibility curve was found to be

$$V = 2^{-\frac{x^2}{24^2}} \cos \frac{0{\cdot}7}{28},$$

so that here again is a double line with 10 : 7 as the ratio of intensity of the components, $\lambda_1 - \lambda_2 = 0{\cdot}08$ A.U. and $\delta = 0{\cdot}057$ A.U.

The radiations from oxygen, sodium, zinc, cadmium, thallium, and mercury were also examined, and in many cases, notably that of the mercury green line, the sources were found to be very complex. The visibility curves are shown in Fig. 123, with the probable intensity curves of the radiations.

The cadmium lines were especially interesting on account of their narrowness. The curve of the red line at $\lambda = 6439$ agreed extremely well with the simple exponential curve—

$$V = 2^{-\frac{x^2}{138^2}}.$$

This line is evidently, therefore, a single line whose half width = 0·0065.

The green line at 5086 was found to be a close double, the intensity of whose components are in the ratio of

5 to 1; their distance apart is 0·022, and the half-width of each is 0·0048, in Ångström units.

Michelson and Benoit afterwards applied this interferometer to the determination of the length of the standard metre in terms of the wave-lengths of the cadmium lines,[1] these rays especially being chosen on account of their width being so small; they were found to be the most homogeneous of any rays examined. A description of the method would take up too much space, and it must suffice to give the final results obtained in air at 0° and 760 mm. pressure.

Red line, 1 metre = 1553163·5 λ, ∴ λ = 6438·4722 tenth metres.
Green line, 1 metre = 1900249·7 λ, ∴ λ = 5085·8240 „ „
Blue line, 1 metre = 2083372·1 λ, ∴ λ = 4799·9107 „ „

In the two last cases the principal component was measured.

For a description of the application of the interferometer to the study of long waved radiation see the Chapter on Infra-red, p. 282.

Following on Michelson's work, Fabry and Perot have applied interference methods to spectroscopy, and have devised an apparatus by means of which observations can be made with beautiful simplicity. The principle of Fabry and Perot's apparatus consists in the use of a film or layer of air enclosed between two plane parallel plates of glass. These two plates are half silvered on the inner sides, and set parallel to one another. The interference phenomena are obtained by allowing a beam of monochromatic light to pass through at normal incidence, and the fringes are observed in a telescope.

If a source of monochromatic light be examined through a thin layer of air enclosed between two parallel surfaces of glass a series of rather confused fringes will be seen on a uniformly illuminated background. It is clear that these fringes are produced by the interference between those rays which pass directly through the apparatus, *e.g.* the ray A, Fig. 124, and those which undergo double reflection, *e.g.* the ray B. After the ray B has been twice reflected, of course a small portion will undergo a further double reflection; the

[1] *Mém. du Bureau internat. des poids et mesures*, 11. 1 (1895).

intensities of this and of the multiple reflections generally, in the case of plain glass surfaces, are so small as to have no material influence. If f is the reflecting power of the glass[1] the relation between the minimum and maximum intensities of the fringes produced is given by the expression—

$$\rho = \left(\frac{1-f}{1+f}\right)^2.$$

With a glass having an index of refraction of 1·52, the value of f at normal incidence is equal to 0·042, whence $\rho = 0{\cdot}84$. There is thus but little difference between the intensity of the maxima and minima. If now by slightly silvering the surfaces the reflecting power be increased, the phenomena will present quite a different appearance. If, for example, $f = 0{\cdot}74$, then ρ is reduced to 0·02, that is to say, the minima become almost absolutely black. Further, the fringes are to be seen as very narrow brilliant lines separated by wide dark intervals. This effect is due to the multiple reflections, which become of considerable importance now that the reflecting power is increased, and it is necessary in dealing with the rays emerging from the apparatus to consider the interference which takes place between the rays directly transmitted and those which have undergone 2, 4, 6, etc., reflections. The fringes seen are due to the superposition of all these rays.

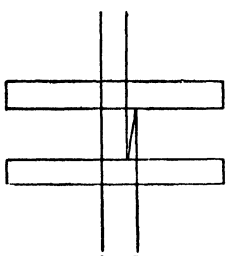


FIG. 124.

If Δ be the difference of path between the direct ray and the ray which has been twice reflected, then the successive rays will differ in their paths from the direct ray by Δ, 2Δ, 3Δ, and so on ; their intensities will decrease, but not very rapidly. If Δ be a round number of wave-lengths, *i.e.* if $\frac{\Delta}{\lambda}$ be a whole number, all the waves will agree in phase, and there will be a maximum of intensity ; but if $\frac{\Delta}{\lambda}$ differ a very little from a whole number,

[1] *Ann. Chim. et Phys.*, **12**. 459 (1897).

then amongst the successively reflected rays there will be found one which will differ very much in phase from the direct ray, and will thus considerably detract from the intensity; and therefore it follows that the higher the value of f, the smaller is the change necessary in $\frac{\Delta}{\lambda}$ from a whole number in order to produce a considerable decrease in the intensity. This is due to the fact that the more f increases, the greater is the effect of the multiple reflections.

Fabry and Perot give a rigid proof of this, and show that if, again, f be the reflecting power of each silvered surface, θ the fraction of the incident light each face allows to pass through, and Δ the difference in path between the direct and twice reflected rays, then the intensity will be given by—

$$I = \frac{\theta^2}{(1-f)^2} \times \frac{1}{1 + \frac{4f}{(1-f)^2}\sin^2 \pi \frac{\Delta}{\lambda}}.$$

Considering the second factor on the right-hand side, and putting $f = 0{\cdot}75$, then this factor becomes equal to—

$$\frac{1}{1 + 48 \sin^2 \pi \frac{\Delta}{\lambda}}.$$

When, therefore, $\frac{\Delta}{\lambda}$ is a whole number, this factor is equal to unity, and the intensity reaches a maximum of $\frac{\theta^2}{(1-f)^2}$; but if $\frac{\Delta}{\lambda}$ differs from a whole number, the above second factor becomes rapidly smaller than unity; and thus with a small change in $\frac{\Delta}{\lambda}$ from a whole number a great decrease in intensity is produced. In other words, close on each side of a maximum the intensity falls very rapidly to almost zero, and the maxima are therefore very sharply defined. At the distance of one-tenth of a fringe from the maximum the intensity falls to one-sixth of the maximum.

The definition of the bright fringes thus depends directly

upon f, but it must be remembered that as f is made greater, the absorption of light by the films increases, and therefore the whole quantity of light passing through the apparatus is diminished. The fact of this absorption limits the thickness of the silver films; in practice the thickness should depend upon the intensity of the light to be employed. The best process for silvering is that given by Martin.[1] By addition of water the strength of the solutions can be varied so as to give anything from a thin veiling to an almost opaque coating. The two plates should be silvered in the same bath in order to produce the same thickness of layer on each.

The appearance of the fringes depends absolutely upon the shape of the limiting surfaces of the layer of air, since each fringe defines the points of equal thickness of the air layer. With a beam of monochromatic light at normal incidence one series of very narrow fringes will be formed; these fringes are localised in the air layer, and are thus rectilinear when the glass surfaces are plane but not parallel, and they are circular when the surfaces are slightly convex or concave. The best way to obtain them is to adjust two optically plane silvered glass surfaces until they are perfectly parallel, and then to observe the fringes with a telescope focussed for parallel rays. A complete system of rings is then obtained, of which, probably, only a small section can be seen at one time in the telescope.

If, now, instead of monochromatic light, light consisting of two different radiations be examined through the interference apparatus, two systems of fringes will be seen, the first due to one radiation and the second due to the other. If the two radiations differ in colour, then the two systems of fringes will be easily distinguishable by their appearance, and also by the different intervals between two consecutive fringes in the two systems; for the greater the wave-length of a ray the wider apart are the fringes it produces.

Let us put the wave-lengths of the two radiations as equal to λ_1 and λ_2, and let also $\lambda_1 > \lambda_2$. If e be the thickness of the air layer, then there will be a maximum for the ray λ_1 when

[1] See Appendix, p. 652.

$e = k_1\frac{\lambda_1}{2}$, k_1 being some whole number which represents the number of the order of the fringe. In the same way there will be a maximum for the ray λ_2 when $e = k_2\frac{\lambda_2}{2}$, k_2 also being some whole number. If the two silvered surfaces are put in contact and then slowly separated, keeping them perfectly parallel, the two systems of fringes will be comparable to two scales, the divisions of which mark the thicknesses of the layer, which are multiples of $\frac{\lambda_1}{2}$ and $\frac{\lambda_2}{2}$ respectively. The appearance of the fringes in the telescope at very small thicknesses is that the fringes of the two systems are not properly separated from one another, and as the thickness of the layer increases and the fringes cross the field of view the fringes belonging to the two systems become more separated, until a region is reached when a fringe from one ray is situated exactly between two fringes from the other ray. After this point the fringes of the two systems get closer together, until two quite, or very nearly, coincide. After this they become wider apart, and then closer together again, and so on.

The first coincidence between a fringe of the one system and a fringe of the other is when $k_2 = k_1 + 1$.

Then $$2e = k_1\lambda_1 = (k_1 + 1)\lambda_2$$

and $$k_1 = \frac{\lambda_2}{\lambda_1 - \lambda_2}.$$

The second coincidence takes place when $k_1 = 2\frac{\lambda_2}{\lambda_1 - \lambda_2}$, and, generally, the fringes coincide when—

$$k_1 = n\frac{\lambda_2}{\lambda_1 - \lambda_2}.$$

Evidently, therefore, the nearer λ_1 and λ_2 are together, *i.e.* the nearer the two rays are in the spectrum, the greater are the intervals between the coincidences. For example, with the D rays of sodium for the first coincidence—

$$k_1 = 1000 \text{ nearly,}$$

Let us consider again the apparatus to be illuminated by two rays closely situated together, of wave-lengths λ and $\lambda + \epsilon$, and let Δ, the difference of path, $= 2e$; then the pth fringe of the first ray corresponds to $\Delta = p\lambda$, and the pth fringe of the second ray corresponds to $\Delta = p(\lambda + \epsilon)$. If p be very small, the two sets of fringes will not appear separated; but as p increases, the fringes will appear to double themselves and to give two sets of fringes, one belonging to one radiation and one to the other. The fringe from the ray having the greater wave-length will appear on the side corresponding to an increased length of path. In the case of the D rays of sodium we have $\frac{\epsilon}{\lambda} = 10^{-3}$, and we find the doubling to be quite plain when we reach the two-hundredth fringe, for then the distance between the components is one-fifth of the interval between two successive fringes. Generally speaking, therefore, at the pth fringe we can separate two rays, for which

$$\frac{\epsilon}{\lambda} = \frac{1}{5p}$$

Thus with an air layer 5 cm. thick ($\Delta = 10$ cm.) and $\lambda = 5000$ A.U., $p = 200{,}000$, and therefore rays can be separated for which $\frac{\epsilon}{\lambda} = 10^{-6}$; that is, rays differing in wave-length by 0·005 A.U.

It is easy to calculate the difference in wave-length of two radiations which are examined in the above way. The relative value is best found, namely, $\frac{\epsilon}{\lambda}$, which corresponds to the limit of resolution (Rayleigh).[1] In order to do this the apparatus is illuminated with the required rays, and the air layer slowly widened until the two sets of fringes are seen clearly separated, and until the fringes belonging to one radiation are exactly situated in the centre between the fringes belonging to the other radiation. This condition can at once be seen by the eye; we then have the pth fringe of the rays of wave-length

[1] See p. 74.

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[1] See p. 74.

$\lambda + \epsilon$ exactly situated in the centre between the pth and the $(p + 1)$th fringes of the rays of wave-length λ.

The pth fringe of the rays λ then corresponds to the difference of path Δ, and the pth fringe of the rays $\lambda + \epsilon$ corresponds to the difference $\Delta + \frac{\lambda}{2}$.

Then
$$p = \frac{\Delta}{\lambda} = \frac{\Delta + \frac{\lambda}{2}}{\lambda + \epsilon},$$

and
$$\frac{\epsilon}{\lambda} = \frac{\lambda}{2\Delta} = \frac{1}{2p}.$$

If, therefore, we know Δ or p and λ, we can calculate $\frac{\epsilon}{\lambda}$.

Let us imagine now that the air layer be still further increased little by little; the two systems of fringes will then get closer together until they coincide; this takes place when Δ is twice what it was before. If Δ be increased to three times its first value, there will again be observed the first condition, which may be called the condition of complete disagreement.

Now, it may easily be seen that,[1] if the beam of light fall upon the air layer at an angle of incidence i, and e be the thickness of the layer,

then
$$\Delta = 2e \cos i.$$

A small correction has, in fact, to be added here, but, as it does not concern the present case, its consideration may be postponed. If the beam of light be truly parallel and normal to the layer, then $i = o$ and $\Delta = 2e$. This method is convenient in cases when e is small, and therefore small errors in parallelism have little influence; but when e becomes very large, a very small error in parallelism produces confusion in the fringes. Under these circumstances it is always preferable to work with a slightly convergent beam of light, and observe the fringes with a telescope focussed for parallel rays. At each point of the field there will be found a single value of i, and thus one single value of Δ, so that perfect clearness of fringes will be

[1] *Ann. Chim. et Phys.*, **16**. 115 (1899).

obtained. As the angular field of the telescope is very small and i thus small, we may put—

$$\Delta = 2e\left(1 - \frac{i^2}{2}\right)$$
$$= 2e - ei^2;$$

Δ therefore decreases with increasing values of i, and is therefore a maximum in the centre of the field. The fringes are therefore to be seen as rings centred round the axis of the beam of light, and the effect of increasing e is to cause the ring to expand. In observing these fringes, therefore, it must be remembered that in the system of fringes seen in the telescope field any one fringe corresponds to a smaller difference of path than does the next fringe nearer the centre. If the fringe nearest the centre were the pth of a series, then the next fringe, counting from the centre, of that series would be the $(p - 1)$th, and the next the $(p - 2)$th, and so on.

Diagrams of Fabry and Perot's apparatus[1] are shown in Figs. 127 and 128 in side and end elevation respectively. It is absolutely necessary in such an interferometer that the silvered glass surfaces be always kept absolutely parallel to one another; very delicate adjustments must therefore be provided to correct for the errors in parallelism produced when the thickness of the air layer is altered. In the present apparatus there are the following adjustments: first, for altering the distance between the silvered surfaces there is a rapid adjustment, a fine adjustment which allows one to count the fringes, and finally a very delicate adjustment, which is limited to a few thousandths of a millimetre; secondly, the orientation adjustments are of two kinds, one a rapid and coarse adjustment, and the other a very fine and slow adjustment. The fine adjustments in each case are obtained by the pressure of a small rubber bag full of water against steel plates; this method is capable of giving extraordinarily small movements.

L and L′ (Fig. 127) are the two supports for the silvered glass plates; each of the latter is 40 mm. in diameter. One face of each is perfectly plane, one being silvered, while

[1] *Ann. Chim. et Phys.*, **22**. 564 (1901).

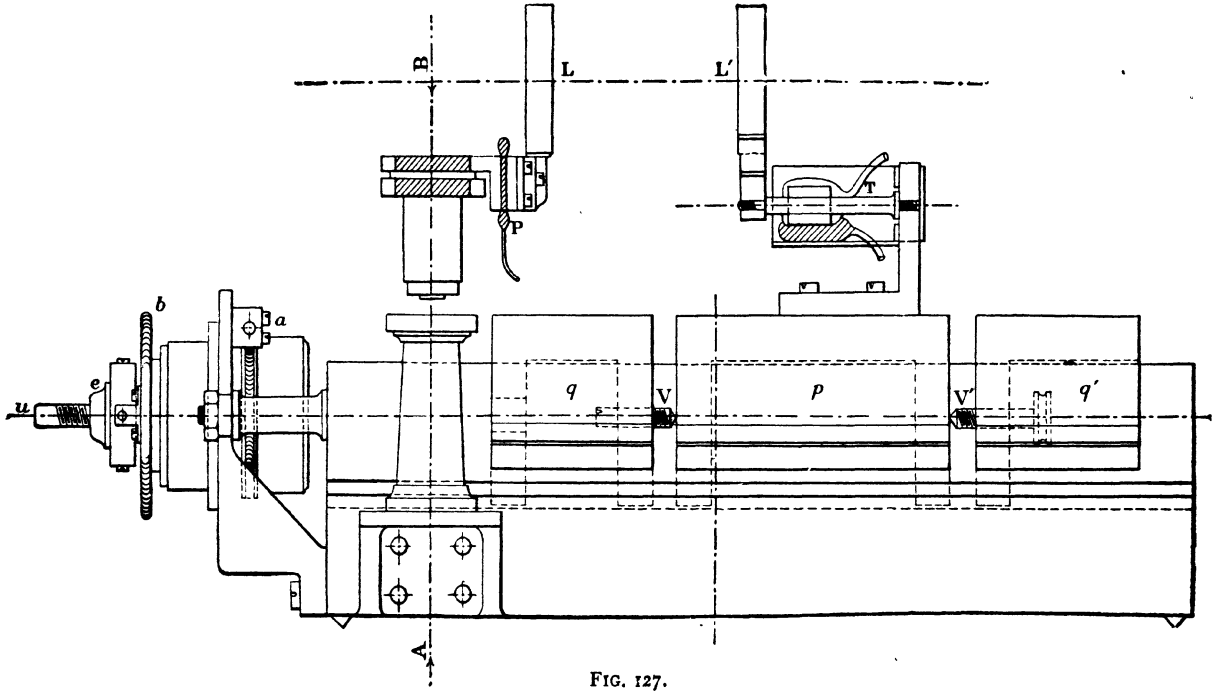


FIG. 127.

the other is very nearly plane. The two faces of each disc are not parallel to one another, but enclose an angle of about 1′, so as to evade any possibility of interference being set up by the glass discs themselves.

L, which is next to the observer, can be subjected to very rapid orientation movements and very small and delicate adjust-

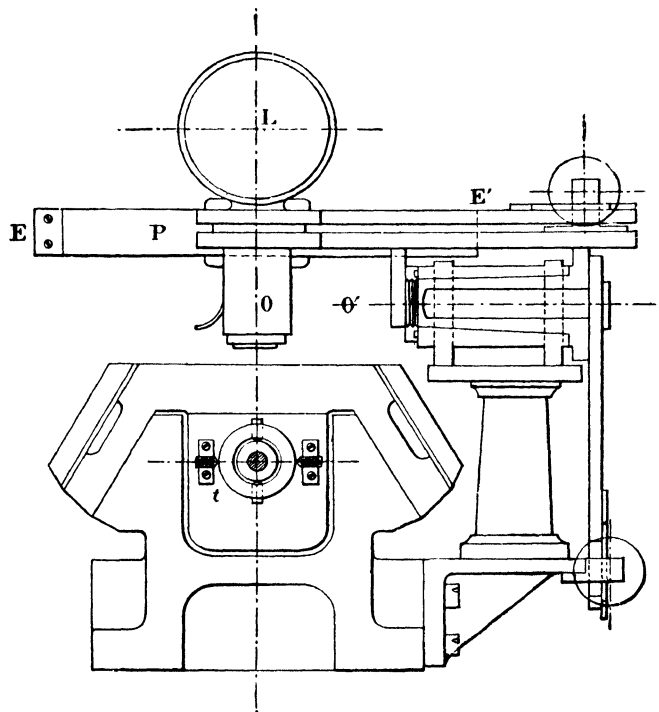


FIG. 128.

ments parallel to the path of the light. The first of these motions is obtained by rotation round two axes, O and O′ (Fig. 128), which are vertical and horizontal respectively. The fine parallel adjustment is obtained by the deformation of a strong steel spring, P, the centre of which is fixed on one side to the axis O, and on the other to the carrier L. This spring

is formed of two steel strips, 16 × 2 × 0·4 cm., which are joined together at the ends; stopping pieces are placed between the strips at the ends E and E', to keep them a short distance apart. A small caoutchouc bag full of water is put between the centres of the strips; this bag is connected by a tube to a movable reservoir of water. An alteration of 1 cm. in the height of this reservoir produces a displacement of the disc of 0·15 μ.

The carrier L' can be subjected to small orientation displacements and large movements parallel to the path of the light. L' is fixed at the end of the steel pillar T, on which is screwed a cube of bronze; two rubber bags, one underneath and the other at the side, serve to give very small horizontal and vertical displacements to L'. A change of 1 cm. in the height of the attendant water reservoirs produces an angular displacement of 0·25″. The parallel movement is obtained as follows: the bracket carrying L' is fixed to p, which is a bronze block, working extremely smoothly and truly upon V-shaped slides.

The block p sits between two smaller blocks, q, q', and as these two blocks move one way or the other, they push the block p by means of the pointed thrust pieces V, V'. In this method of moving p it can be seen that p is entirely free upon its slides, and rests thereon by its own weight, the only force applied to it being truly parallel to its movements. There is thus no chance of any rocking motion, such as would certainly be produced were p moved directly by the micrometer screw. Fabry and Perot found it possible in this way to follow the fringes while moving p, which would otherwise have been impossible. The two blocks q and q' are both rigidly fastened to the micrometer screw, which can be seen projecting from the apparatus at u; this screw is moved backwards or forwards by the rotation of the nuts a or b, a having a tangent-screw arrangement for slow motion.

In order to gain some idea of the distance between the silvered surfaces at any time, a micrometer scale is fitted to the instrument, upon which the position of p can be read at any instant by means of a microscope with a micrometer eyepiece.

This scale is graduated in $\frac{1}{5}$th mm., and the zero is determined upon it by direct observation, such as the first complete disagreement of the two mercury yellow rays. The instrument is shown in its complete form in Fig. 129.

One of the first applications of this interferometer was to the study of the structure of certain spectrum lines by the examination of the fringes they produce. It is necessary for this purpose that the apparatus be only illuminated with the rays it is required to examine; if these rays form part of a very simple spectrum it may be sufficient to cut off the other rays by means of absorbing solutions, but the best method is to

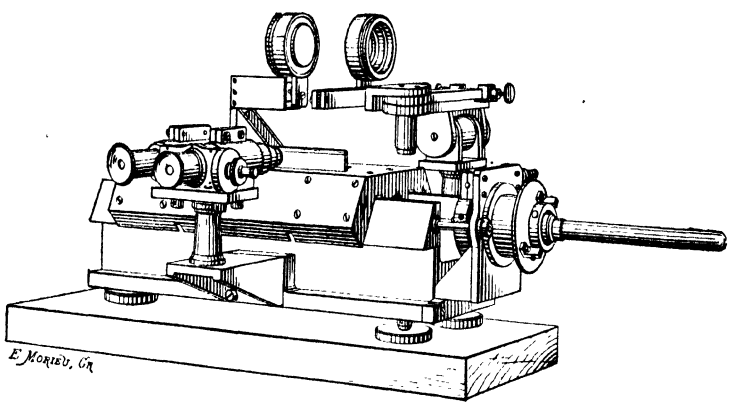


FIG. 129.

analyse the light by passage through one or two carbon bisulphide prisms, and to focus the required rays upon a slit by means of a lens. A second lens receives the rays coming through the slit, and directs them as a converging beam upon the silvered surfaces. At first the air layer is made as small as possible, and then it is slowly widened until the fringes double themselves, and the first condition of disagreement is reached. As was pointed out before, the nearer a fringe ring is to the axis of the beam of light, *i.e.* the smaller the radius of a fringe, the greater the corresponding difference of path.

The following rays were examined, the various substances

being excited in tubes similar to those used by Michelson and by Hamy:[1]—Thallium: $\lambda = 5351$ A.U.

This ray doubles itself very easily, the first effect showing itself when the thickness of the layer ($= e$) is equal to 1·5 mm.; a weaker ring is then to be seen just inside each bright ring, showing that the weaker component has the larger wave-length. The condition of complete disagreement is obtained when $e = 6{\cdot}35$ mm.

From these numbers the number of the order $\left(= \frac{12{\cdot}7}{0{\cdot}0005351}\right)$ is found to be nearly 23,800, whence $\frac{\epsilon}{\lambda} = 21 \times 10^{-6}$.

On still further increasing e it is found that the principal component itself is double, being composed of a brighter and weaker component, the weaker component having the greater wave-length; for this pair $\frac{\epsilon}{\lambda}$ was found to be 3×10^{-6}. It follows that the green thallium radiation is triple, being composed of one bright and two weaker components. The last two are apparently of the same intensity, and are both on the red side of the principal component, the values of $\frac{\epsilon}{\lambda}$ being respectively 3×10^{-6} and 21×10^{-6}.

The cadmium radiations were examined, and it was found that the red ray is quite simple, as was shown originally by Michelson.

The results obtained by Fabry and Perot[2] differ to a certain extent from those obtained by Michelson by his method of plotting the visibility curves. The reason of this lies in the fact that in the case of a given visibility curve, especially if complex, many hypotheses may be chosen which give on calculation a curve of similar form to that observed. For example, one cannot be certain in the case of a double source of two lines of unequal brightness as to how these are situated with regard to one another. It is important to notice that, if the values obtained from the above measurements be substituted in Michelson's expression for visibility, the visibility curves

[1] See p. 395. [2] See p. 345.

obtained agree with those actually observed by him; these results are, therefore, really in perfect accord with those of Michelson.

The next application by Fabry and Perot of their interferometer was in the direction of the comparison of wave-lengths among themselves and the measurement of length in terms of wave-lengths.[1] According to the equation $p = \frac{\Delta}{\lambda}$, as has already been said, when p is a whole number a bright fringe is produced, of which p is the number of the order; when p is not a whole number, the fractional part represents the difference of phase between the two first interfering waves, and therefore p should be defined as the order of interference corresponding to a difference of path Δ. Let us imagine that the incident light consists of two vibrations, red and green, of wave-lengths λ and λ' ($\lambda > \lambda'$). The two systems of fringes then seen can easily be distinguished by their difference of colour. When we pass from one red fringe to the next, the difference of path increases by λ, and similarly from one green fringe to the next, by λ'; as λ' is smaller than λ, the green fringes are closer together than the red. It is possible then to find a region where two green fringes are placed between two red fringes; this is an approximate coincidence of the two systems.

In Fig. 130 A and A′ are two consecutive red fringes, B and B′ two consecutive green fringes. Let K and K + 1 be the order numbers of A and A′, and K′ and K′ + 1 the orders of B and B′, and let $K' - K = m$.

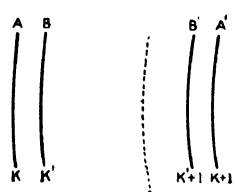


FIG. 130.

Now, at each point in the field of view there is a definite value of Δ, and therefore a definite value of the order of interference, $p = \frac{\Delta}{\lambda}$ for the red, and $p' = \frac{\Delta}{\lambda'}$ for the green rays.

Along the curve B, p' is a whole number and equal to K′,

[1] *Ann. Chim. et Phys.*, **16**. 289 (1899).

while p, which is equal to K along A, is a little larger than K; along B, therefore, we have—

$$p' - p < m.$$

Similar reasoning shows that along B′—

$$p' - p > m.$$

It follows that $p' - p$ increases with Δ, and that there must be a particular value, Δ_0, for which—

$$p' - p = m.$$

This value of the difference of path, called by Fabry and Perot the difference of path at coincidence, occurs when the difference $p' - p$ between the orders of interference is a whole number, m. It corresponds to an ideal line in the field of view, and is defined by the equation—

$$\frac{\Delta_0}{\lambda'} - \frac{\Delta_0}{\lambda} = m.$$

It follows that

$$\Delta_0 = m\frac{\lambda\lambda'}{\lambda - \lambda'}.$$

The phenomenon is thus periodic, for the differences of path at coincidence are multiples of a length which may be called the period—

$$\mathrm{P} = \frac{\lambda\lambda'}{\lambda - \lambda'}.$$

One can express this period in terms of the wave-length of any ray, *e.g.* in terms of λ—

$$\omega = \frac{\mathrm{P}}{\lambda} = \frac{\lambda'}{\lambda - \lambda'},$$

and similarly in terms of λ'—

$$\omega' = \frac{\mathrm{P}}{\lambda'} = \frac{\lambda}{\lambda - \lambda'}.$$

Evidently $\omega' = \omega + 1$, because at the first coincidence n waves of length λ are equal to $n + 1$ waves of length λ'.

The mth coincidence takes place when $\Delta = m\mathrm{P}$, and the order of interference of waves λ is $m\omega$, and of waves λ', $m\omega'$, which $= m\omega + m$.

If $m\omega$ happens to be a whole number K, then the coincidence will be exact, and the appearance will be as in Fig. 131.

Generally, we put $m\omega = K + \theta$, K being a whole number and θ lying between 0 and 1. When θ is = 0 or 1, then the coincidence is exact, as in Fig. 131; and when θ has some intermediate value, the coincidence is inexact, as in Fig. 130. If a and a' are the distances AB, B'A' in Fig. 130 (strictly speaking the differences in path denoted by the distances AB and B'A'), then—

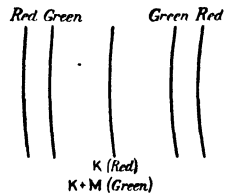


FIG. 131.

$$\theta = \frac{a}{a + a'}.$$

It is possible when λ and λ' are not too close to measure θ from the observations on a coincidence.

Clearly from the above P is inversely proportional to the difference between λ and λ'; if P corresponds to four or five fringes one can observe the coincidences with accuracy. When P is about fifteen fringes, observations of θ are more difficult; but when P is very large, as with the D rays of sodium, it is better to observe the regions of complete disagreement of the fringes, for in this case the observations are impossible on the coincidences, as the fringes belonging to the two systems are so alike in colour and are so confused with one another. The condition of complete disagreement is, however, easily estimated, and then, of course, we have—

$$\Delta = (m + \tfrac{1}{2})\mathrm{P}.$$

In all interference measurements the standards of reference are the red, green, and blue radiations of cadmium, determined by Michelson to have the following wave-lengths—

$\lambda_R = 6438{\cdot}4722$ A.U.
$\lambda_G = 5085{\cdot}8240$,, (principal component)
$\lambda_B = 4799{\cdot}9107$,,

The blue ray is not sufficiently simple in structure to use with anything but small differences of path.

The following method was adopted to measure wave-lengths of the two yellow rays and the green ray of mercury in reference to these standards :—

The rays from both the sources are simultaneously thrown into the apparatus, and it is absolutely indispensable that the two beams of light should be exactly superposed. The method used is shown in Fig. 132, where T and T' are the two sources, and A a half-silvered mirror. E and E' are two movable screens, used when only one source is required. Absorbents may also be used to cut off the rays from either source. The

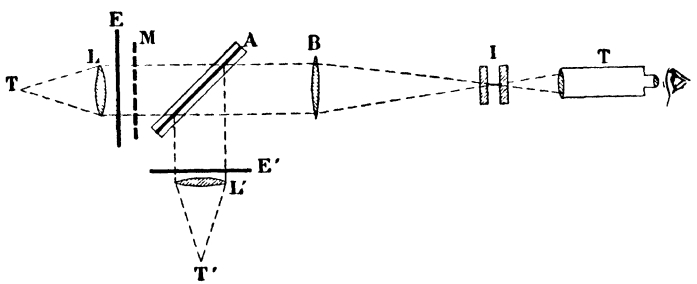


FIG. 132.

interferometer is placed at I ; the rest of the apparatus explains itself.

It is necessary in making these measurements that the wave-lengths of the rays to be dealt with be approximately known ; these may, of course, be readily found with a grating, and the values used in this investigation were—

$$\lambda_{Y_1} = 5790{\cdot}49 = Y_1$$
$$\lambda_{Y_2} = 5769{\cdot}45 = Y_2$$
$$\lambda_{G_m} = 5460{\cdot}97 = G_m$$

All the measurements made were referred to the green ray of cadmium (called G).

From the above values of the wave-lengths of the mercury rays, one approximate value of the period of coincidence in terms of the ray G was calculated for the two yellow rays

of mercury (Y_1 and Y_2). This is given by the expression $\frac{5790{\cdot}49 \times 5769{\cdot}45}{21{\cdot}04 \times 5085{\cdot}824}$, and is equal to 312·2.

Similarly, the period of the rays G_m and cadmium red (R) were found in terms of the ray G to be 14·5569 and 4·759901 respectively.

It is convenient to have the scale of the interferometer calibrated in terms of the coincidences of two rays. The two yellow rays of mercury are very suitable for this purpose; the apparatus is illuminated by these rays alone, and the two silver surfaces are brought as near together as possible. They are then slowly widened until the first coincidence is observed; the reading on the scale is taken, and the plates again separated until the second coincidence is seen, when the scale is again read, and so on. In this way a calibration of the scale is obtained from which at any time when a coincidence is observed the number of it can at once be obtained.

The first series of observations was made as follows:—

1. The silvered plates were so set as to observe, near the centre of the field, a complete disagreement between the fringes of the rays Y_1 and Y_2, and on reference to the scale and the table it was found that this disagreement occurred between the sixth and seventh coincidences.

2. The mercury rays were then removed and the cadmium rays R and G thrown in without altering the interferometer in any way; it was found that an exact coincidence occurred in the same part of the field as did the complete disagreement in the first observation; that is to say, the nth red fringe exactly coincided with the pth green fringe.

3. On comparing the rays G and G_m it was found that the $(p - 5)$th fringe of the former was in complete disagreement with two fringes of the ray G_m.

4. On comparing the rays R, Y_1, and Y_2 it was found that the $(n - 2)$th fringe of the first was in complete disagreement with two fringes, one due to Y_1 and the other due to Y_2, the fringe due to Y_2 being on the inside. The $(n - 2)$th fringe of G therefore exactly coincided with a hypothetical ray of mean wave-length between Y_1 and Y_2.

5. The $(n + 2)$th red fringe was in complete disagreement with a blue and a green cadmium fringe.

Now, from the approximate wave-lengths of Y_1 and Y_2 above given, it follows that the sixth disagreement takes place at the 2028th green cadmium fringe. The period is equal to 312, and therefore the disagreement dealt with occurred at the $\left(312 \times 6 + \frac{312}{2}\right)$th fringe. Therefore p is about 2028, and n about $2028 \times \frac{\lambda_G}{\lambda_R} = 1602$.

In the following table are given the numbers of the red cadmium fringes which coincide with green cadmium fringes, and also the disagreements between green and blue fringes of cadmium expressed in terms of the red ray of cadmium, both calculated from Michelson's measurements :—

Coincidences. red and green cadmium.	Disagreements. green and blue cadmium.
1597·8	1584·7
1601·5	1598·0
1605·3	1611·2
1609·0	1624·5
1612·8	1637·7
1616·5	

Now, it was stated that the nth red and pth green were in *exact* coincidence ; therefore n must be a whole number, about 1602. Evidently 1609 is the only possible value ; further, from (5) the $(n + 2)$th red fringe is situated at a disagreement between a green and a blue cadmium fringe, and this is shown by the 1611·2 in the second column. The corresponding value of p is, therefore, 2037.

Again, from (3) the 2032nd fringe of G was in complete disagreement with two fringes of the ray G_m. The following table gives the numbers of the fringes of the ray G in such disagreement, calculated from the period given above (14·5569) :—

	Number of disagreement.
2015·5	138
2030·0	139
2044·5	140

The 139th disagreement was evidently observed, and as the calculation gives the 2030th fringe, while the observation gives the 2032nd, it follows that the period obtained above from the wave-lengths is wrong A better value is—

$$\omega = \frac{2032}{139{\cdot}5} = 14{\cdot}5663.$$

Again, from (4) the 1607th red cadmium fringe is in exact coincidence with the mean of the two mercury yellow rays. The calculation from the period obtained from the above wave-lengths shows that the 183rd coincidence takes place at the fringe 1605·8; evidently here also the period must be slightly corrected.

From these first series of measurements we thus obtain more accurate values of the period of coincidence of the rays whose wave-lengths are to be determined, and from these the tables of coincidences may be more accurately calculated. It becomes possible then to work with thicker interference layers, when still more accurate measurements may be made. From these new values the periods are again obtained with still greater accuracy, and so on. Fabry and Perot reached layers in these measurements of 32 mm., which correspond to the 125,000th fringe of the green cadmium ray.

The final values obtained were—

$$\lambda = 5460{\cdot}7424$$
$$\lambda = 5790{\cdot}6593$$
$$\lambda = 5769{\cdot}5984$$

The probable error in the green ray is given by $\frac{\delta\lambda}{\lambda} = \pm 10^{-7}$, or about $\frac{1}{10000000}$; in the case of the yellow rays it is somewhat greater.

This beautiful apparatus leaves very little to be desired as an interference apparatus for examination of the structure of radiations and the determination of absolute wave-length. It has further a great advantage over an ordinary apparatus in that absorption lines such as the Fraunhofer lines can be examined. The measurement of wave-length, it is true, is a

very tedious process, and hence Fabry and Perot,[1] profiting by their experience with their interferometer, have adopted fixed air layers as interference apparatus, the widths of which are determined once and for all. They call these apparatus standards (*étalons*), and have made use of three, which are 2·5 mm., 5 mm., and 10 mm. in thickness respectively. With these they have measured the wave-lengths of certain rays in the emission spectrum of the iron arc, and also in the solar spectrum.

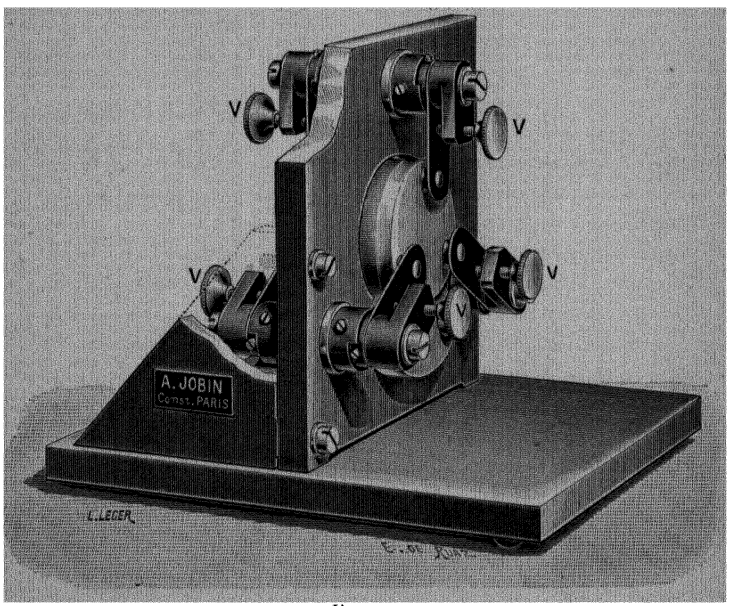


FIG. 133.

These standards consist of two half-silvered glass plates, as before, which are kept apart by polished steel supports. The plates are kept pressed against the supports by binding screws, by means of which they are very carefully adjusted and made parallel. The apparatus is shown in Fig. 133.

The method is as follows: The order of interference at the centre of a system of rings is determined successively for the

[1] *Ann. Chim. et Phys.*, **25**. 98 (1902).

two radiations to be compared; this can be done first for one and then for the other, because the thickness of the interfering layer will not change during a measurement. Let one of these, with wave-length λ, be as usual the green ray of cadmium, and let P be the number of the order of one of the fringe rings obtained with it, and let this be the first ring, counting from the centre. The order of interference at the centre will be $p = P + \alpha$; P is readily found from the knowledge of the thickness of the air layer, supposed previously determined. It only remains to determine the fraction α, which lies usually between 0 and 1.

The diameter of the fringe is evidently proportional to α, and it is therefore possible to determine α from a measurement of the diameter of the ring P.

As shown previously, the order of interference at the centre is—

$$p = \frac{2e}{\lambda}, \text{ if } e \text{ is the thickness of the air layer.}$$

In a direction making an angle i with the normal it is $\frac{2e}{\lambda}\cos i$, or $p \cos i$. If x is the angular diameter of the ring P, then, the telescope being focussed for parallel rays,

$$p \cos \frac{x}{2} = P,$$

and as x is very small, $p = P\left(1 + \frac{x^2}{8}\right)$;

thence
$$\alpha = p - P$$
$$= P\frac{x^2}{8}.$$

Similarly, with a radiation of wave-length λ' we have—

$$\alpha' = P'\frac{x'^2}{8}.$$

Now, since the thickness of the layer is constant—

$$\lambda(P + \alpha) = \lambda'(P' + \alpha'),$$

therefore
$$\lambda' = \lambda\frac{P + \alpha}{P' + \alpha'};$$

and by substitution of the values for α and α' above found we have—

$$\lambda' = \lambda \frac{P}{P'}\left(1 + \frac{x^2}{8} - \frac{x'^2}{8}\right).$$

From this $\frac{\lambda'}{\lambda}$ can be determined by observation.

It is first of all necessary to determine the thickness of the standards to be employed in the investigations. This is done by the method of superposed interfering layers; that is to say, a beam of light is sent through two layers in series, the most satisfactory arrangement being that shown in Fig. 134.[1]

It can readily be shown that if the two thicknesses be the same, a beam of white light will give a white fringe along the points corresponding to equal thicknesses. This also occurs when the thicknesses of the layers are in simple proportion.

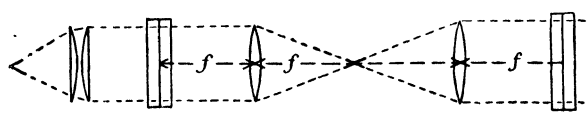


FIG. 134.

As a result of this it is possible to determine accurately the thickness of the air layer in a given standard, by comparison with the interferometer or a graduated standard. The graduated standard is made with the glass plates set at a very small angle to one another. There is a scale ruled on one of the inner glass surfaces, and the thickness of the layer is known from previous measurements at any point on the scale. For the actual method employed, the original memoir must be consulted. It must be imagined that the thicknesses of all the standards used are known in terms of the standard ray (cadmium green, principal component).

Now, changes are readily produced in the thickness of the layer by alteration of temperature, and therefore in practice

[1] *Ann. Chim. et Phys.*, **12**. 459 (1897).

only a small area of the layer is used, and the cadmium green fringes are observed and measured immediately before and after a measurement of the new ray.[1] Since the thicknesses are known, the number of the order of the first ring can always be found at once; in the case of the cadmium green from the standardisation, and in the case of a new ray from its approximate wave-length, supposed already known.

The measurement of the diameter of the ring is carried out by means of a micrometer eyepiece in the telescope, the readings of this instrument having been already calibrated in some convenient way.

A small correction has to be introduced in the measurements due to the change of phase at reflection. In the expression—

$$e = p\frac{\lambda}{2},$$

in which p is the order of interference at the centre, e, it must be remembered, is the optical thickness of the air layer; it is not necessarily the distance between the two silver surfaces. Hitherto we have reasoned as if e did not vary with λ, but in actual practice this is not strictly true, on account of the fact that the change of phase at reflection varies very slightly with the wave-length. In other words, e varies slightly with λ, so that if e be determined for a standard ray, λ, it must not be assumed that e is the same for another ray, λ', if $\lambda - \lambda'$ is large. Let us consider two rays, λ and λ', therefore, for which the optical thicknesses of the air layer are e_λ and $e_{\lambda'}$, and are slightly different; then, if p and p' be the orders of interference—

$$2e_\lambda = p\lambda \text{ and } 2e_{\lambda'} = p'\lambda',$$

whence

$$\lambda' = \frac{e_{\lambda'}p}{e_\lambda p'}\lambda.$$

Hitherto we have assumed $\lambda'_0 = \frac{p}{p'}\lambda$.

[1] The actual expansion of a 10 mm. standard is about 0·0001 mm., *i.e.* about four fringes for 10°.

To the ordinarily found value λ'_0 we must, therefore, add a small correction—

$$\gamma = \lambda' - \lambda'_0 = \frac{p\lambda}{p'} \cdot \frac{e_\lambda' - e_\lambda}{e_\lambda} = 2\frac{e_\lambda' - e_\lambda}{p'} \quad . \quad . \quad (1)$$

This correction is readily found by observations upon two rays whose wave-lengths are absolutely known. The two silvered plates are dismantled from the standard, and mounted upon the interferometer, and brought almost into contact. The apparatus is then illuminated by the two rays, for example, the red and green of cadmium, which we may denote by λ and λ'. The two plates are then slowly separated until an exact coincidence is found; if this be the qth coincidence, then the pth fringe of the ray λ is in exact coincidence with the $(p+q)$th fringe of λ', and thus—

$$2e_\lambda = p\lambda \text{ and } 2e_\lambda' = (p+q)\lambda',$$

therefore

$$e_\lambda' - e_\lambda = \frac{(p+q)\lambda'}{2} - \frac{p\lambda}{2}$$

$$= \frac{q\lambda'}{2} - \frac{p(\lambda - \lambda')}{2}$$

$$= \frac{\lambda - \lambda'}{2}\left(q\frac{\lambda'}{\lambda - \lambda'} - p\right)$$

$$= \frac{\lambda - \lambda'}{2}\rho,$$

where

$$\rho = \frac{q\,\lambda'}{\lambda - \lambda'} - p.$$

It will be seen that $\frac{\lambda'}{\lambda - \lambda'}$ is the period of coincidence in terms of λ. The following are the results obtained with one of the standards by Fabry and Perot:—

(*a*) Two cadmium rays, $\lambda = 6438$ and $\lambda' = 5085$.

$$\rho = 0{\cdot}065,$$

therefore

$$e_\lambda - e_\lambda' = -4{\cdot}4\mu\mu.$$

(*b*) Cadmium red and mercury green rays, $\lambda = 6438$ and $\lambda' = 5461$.

$$\rho = 0{\cdot}042,$$

therefore $$e_\lambda - e_{\lambda'} = -2{\cdot}1\mu\mu.$$

(*c*) Mercury green and blue rays, $\lambda = 5461$ and $\lambda' = 4358$.

$$\rho = 0{\cdot}12,$$

therefore $$e_\lambda - e_{\lambda'} = +6{\cdot}6\mu\mu.$$

These are then all reduced to the standard of the cadmium green, and the values of the correction γ obtained from

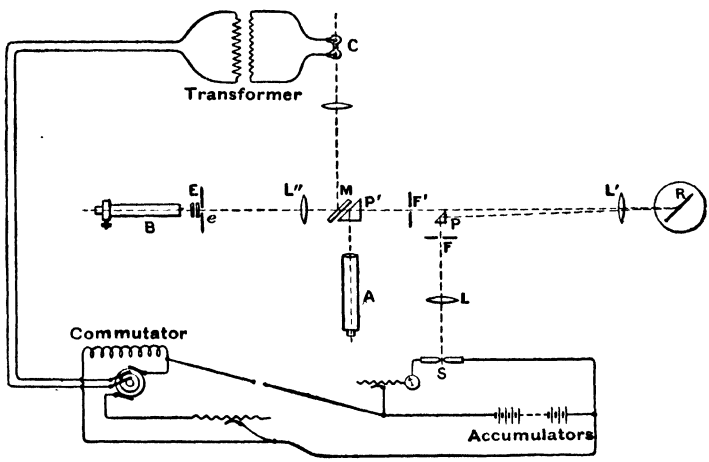


FIG. 135.

equation (1). These values are then put upon a curve; they vary from $-0{\cdot}003$ A.U. at $\lambda = 6500$ to $+0{\cdot}002$ A.U. at $\lambda = 4500$.

By means of three standards Fabry and Perot measured the wave-lengths of fourteen lines in the arc spectrum of iron, and thirty-three in the solar spectrum. In both series of measurements the apparatus was so arranged that either the cadmium green ray or the required ray in the iron or solar spectrum could be thrown upon the interference standard; in

the case of the iron spectrum, the arrangement used is shown in Fig. 135.

S was the iron arc, an image of which was focussed in the slit F by the lens L; the rays coming through the slit passed through the totally reflecting prism P, and thence through the lens L′ on to the plane grating R; the diffracted rays passed back, and were focussed by the lens L′ on to the slit F′. By rotating the grating R any required line could be brought on to the slit F′. The rays coming through F′ passed straight on through the half-silvered parallel plate M, and were directed as a converging beam on to the interference standard E by the lens L″. The prism P′ could, if desired, be raised and brought into the path of the rays in order to examine the spectrum at the telescope A. The cadmium tube was at C, and the rays therefrom were reflected at M, and thence passed into the apparatus. Screens were employed to cut off either one or the other beams of light; *e* was a fixed screen pierced with a small hole of 3 mm. diameter, to localise the region of the standard E which was employed. The apparatus used for the solar spectrum was somewhat similar, with this difference, that a concave grating was employed in place of the plane one. In the case of iron, only a few lines could be measured with a very great degree of accuracy, because they are not, as a rule, of sufficient fineness.

For a description of the actual experimental details, the original memoir must be consulted.

The following is the first list of wave-lengths[1] determined by Fabry and Perot, both with the interferometer and with the interference standards as last described:—

[1] *Comptes Rendus*, **130**. 492 (1900), and *Ann. Chim. et Phys.*, **25**. 98 (1902).

Element.	Wave-length in tenth metres.	Source.
Mercury	5790·6593	Arc in vacuo
	5769·5984	,, ,,
	5460·7424	,, ,,
	4358·343	,, ,,
Zinc	6362·345	"Vibrator" in vacuo[1]
	4810·535	,, ,,
	4722·164	,, ,,
	4680·138	,, ,,
Copper	5782·159	"Vibrator" in vacuo
	5782·090	,, ,,
	5218·202	,, ,,
	5153·251	,, ,,
	5105·543	,, ,,
Silver	5465·489	"Vibrator" in vacuo
	5209·081	,, ,,
Sodium	5895·932	Flame spectrum
	5889·965	,, ,,
Lithium	6707·846	Flame spectrum
Iron	6494·992	Arc
	6230·733	,,
	6065·489	,,
	5763·323	,,
	5615·657	,,
	5586·775	,,
	5506·783	,,
	5434·525	,,
	5302·321	,,
	5232·954	,,
	5083·345	,,
	5001·887	,,
	4859·763	,,
	4736·785	,,

[1] For a description of this apparatus, see p. 394.

The wave-lengths of the following lines were also determined in the solar spectrum :—

Fabry and Perot. λ	Rowland. λ_R	$\frac{\lambda_R}{\lambda}$
6471·666	6471·885	1·0000338
6408·027	6408·233	1·0000321
6322·700	6322·907	1·0000327
6230·746	6230·943	1·0000316
6151·639	6151·834	1·0000317
6065·506	6065·709	1·0000335
6016·650	6016·861	1·0000351
5987·081	5987·290	1·0000349
5934·666	5934·881	1·0000362
5862·368	5862·582	1·0000365
5763·004	5763·218	1·0000371
5715·095	5715·308	1·0000373
5586·778	5586·991	1·0000381
5506·794	5507·000	1·0000374
5497·536	5497·735	1·0000362
5434·544	5434·740	1·0000361
5409·800	5410·000	1·0000370
5367·485	5367·669	1·0000343
5345·820	5345·991	1·0000320
5339·956	5340·121	1·0000309
5247·587	5247·737	1·0000286
5247·063	5247·229	1·0000316
5171·622	5171·778	1·0000302
5123·739	5123·899	1·0000312
5090·787	5090·954	1·0000328
5001·881	5002·044	1·0000326
4923·943	4924·107	1·0000333
4859·758	4859·928	1·0000350
4783·449	4783·613	1·0000340
4736·800	4736·963	1·0000344
4704·960	4705·131	1·0000363
4643·483	4643·645	1·0000349

The last column in the table of solar wave-lengths expresses the ratio of Rowland's measurements to those given, and in Fig. 136 these ratios are plotted against the wave-lengths, the ratios being taken as the ordinates, and the wave-lengths as the abscissæ.

The curve should be, of course, a horizontal straight line, but as the differences from a mean straight horizontal line are enormously greater than the errors of experiment, this curve

points to there being a periodic error in Rowland's determinations.

I have given this full account of Fabry and Perot's work because it is the first determination of wave-lengths made by interference methods, and based upon Michelson's standards, and further, because the wave-lengths determined by this method have been adopted as the standard of reference in place of those of Rowland. The discrepancy between the grating and interference measurements gave rise to considerable discussion, because it had always been thought that even if the determination of the D_1 line were in error it would only be necessary to multiply Rowland's measurements by a

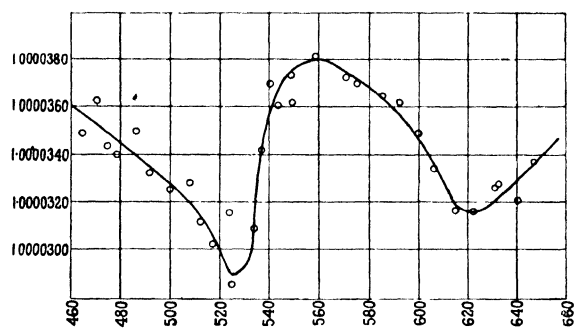


FIG. 136.

constant factor in order to make them absolutely accurate. The curve of ratios, however, shown in Fig. 136 proved that this was not the case, but that there must be a periodic error in Rowland's measurements which is not a simple function of the wave-length. If Fabry and Perot's measurements are truly accurate, as there seems absolutely no reason to doubt, it is evident that some fundamental source of error must underlie the method Rowland used. A very striking paper has been published by Kayser,[1] in which he shows that the accuracy of the coincidences between different orders with gratings is not to be depended upon. Kayser remarked that from an extensive use of Rowland's tables he had found that

[1] *Astrophys. Journ.*, **19**. 157 (1904).

the system is less correct than had generally been supposed, and that he had attempted to amend it in his measurements of the spectrum of iron;[1] the iron standards had, however, the same general features as Rowland's standards. There are two reasons for the bad results: first, Rowland did not know of the difference between the position of arc and solar lines. Even the taking of the solar D lines for the arc spectra was doubtful. According to Jewell,[2] as Rowland was not convinced that the displacement was due to any other cause than the accidental movement of the apparatus, when changing from the spectrum of the sun to that of the arc, the displacement was treated as being due to this cause, and the wave-lengths of all metallic lines corrected for the average displacement of the stronger "impurity lines" (generally iron) upon the plate, thus reducing them to an approximate agreement with the corresponding solar lines. Kayser pointed out that Rowland thus shifted different parts of the spectrum to smaller or greater wave-lengths, and as from such parts by the method of coincidences other parts were determined, perhaps with another shifting, it is impossible to know to what extent the errors may have accumulated in different parts. If this were the only error, it would be possible to avoid it by applying the method of coincidences, using only the arc lines as determined by Fabry and Perot.

There may, however, be another cause for the inaccuracy of Rowland's measurements. As it is impossible to get absolute measurements with the grating, the method of coincidences may also have led to errors. Indeed, Michelson showed that an error in the ruling of gratings is possible, which falsifies the results of this method, and there may be other causes not yet found with the same effect. Kayser, therefore, carried out some tests of the method with the help of two of Rowland's largest gratings, which were ruled on different engines. With the first grating plates were taken containing Fabry and Perot's lines at $\lambda = 5302$, and $\lambda = 5434$ in the second order, coinciding with $\lambda = 3550$ and $\lambda = 3630$ in the third order. The wave-lengths of the third order lines

[1] *Ann. der Phys.*, **8**. 195 (1900). [2] *Astrophys. Journ.*, **3**. 89 (1896).

were determined from Fabry and Perot's values. Then other plates were taken of these lines in the fourth order, together with Fabry and Perot's lines at $\lambda = 4736$ and $\lambda = 4859$ in the third order. The wave-lengths of the last two lines were thus determined direct, with one intermediate stage, from Fabry and Perot's lines at $\lambda = 5302$ and $\lambda = 5434$. The wave-lengths as determined by the grating, however, did not agree with the value found by the interference comparison; for example, Kayser found the wave-length $\lambda = 4736{\cdot}804$, instead of Fabry and Perot's number, $\lambda = 4736{\cdot}785$. As the individual grating measurements agreed to 0·003 A.U., it is clear that either the coincidence method is unsound, or that Fabry and Perot's values are wrong. With the second grating, proceeding in exactly the same way, a discrepancy of 0·108 A.U. was obtained between the grating coincidence and the interference value. The two gratings were then compared directly together. With each grating two plates of the region $\lambda = 5302$ to $\lambda = 5434$ in the second order were taken, and the third order lines were measured. While the two plates taken with each grating agreed to within 0·003 A.U., there was a constant difference of 0·03 A.U. between the values found with the two gratings. Kayser, therefore, concluded that there is no reason to doubt Fabry and Perot's values, but that the method of coincidences is not applicable for his gratings. Perhaps there may exist gratings free from this fault, but every one must be carefully tested before using. He showed, therefore, that it is necessary to determine more lines by the interference method, especially in the ultra-violet, so that we have a spectrum of lines between which we may interpolate without using the coincidence method.

Certain improvements have been recently made in Fabry and Perot's apparatus. In the first place, the rubber bags full of water for producing the fine adjustments have been done away with, and owing to improved workmanship it has been found possible to control the fine adjustments by simple mechanical means. Then, again, the silvering of the interferometer plates by means of silvering solutions has given place to the deposition of the silver by cathode streams in high

vacua.[1] A very much better silver layer is obtained in this way, and the fringes are very much improved in definition and in brilliancy.

A notable improvement has also been made in the étalon described above, for in place of the steel supports a quartz tube with optically worked ends is now used by Hilger in making these apparatus, as first employed by Rentschler.[2] The linear expansion of quartz is so small, being far below that of any other known substance, that the effect of temperature on the fringes is lessened very much. The linear expansion of quartz is 0·00000059 for 1° C., which is about $\frac{1}{18}$th of that of steel so that the great advantage gained is apparent. For work in the ultra-violet the étalon is also made with quartz plates and with the silver layer replaced by a nickel layer, this being rendered necessary by the fact that the reflecting power of silver falls to a very low value for the shorter wave-lengths. The nickel layer is also produced cathodically.

As a result of the discussions at the meetings of the International Union for Solar Research, it has been decided to determine the wave-lengths of a number of lines, not more than 50 Ångströms apart, in the visible and ultra-violet regions. The iron arc has been especially chosen for this purpose, and Fabry and Buisson[3] have published a list of wave-lengths in this spectrum. In certain places the iron lines fail and these have been supplemented by four lines of nickel, two of manganese, and three of silicon. Some of the lines on this list have been confirmed as to their wave-lengths within very small limits by two other and quite independent observers. The means of the three values have been adopted therefore towards the formation of the International Standard of wave-length (see p. 49). In this investigation Fabry and Buisson used photographic methods, the measurements of the interference rings obtained with the étalon being made on the negatives. The methods are described in great detail in the paper. The following is a list of the lines, and it may be pointed out that

[1] *Houllevigue. Comptes. Rendus.*, **135**. 626 (1902).
[2] *Astrophys. Journ.*, **28**. 345 (1908).
[3] *Ibid.*, **27**. 169 (1908).

each wave-length has a great inherent probability of accuracy since it is a mean of several close measurements. It must be pointed out that these measurements are based upon the new value for the cadmium red line, viz. $\lambda' = 6438{\cdot}4696$ Ångströms, while the older Fabry and Perot wave-lengths were based on the older value for this constant, viz. $\lambda = 6438{\cdot}4722$ Ångströms.

6494·994	5455·616	4678·855	3724·379	2679·065
6430·859	5434·530	4647·437	3677·628	2628·296
6393·612	5405·780	4602·944	3640·391	2588·016
6335·343	5371·498	4592·658	3606·681	2562·541
6318·029	5324·196	4547·854	3556·879	2528·516 Si
6265·147	5302·316	4531·155	3513·820	2506·904 Si
6230·732	5266·568	4494·572	3485·344	2435·159 Si
6191·569	5232·958	4466·554	3445·155	2413·310
6137·700	5192·362	4427·314	3399·337	2373·737
6065·493	5167·492	4375·935	3370·789	
6027·059	5127·364	4352·741	3323·739	
6003·039	5110·415	4315·089	3271·003	
5952·739	5083·343	4282·407	3225·790	
5934·683	5049·827	4233·615	3175·447	
5892·882 Ni	5012·072	4191·441	3125·661	
5857·760 Ni	5001·880	4147·677	3075·725	
5805·211 Ni	4966·104	4134·685	3030·152	
5763·013	4919·006	4118·552	2987·293	
5760·843 Ni	4903·324	4076·641	2941·347	
5709·396	4878·226	4021·872	2912·157	
5658·835	4859·756	3977·745	2874·176	
5615·658	4823·521 Mn	3935·818	2851·800	
5586·770	4789·657	3906·481	2813·290	
5569·632	4754·046 Mn	3865·526	2778·225	
5535·418	4736·785	3843·261	2739·550	
5506·783	4707·287	3805·346	2714·419	
5497·521		3753·615		

Some measurements have also been made by Rayleigh, who used an interference apparatus differing somewhat from that designed by Fabry and Perot. In place of the air layer bounded by half-silvered surfaces and normal incidence the interference rings were observed dependent on obliquity as first described by Haidinger. The results of Fabry and Perot for four mercury lines, four zinc lines, two sodium lines, and the cadmium lines were confirmed to one part in one million. The following values were also obtained for 7 helium lines :—

$\lambda\lambda = 7065{\cdot}200$, $6678{\cdot}150$, $5875{\cdot}625$, $5015{\cdot}680$, $4921{\cdot}930$, $4713{\cdot}144$ and $4471{\cdot}482$.

Lummer has described an interference apparatus, which is especially suited to the examination of the structure of the finest spectrum lines.[1] This instrument can be best understood from a diagram, which is given in Fig. 137.

AB is a glass plate 5·4 mm. thick and 20 cm. long, of which the upper and lower sides are made as plane as possible, and parallel to one another. C is a prism cemented to the plate; a beam of parallel light falls upon C, as is shown. The ray undergoes a series of reflections inside the glass plate, and at each reflection some of the light is refracted into the air, and the two pencils *a* and *b* are formed, one by the rays escaping from the upper side, and the other by the rays escaping from the lower side of the plate. These two pencils enter

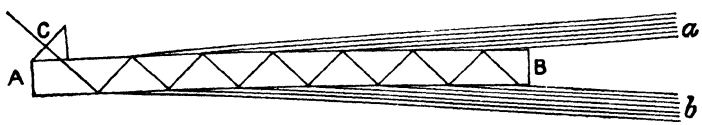


FIG. 137.

the telescope, and the interference rings are observed at the focus of the objective. Lummer and Gehrcke have employed this apparatus for the resolution of the lines of the spectrum of mercury.

Gehrcke[2] has shown that a considerable advantage is gained by using two of these plane-parallel interference plates which are set at right angles to one another, so that a series of bright point maxima are seen. In this way the false maxima due to errors in the plate are readily differentiated from the real maxima, and hence certain errors which may arise from the use of a plate that is not quite perfect may be eliminated. In a later paper Gehrcke and von Baeyer[3] show how small differences of wave-length may be measured with these crossed plates (see page 505).

A similar type of interferometer has also been described

[1] *Verh. d. Deutsch. Phys. Ges.*, **7**. 85 (1901), and *Berl. Ber.* (1902), 11.
[2] *Ibid.*, **13**. 236 (1905).
[3] *Ann. d. Physik.*, **2**. 269 (1906).

by Barnes;[1] this is a reflecting instrument, and is shown in Fig. 138. It consists of two perfectly plane parallel pieces of glass; the under surface of the upper plate is heavily silvered and carefully polished, while the lower plate is almost completely silvered on its upper side, so that its reflecting power is about 0·9. The light is incident upon the upper plate, as is shown, and, due to multiple reflections between the

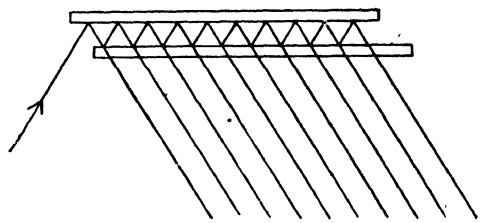


FIG. 138.

silver plates, we have transmitted a number of rays whose path differences are in arithmetical progression. The rays escaping through the lower plate are focussed by a lens, and the interference fringes are examined in the focal plane. The two plates are mounted upon an interferometer similar to that described for Michelson's apparatus (see Fig. 120, p. 306). Barnes claims that with this apparatus the bright interference bands are much stronger than those obtained with the Fabry and Perot method, and hence the weaker components are more readily seen.

[1] *Astrophys. Journ.*, **19**. 190 (1904).

CHAPTER X

THE PRACTICAL RESOLVING POWER OF THE SPECTROSCOPE

IT was shown in Chapter III. page 74, *et seq.*, how Lord Rayleigh deduced his well-known expression for the resolving power of a prism spectroscope. Lord Rayleigh found the relation

$$R = a\frac{d\theta}{d\lambda}$$

where R is the resolving power, a the aperture, and $\frac{d\theta}{d\lambda}$ the dispersion of the prism train. By the resolving power is meant the ratio $\frac{\lambda}{d\lambda}$, *i.e.* the ratio between the mean wave-length of a pair of lines that can just be resolved by the spectroscope and the difference in wave-length between the two components of the pair. It must be remembered that this refers strictly to an infinitely narrow slit, a condition that does not obtain in actual practice, and it is proposed to devote a short space to the consideration of the resolving power when the slit is given a definite width, as of course it must have under ordinary working conditions. It will be seen from what follows that the practical resolving power differs very considerably from the theoretical value with slit of infinitely narrow width, and since we are met with the fact that the giving of a finite width to the slit increases the amount of light available, and at the same time decreases the resolving power, we must, in designing any spectroscope, preserve the balance between the two best suited for the object in view. For this

intensity at the centre. Two lines at a distance of 2δ from each other may then be said to be completely resolved, but as a result of observation it is known that visual resolution begins when the distance apart is only δ. This distance Schuster adopts as the criterion of visual resolution. Now, if a point of the spectrum defined by λ be encroached upon according to the above definition by waves on either side as far as $\lambda + \delta\lambda$ and $\lambda - \delta\lambda$, then we may put

$$P = \frac{\lambda}{\delta\lambda}$$

and call P the purity of the spectrum. Two lines will be completely resolved when they are at a distance $\delta\lambda$, which is equal to $\frac{\delta\lambda}{P}$, and visual resolution will begin when their difference of wave-length is $\frac{\lambda}{P}$.

In the case of very narrow slits we have the same equations with the resolving power R in place of the purity P; the purity is proportional to the resolving power, but it also depends on the width of the slit. We may, therefore, put

$$P = pR$$

and call p the purity factor.

As Schuster points out, the above definitions assume a definite limit to which wave-lengths spread out on either side, and neglect all the light which may be beyond these limits. For narrow slits the neglected light is approximately that which lies outside the central diffraction image. Schuster gives a table showing the distribution of the energy of the light amongst the various diffraction bands, and shows that 90 per cent. is concentrated in the central band. A considerable amount of the light therefore is neglected in the above convention as regards the extent of encroachment, but, as is pointed out, this leads to no practical disadvantage, as the light so neglected is spread over a considerable range of

diameter of the collimating lens at the slit, d the width of the slit, and λ the wave-length. Moreover, he showed that two wave-lengths differing by $\delta\lambda$ are resolved when $\delta\lambda = \frac{\lambda}{P}$.

Owing to the finiteness of light waves, each wave-length, even in a so-called pure spectrum, encroaches to some extent on a neighbouring one. In endeavouring to obtain a simple measurement of the encroachment Schuster neglected everything in the diffracted image beyond the first band. On this assumption each wave-length spreads over a certain finite range and not beyond. If 2ϵ be the width of the first band in the diffraction image of a narrow line, and σ the width of the slit image, each wave-length will spread through a distance of $\frac{1}{2}\sigma + \epsilon$ to either side of its centre. Two lines then will be completely separated when their distance apart is $\sigma + 2\epsilon$. Lord Rayleigh, however, has shown that they are distinctly resolved when their distance apart is only ϵ. Schuster then made the assumption that in the case of wide slits resolution begins when the distance between the lines is $\sigma + \epsilon$. The above equation was deduced under this condition.

Wadsworth criticised the above equation, showing conclusively that, owing to the rapid falling off of the light near the edge of the image of an extended luminous surface, the distance between the two lines at which they would be resolved is appreciably less than that given by the equation. In his later paper Schuster[1] accepts the major portion of this criticism and puts the following proposals forward.

In the image of a very narrow slit at a distance ϵ from the centre the intensity of illumination is zero, while the intensity at a distance $\frac{1}{2}\epsilon$ is 0·40528 of that at the centre. It may, therefore, be said that the line spreads out on either side to a point which is at twice the distance of the point at which the intensity is equal to the above fraction. Let this definition be generalized as follows: the sensible image of a slit of finite width spreads through a distance δ to either side of its centre, such that the intensity at a distance $\frac{\delta}{2}$ is 0·40528 that of the

[1] *Astrophys. Journ.*, 21. 197 (1905).

intensity at the centre. Two lines at a distance of 2δ from each other may then be said to be completely resolved, but as a result of observation it is known that visual resolution begins when the distance apart is only δ. This distance Schuster adopts as the criterion of visual resolution. Now, if a point of the spectrum defined by λ be encroached upon according to the above definition by waves on either side as far as $\lambda + \delta\lambda$ and $\lambda - \delta\lambda$, then we may put

$$P = \frac{\lambda}{\delta\lambda}$$

and call P the purity of the spectrum. Two lines will be completely resolved when they are at a distance $\delta\lambda$, which is equal to $\frac{\delta\lambda}{P}$, and visual resolution will begin when their difference of wave-length is $\frac{\lambda}{P}$.

In the case of very narrow slits we have the same equations with the resolving power R in place of the purity P; the purity is proportional to the resolving power, but it also depends on the width of the slit. We may, therefore, put

$$P = pR$$

and call p the purity factor.

As Schuster points out, the above definitions assume a definite limit to which wave-lengths spread out on either side, and neglect all the light which may be beyond these limits. For narrow slits the neglected light is approximately that which lies outside the central diffraction image. Schuster gives a table showing the distribution of the energy of the light amongst the various diffraction bands, and shows that 90 per cent. is concentrated in the central band. A considerable amount of the light therefore is neglected in the above convention as regards the extent of encroachment, but, as is pointed out, this leads to no practical disadvantage, as the light so neglected is spread over a considerable range of

wave-lengths, with the result that within any small range of periods the total energy is exceedingly small.

Schuster then calculated the distribution of intensity of light energy in the images of slits of finite widths, and the results are given in the table below. In dealing with the widths of the slit it is an advantage to express them all in terms of one convenient width called the normal width. In his investigation of the question of the deterioration of images owing to aberrations or other defects, Lord Rayleigh has generally admitted $\frac{\lambda}{4}$ as the limit of the allowable deviation from the ideal wave-front, if the image is not appreciably to suffer. Schuster, therefore, assumes that an extreme difference of path of $\frac{\lambda}{4}$ from one of the edges of the slit to the nearest and farthest points of the collimating lens will give images as good as if the slit were indefinitely narrow. He, therefore, fixes on this as being the "normal width," and his "slit factor" is the width of the slit in terms of this normal width. In the given table of intensity distributions the widths of slit σ are given in terms of the slit factor, and may be reduced to centimetres by multiplying them by $\frac{f\lambda}{D}$, where f and D are the focal length and effective diameter of the collimating lens, and λ is the wave-length. In the first column the distances from the centre are expressed in terms of the unit distance, viz. the half width of the central diffraction band in the focal plane of the telescope. These distances may be reduced to centimetres by multiplying them by $\frac{f_1\lambda}{D_1}$, where f_1 and D_1 are the focal length and effective diameter of the telescope lens, and λ is the wave-length.

DISTRIBUTION OF INTENSITY IN IMAGES OF SLITS OF FINITE WIDTH.

Distance from centre.	$\sigma = 0{\cdot}0$	$\sigma = 0{\cdot}8$	$\sigma = 1{\cdot}6$	$\sigma = 2{\cdot}4$	$\sigma = 3{\cdot}2$	$\sigma = 4{\cdot}0$	$\sigma = 8{\cdot}0$	$\sigma = 12{\cdot}0$
0·0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·1	0·9675	0·9680	0·9695	0·9719	0·9752	0·9792	0·9999	0·9994
0·2	0·8751	0·8770	0·8825	0·8916	0·9040	0·9192	0·9983	0·9978
0·3	0·7368	0·7406	0·7518	0·7702	0·7954	0·8265	0·9917	0·9962
0·4	0·5728	0·5785	0·5956	0·6239	0·6627	0·7108	0·9753	0·9952
0·5	0·4053	0·4126	0·4345	0·4708	0·5209	0·5834	0·9441	0·9949
0·6	0·2546	0·2627	0·2872	0·3279	0·3845	0·4560	0·8946	0·9946
0·7	0·1353	0·1434	0·1676	0·2082	0·2652	0·3384	0·8252	0·9918
0·8	0·0547	0·0617	0·0830	0·1190	0·1705	0·2379	0·7374	0·9831
0·9	0·0119	0·0173	0·0336	0·0618	0·1030	0·1588	0·6356	0·9640
1·0	0·0000	0·0034	0·0138	0·0325	0·0610	0·1017	0·5261	0·9306
1·1	0·0080	0·0095	0·0143	0·0237	0·0395	0·0646	0·4166	0·8797
1·2	0·0243	0·0243	0·0247	0·0266	0·0320	0·0436	0·3146	0·8105
1·3	0·0392	0·0384	0·0362	0·0334	0·0319	0·0339	0·2261	0·7243
1·4	0·0468	0·0457	0·0427	0·0383	0·0338	0·0308	0·1550	0·6252
1·5	0·0450	0·0442	0·0420	0·0385	0·0343	0·0304	0·1027	0·5190
1·6	0·0358	0·0356	0·0349	0·0337	0·0321	0·0302	0·0681	0·4128
1·7	0·0230	0·0233	0·0244	0·0259	0·0274	0·0287	0·0481	0·3136
1·8	0·0108	0·0116	0·0139	0·0174	0·0216	0·0258	0·0387	0·2272
1·9	0·0027	0·0036	0·0064	0·0108	0·0162	0·0221	0·0356	0·1575
2·0	0·0000	0·0008	0·0033	0·0072	0·0123	0·0181	0·0352	0·1059

From the numbers in the above table Schuster calculated the factors of purity which express the fractions of the highest possible resolving power that are obtained under the different conditions of slit width. These values are given in the following table, which also includes a column (V) showing the central intensities of the image in terms of the intensity with the normal width of slit, and a column (VI) showing the same intensities in terms of the maximum intensity, *i.e.* that with an infinitely wide slit.

CONNECTION BETWEEN PURITY AND WIDTH OF SLIT.

I	II	III	IV	Relative Intensities. V	Relative Intensities. VI
Width of slit.	Slit factor.	Distance of resolution.	Purity factor.	Intensity = 1 for normal width.	Intensity = 1 for infinite width.
0·0	0·0	1·000	1·000	0·000	0·000
0·1	0·4	1·002	0·998	0·406	0·100
0·2	0·8	1·009	0·991	0·805	0·198
0·25	1·0	1·014	0·986	1·000	0·246
0·3	1·2	1·021	0·980	1·191	0·293
0·4	1·6	1·038	0 964	1·558	0·383
0·5	2·0	1·060	0·943	1·902	0·467
0·6	2·4	1·089	0·918	2·217	0·545
0·7	2·8	1·124	0·889	2·500	0·615
0·8	3·2	1·168	0·856	2·751	0·676
0·9	3·6	1·221	0·819	2·967	0·729
1·0	4·0	1·283	0·780	3·148	0·774
1·2	4·8	1·438	0·695	3·415	0·839
1·4	5·6	1·624	0·616	3·571	0·878
1·6	6·4	1·823	0·549	3·646	0·896
1·8	7·2	2·022	0·495	3·670	0·902
2·0	8·0	2·221	0·450	3·674	0·903
3·0	12·0	3·214	0·311	3·789	0·931
D very large		D+0·096		4·0689	1·000

A comparison of columns IV and V will help to determine the choice as to the width of the slit. For example, the normal slit width (slit factor = 1) gives a purity which is 1·4 per cent. less than the maximum possible. Nearly double the amount of light can be obtained by widening the slit until the factor is 2, and the purity only falls to 5·7 per cent. below the maximum. A gain of three times the light will mean a loss of about 20 per cent. of the purity, but a total intensity of 3·67 times that with the normal slit width is accompanied by a loss of just upon half the resolving power. Beyond this point a further widening of the slit greatly decreases the purity without much gain in the light.

The general conclusion gained is that in the case of spectroscopes which are designed for use with weak sources of light, they should be so made that the resolving power is about twice that actually aimed at. The slit may then be set

so that its factor is 7·2 which will give an intensity of 3·67 times that with the normal slit or $\frac{9}{10}$ths of the maximum possible, and a purity of about one half the theoretical maximum. Schuster goes on to say that the above calculations are based upon the supposition that the slit acts as a self-luminous source. In the laboratory this may be secured by the use of a condensing lens. The loss of light, however, may be very large unless the condensing lens subtends a much larger angle at the slit than does the collimating lens; in the case of the normal slit width it should be four times as great. If the slit have the width 8 the loss would not be great and so Schuster suggests the designing of spectroscopes with $2\frac{1}{4}$ times the required resolving power and the use of a slit factor of 8.

Morris-Airey [1] has pointed out that Schuster's expressions for purity do not appear to contain a factor depending upon the position of the grating or prism, but as a matter of fact the purity becomes greater as the angle of incidence of the light on the grating increases. When the slit has a finite width the light falling on the grating may be considered as a number of beams of parallel rays making slightly different angles with the normal to the grating. Let ϕ be the angle of incidence and θ the angle which the corresponding diffracted beam makes with the normal. Then if b is the grating space we have $b(\sin\phi - \sin\theta) = \pm\frac{n\lambda}{2}$ from which $d\theta = \frac{\cos\phi}{\cos\theta}d\phi$ and $\frac{d\theta}{d\lambda} = \frac{n}{2b\cos\theta}$, for any value of ϕ. The diffracted beams, therefore, make slightly different angles with the normal, the total variation being $d\theta$. This variation can be made as small as we please by increasing the value of ϕ. In the limit when the light falls at grazing incidence the different beams corresponding to any particular wave-length and order of spectra make the same angle with the normal and will be received by the telescope very nearly as if the slit had been very narrow. Again $\frac{d\theta}{d\lambda}$ is also increased so that the total effect is greatly to increase the purity. Morris-Airey points out that this

[1] *Phil. Mag.*, 11. 414 (1906).

result is really included in Schuster's formula, the term ψ has always been interpreted to mean the angle subtended by the collimator lens at the slit, but when the prism or grating is sufficiently tilted only part of the light passing through the lens is effective and it is only the width of this effective portion which should be considered in determining the value of the angle ψ. That angle, therefore, depends on the position of the prism or grating and may in the limit be reduced to zero. The smaller ψ is the greater is the purity, and ultimately by reducing its value the full resolving power is reached with a great width of slit. In fact, Morris-Airey finds that with a small grating of about 1300 lines to the inch it is easily possible to separate the D lines when the slit is half a centimetre wide. It must not be forgotten that the application of this is limited by the great loss of light by reflection when large angles of incidence are used.

CHAPTER XI

THE PHOTOGRAPHY OF THE SPECTRUM

No attention has as yet been paid to the actual methods of photography employed in spectrum work, and a few pages may well be devoted to their description. Chiefly, however, we must discuss the special methods used in the preparation of plates for the photography of the regions to which the ordinary commercial plate is not sensitive. The ordinary dry plate of the market is quite sensitive between the limits $\lambda = 5000$ and $\lambda = 2200$, and may, therefore, be used for these regions. It must be remembered, however, that the slower speed plates generally produce a much finer grained image than do the rapid plates, so that it is always advisable to use slow plates where possible for spectrum work. With the very rapid plates the spectrum lines become badly defined, and very difficult to measure with any degree of accuracy. The maximum of sensitiveness of an ordinary dry plate as made at present lies in the violet or indigo region of the spectrum; on the red side of this maximum the sensitiveness falls away rapidly, becoming very small beyond the limit given above of $\lambda = 5000$. It is quite possible, with bright illumination and sufficiently long exposure, to photograph the green, yellow, and even the red regions with certain commercial slow plates, but this is impracticable on account of the great exposures required. On the more refrangible side of the maximum the sensitiveness falls off more slowly, and extends to $\lambda = 2100$, where the absorption due to the gelatine begins to make its appearance.

In 1873 Vogel[1] discovered that if the emulsion of a photographic plate is mixed with one of certain dyes, or if the plate

[1] *Berichte*, 6. 1302 (1873); 7. 976 (1874).

is simply allowed to stand for a short time in the solution of the dye, it becomes sensitive to those rays which are absorbed by the dye. Thus corallin absorbs the green and yellow rays of light, and Vogel found that a collodio-bromide plate on treatment with this dye became sensitive to those rays. Vogel experimented with many other dyes, amongst others cyanin, naphthalene red, fuchsine, etc. A great deal of work upon the subject has been done, and various theories proposed, but the inner meaning of the action of the dye is still not quite understood. An interesting and very important fact is that the strength of the solution of the dye must be very weak (0·001 to 0·01 per cent.), as otherwise the whole sensitiveness of the plate is reduced. We are indebted to Eder [1] for an extended investigation into the effects of various dyes ; he found, amongst other facts, that the new maximum of sensitiveness is always about 30 A.U. on the red side of the absorption maximum of the dye used.

A very great number of dyes have been recommended for sensitising plates, and it is impossible to quote them all here. There are so many brands of orthochromatic plates upon the market which are suitable for the photography of the spectrum from Fraunhofer's C to the ultra-violet, that it is hardly worth one's while preparing the plates, except for the extreme ends of the spectrum.

The following, however, may be given as typical recipes for sensitising plates for the regions specified.

Erythrosin, recommended by Eder,[2] for the region from D to the ultra-violet—

25 c.c. erythrosin solution (1 part in 1000 parts of water),
1 c.c. silver nitrate solution (1 part in 80 c.c. of water),
½ c.c. = 8 drops of ammonia (sp. g., 0·91),
75 c.c. of water.

The plates are soaked in this for three or four minutes, and then quickly dried.

[1] *Wien. Ber.*, **90.** I, 1097 (1884) ; **92.** II, 1346 (1885) ; **93.** II, 4 (1886) ; **94.** II, 75 and 378 (1886).

[2] Eder's *Handbuch d. Photographie*, I, 226 (Wilhelm Knapp, Halle, 1891).

Cyanin, for the region from C to D, with a minimum in the green; the solution recommended by Eder is as follows:—

2 parts of a 0·25 per cent. solution of cyanin in alcohol,
100 „ water,
½ part of ammonia.

The plates to be soaked in the bath for four minutes with continual rocking, and dried. They keep from one to two weeks.

Hübl[1] recommends the conversion of the commercial cyanin, which is the hydriodide of the free base, into the hydrochloride by evaporation with concentrated hydrochloric acid over a water bath; 300 c.c. of a saturated solution of borax are mixed with 3 c.c. of a 0·2 per cent. solution of the dye in alcohol. The plates are soaked in this for five to ten minutes, and are used at once while wet, or are rinsed in water and dried.

Burbank[2] also makes use of cyanin, this compound being treated in rather a novel way: 1 grm. of cyanin, 31 grms. chloral hydrate, and 125 c.c. of water (best in an Erlenmeyer flask) are heated for half to three-quarters of an hour on a water bath with vigorous stirring; 35 c.c. of strong ammonia are now added, which causes a considerable evolution of chloroform. The cyanin is at the same time deposited as a liquid on the sides of the flask (probably because it contains chloroform). After allowing to settle for a few minutes, the supernatant liquid is carefully poured off, so as not to disturb the cyanin; 100 c.c. of methylated spirit are added to dissolve the cyanin, and then also a solution of 8 grms. of quinine sulphate in methylated spirit. The quinine may be dissolved in 120 c.c. of the spirit with the aid of heat. The whole is then made up to about 250 c.c., this being the stock solution, which must be kept in the dark, as it is very apt to become decomposed. The above preparation should be carried out in as little light as possible, and the following staining and drying processes must be conducted in absolute darkness. To 850 c.c. of water

[1] Eder's *Jahrbuch f. Photog.*, **11**. 168 (1897).
[2] *Phil. Mag.* (5), **26**. 391 (1888).

are added 6 c.c. of the stock cyanin solution, and 6 c.c. of strong ammonia. The plates are placed in this solution for about four minutes, and dried; they may be developed with a pyro-potash developer. I have used this process with excellent results.

Two very important dyes for use in sensitisers for the red are alizarin blue and cœrulin, and these have been employed as the sodium bisulphite compounds with great success by Higgs,[1] as well as by others after him. Higgs gives the following rather lengthy method of preparation of the compounds, at the same time pointing out the necessity of using pure substances for the best results. He says—

"To a saturated solution of sodium bisulphite in a mortar is added alizarin blue paste. This is disintegrated with a pestle, and poured into a glass vessel capable of holding an additional quantity of sodium bisulphite, in all 10 parts of the paste to 20 parts of the bisulphite, and another 10 parts of water. The vessel is well stoppered, set aside in a cool place for five or six weeks, and shaken daily, but left undisturbed during the last eight or ten days.

"The solution is decanted, filtered, and treated with alcohol, to precipitate the greater portion of the remaining sodium bisulphite. Fifty parts of water are now added with a sufficiency of sodium chloride to form a concentrated solution. Again set aside in an open-mounted glass jar, covered with bibulous paper, for seven or eight days, a deposition of the dye in a crystalline state, together with sulphite of calcium, will take place, which latter, owing to its insolubility in water, may be removed by filtration.

"The alizarin blue S is separated from any unaltered substance left in the original stoppered vessel by solution, and added to the brine, now purified from lime salts, and once more set aside to crystallise; the final purification is effected in a beaker containing alcohol and a small percentage of water to remove the last traces of sodium chloride, collecting the crystals on a filter paper and drying at ordinary temperatures.

[1] *Proc. Roy. Soc.*, **49**. 345 (1891).

"The needle-shaped crystals are of a deep-red colour. Dilute solutions are of a pale sherry colour, changing with the addition of a few drops of ammonia to a green, which immediately gives way to magenta and every shade of purple till it assumes a blue colour.

"Plates immersed in a solution containing 1 : 10,000 of the dye and 1 per cent. of ammonia give the most perfect results the day after preparation, but rapidly deteriorate unless kept quite dry.

"An exposure of forty minutes with a slit width of 0·001 inch gave the region of A in the second order of a grating with perfect detail; $\lambda = 8400$ has also been reached."

The process for the preparation of pure cœrulin S is a slight modification of the preceding. The results obtained, as well as the actinic curve, are almost identical. The pure substance is almost white.

Alizarin blue bisulphite in combination with other dyes has been used with considerable success by Lehmann,[1] who after making trial of several dyes, amongst which were cœrulin and cyanin, found that the following solution gave the best results :—

Alizarin blue bisulphite (1 in 500)	2 c.c.
Nigrosin (water soluble) (1 in 500) . . .	1·5 c.c.
Ammonia (sp. g., 0·910)	1·0 c.c.
Distilled water	100 c.c.
Silver nitrate (1 in 40)	5 drops.

The solution is filtered, and the plates are soaked therein for four or five minutes, and quickly dried. As a developer, Lehmann recommends ferrous oxalate, containing 3 to 4 c.c. of potassium bromide solution to each 50 c.c. of developer. All processes should be conducted in absolute darkness, but if one prefers not to have complete darkness, light as nearly monochromatic as possible should be used of about the wave-length of Fraunhofer's E. The plates do not keep for more than four days at the longest, and are sensitive to $\lambda = 9200$, and even to $\lambda = 10{,}000$ with longer exposure. It is preferable

[1] *Arch. f. Wissenschaftliche Photogr.*, II, 216 (1900).

to recrystallise the dye-stuffs in the dark before using them, because the sensitiveness of the plates is materially increased thereby, especially for the longer wave-lengths.

Nigrosin has also been used by Eckhardt,[1] who found that plates could be rendered sensitive to the region between Fraunhofer's A and B, and also to the orange, though in less degree by the following solution :—

Nigrosin B. (Beyer & Co., Elberfeld) (1 in 500)	10 parts,
Ammonia	1 part,
Distilled water	100 parts.

The plates are soaked in this solution, and then washed with alcohol.

I have used Lehmann's recipe with excellent results, especially when Lumière's B plates (sensitive to red and orange) are used. One other dye for the extreme red may be mentioned, namely, the diazo-black, BHN, of Beyer & Co., which Valenta [2] considers far superior to nigrosin, as the plates are four times as sensitive.

As is well known, Abney succeeded in preparing a special photographic emulsion which was sensitive to rays with a wave-length of $\lambda = 20{,}000$, and by means of this has photographed the solar spectrum to $\lambda = 10{,}000$ A.U. Abney commenced his work upon the dyeing of plates, and found that the maximum of sensibility always lay in the same spectral region as the absorption maximum of the dyed emulsion. Arguing from these results, Abney [3] conceived the idea of making a silver emulsion, which of itself should absorb red light, in distinction from the ordinary emulsions which absorb blue light, and hence appear red by transmitted light. This he succeeded in doing, and obtained an emulsion essentially blue by transmitted light, which was extremely sensitive to red rays, even in some cases to the rays from boiling water. Before describing the methods employed, it may be pointed out that Abney found that his emulsion had two maxima of sensitiveness,

[1] *Phot. Correspondenz*, **34.** 121 (1897).
[2] *Ibid.*, **35.** 314 (1898).
[3] *Phil. Trans.*, **171.** II, 653 (1880).

one at $\lambda = 7600$, and the other at $\lambda = 3800$; and he therefore suggested, as one maximum was the octave of the other, that the silver bromide which is blue by transmitted light is more associated than the bromide which is red. He also found that the new emulsion when rubbed became converted into the ordinary variety, red by transmitted light, and lost its power of responding to the longer wave-lengths. The following method is given by Abney:—

A normal collodion is first made according to the formula—

Pyroxylin (any ordinary kind)	16 grains,
Ether (sp. g., 0·725)	4 ozs.,
Alcohol (sp. g., 0·820)	2 ozs.

This is mixed some days before it is required for use, and any undissolved particles allowed to settle, and the top portion is decanted off. Three hundred and twenty grains of pure zinc bromide are dissolved in ½ to 1 oz. of alcohol (0·820), together with 1 drachm of nitric acid. This is added to 3 ozs. of the above normal collodion, which is subsequently filtered. Five hundred grains of silver nitrate are next dissolved in the smaller quantity of hot distilled water, and 1 oz. of boiling alcohol added. This solution is gradually poured into the bromised collodion, stirring briskly while the addition is being made. Silver bromide is now suspended in a fine state of division in the collodion, and if a drop of the fluid be examined by transmitted light it will be found to be of an orange colour.

Besides the suspended silver bromide, the collodion contains zinc nitrate, a little silver nitrate, and nitric acid, and these have to be eliminated. The collodion emulsion is turned out into a glass flask, and the solvents carefully distilled over with the aid of a water bath, stopping the operation when the whole solids deposit at the bottom of the flask. Any liquid remaining is carefully drained off, and the flask filled with distilled water. After remaining a quarter of an hour the contents of the flask are poured into a well-washed linen bag, and the solids squeezed as dry as possible. The bag with the solids is again immersed in water, all lumps being previously crushed, and after half an hour the squeezing is repeated. This operation

is continued until the wash water contains no trace of acid when tested by litmus paper. The squeezed solids are then immersed in alcohol (0·820) for half an hour to eliminate almost every trace of water, when, after wringing out as much as possible of the alcohol, the contents of the bag are transferred to a bottle, and 2 ozs. of ether (0·720) and 2 ozs. of alcohol (0·805) are added. This dissolves the pyroxylin, and leaves an emulsion of silver bromide, which when viewed in a film is essentially blue by transmitted light.

All these operations must be conducted in very weak red light, such a light, for instance, as is thrown by a candle shaded by ruby glass, at a distance of 20 feet. It is pointed out in a footnote that a faint green light of a wave-length midway between E and D would be best.

It is most important that the final washing should be conducted almost in darkness. It is essential to eliminate all traces of nitric acid, as it retards the action of light on the bromide, and may destroy it if present in appreciable quantities. To prepare the plate with this silver bromide emulsion, all that is necessary is to pour it over a clean glass plate, as in ordinary photographic processes, and to allow it to dry in a dark cupboard. (It has been found advantageous to coat the plate in red light, and then to wash the plate and immerse it in a dilute solution of hydrochloric acid, and again wash, and finally dry. These last operations can be done in dishes in absolute darkness; the hydrochloric acid gets rid of any silver sub-bromide which may have been formed by the action of the red light.)

Abney recommends the ferrous oxalate developer mixed with an equal volume of potassium bromide solution containing 20 grains to the ounce. The film is first softened by flowing over it a mixture of equal parts of alcohol and water, and is then well washed. The developer is now poured over the plate, taking care not to touch the film with the fingers.

By diminishing the amount of nitric acid to one-fourth the amount given above, it is possible in very cold weather to obtain plates which are sensitive to the radiations from boiling mercury or even boiling water. In summer-time this emulsion

produces what is known as foggy pictures; but it can be rendered of use by flooding with hydrochloric acid. In the preparation of such an emulsion the water bath must be kept at a temperature but little above that of the boiling-point of ether.

Ritz[1] varied the proportions of Abney's mixture, and in all cases found that the sensibility is much increased when the silver nitrate or bromide is in excess. It is preferable to use the latter. An emulsion obtained by means of concentrated solutions of silver nitrate and zinc or ammonium bromide, reducing the quantity of pyroxiline almost to vanishing point, is more sensitive than emulsions prepared in the usual way. The characteristics of such an emulsion are: (1) the greatest concentration possible of the reacting solutions; (2) the minimum possible of the pyroxiline, with reasonable precautions; (3) the formation of a homogeneous emulsion.

The bromides of zinc and ammonium act in an almost similar way, and we can also replace the mixture of alcohol and ether by methyl alcohol or acetone. The transformation of the silver bromide is then of a purely physical order, and is always accompanied by an increase in the diameter of the grains. Finally, the emulsion is submitted to pressure at about 100° C. for one hour, and at 40° C. for twenty-four hours. Still, however, Ritz found that Abney's limit was not passed, the bromide becoming granular and decomposing under the influence of longer wave-length radiation.

He therefore found it better, after having distilled the ether, to allow it to cool; then return it to the mixture and once more distil. He could then use solutions two or three times weaker than those employed by Abney, and so obtain much more homogeneous emulsions. It was also found that the sensitiveness to white light is increased to a slight degree.

It is known that under the action of heat an emulsion of gelatine bromide becomes much more sensitive to the very refrangible rays, but less so to the yellow and red. Ritz also found that the variations in the concentrations of the salts and of the gelatine have the same influence as in Abney's emulsion.

[1] *Comptes Rendus*, **143**. 167 (1906).

This leads to the conclusion that this characteristic is a quantitative difference only of the same property of silver bromide. He performed the following experiment to confirm this theory. A precipitate of silver bromide, obtained either in water or in alcohol, was washed and heated for some minutes under pure water, or, if found to be more advantageous, water with a few drops of silver nitrate added. After emulsification in gelatine and a further action of heat, plates more sensitive to infra-red radiations than those of Abney were given. After five minutes' exposure to the spectrum of a Nernst lamp much less rich in heat-rays than the sunlight used by Abney, a spectrum was shown which decreased regularly from the blue end to $1{\cdot}4\mu$ without showing any of the rough variations of plates treated with dyes. The characteristic blue colour of Abney's emulsion appeared in this case immediately, and in the cold.

There are at present upon the market many brands of plates which have been specially sensitised for the red and yellow, and for the yellow and green regions. Amongst several may be mentioned Lumiere's series A for the yellow and green, and the series B for the red and yellow. The best plates now to be obtained, in my opinion, are those of Wratten and Wainwright. This firm make three kinds, which differ in their colour sensitiveness—the allochrome plate, which is sensitive to the yellow-green; the panchromatic plate, which is sensitive to the red as far as $\lambda = 6800$; and the spectrum panchromatic plate, which is sensitive up to as far as $\lambda = 8000$. The allochrome plate is thoroughly suited for all ordinary work in spectrum photography, from the extreme ultra-violet up to the yellow-green, and gives most excellent results. For the yellow and red regions one of the other two kinds should be used.

Millochau[1] has applied the Waterhouse method to the photographic registering of the infra-red spectrum. This process depends on the fact that the infra-red rays destroy the photographic action on a plate which has previously been "solarised." Very sensitive gelatine bromide plates are immersed for ten minutes in distilled water which contains a few

[1] *Comptes Rendus*, **144.** 725 (1907).

drops of acetic acid, and then are placed for the same time in a saturated alcoholic solution of malachite green. The plates are then rinsed rapidly and dried, the whole process being carried out in the dark. When required for use, the plates are solarised by exposure for thirty seconds to a four candle-power electric lamp at 75 cms. distance, and are then exposed in the spectrograph. With these plates Millochau succeeded in photographing the solar spectrum from $\lambda = 7500$ to $\lambda = 9500$. Trials were also made with these plates in a spectrograph of low dispersion, and it was found that the inverse action extends from $\lambda = 6000$ to as far in the infra-red as the optical parts of the instrument allowed.

Lehmann[1] succeeded in photographing the spectrum as far as 20,000 Ångström units by means of the phosphoro-photographic process. This process depends upon the property possessed by infra-red rays of extinguishing the phosphorescence of certain substances. Very finely powdered zinc sulphide (which possesses a green phosphorescence) is pressed by means of a glass plate into a film of some transparent medium. Such a screen is exposed to blue light for a quarter to half a minute, which causes the zinc sulphide particles to phosphoresce. It is then immediately exposed to the spectrum for one to two minutes, after which it is at once placed in contact with a photographic plate, sensitive to green light. After two hours the plate is developed in the usual way. The proper ratio of the time necessary for excitation of the screen and exposure must be carefully ascertained by trial. Since the phosphorescence of zinc sulphide is destroyed by infra-red light, it is evident that the presence of a bright line in the spectrum will be denoted by a transparent line in the photographic plate.

As regards the manipulation of the plates there is very little to be said beyond what is to be found in ordinary text-books upon photography. Spectrum photography differs from landscape work in that one strives after as hard contrasts as possible, and therefore the developer should be selected accordingly. Very good results are obtained with hydroquinone or ortol, especially the latter. In such cases an acid

[1] *Zeitschr. für Instrumentenk.*, **26**. 353 (1906).

fixing bath should be used, *i.e.* a bath which contains sodium bisulphite as well as the thiosulphate. This may be obtained by adding some sodium metabisulphite crystals or concentrated sodium bisulphite solution to the fixing solution; Eder[1] recommends 50 c.c. of a concentrated sodium bisulphite[2] solution to 1 litre of 25 per cent. solution of sodium thiosulphate.

In working with the red and yellow sensitive plates it is always better to work in absolute darkness, although sometimes a green screen is recommended, because this style of plate usually possesses a minimum of activity in this region. It is quite simple to find by experiment how long a particular developer takes fully to develope a correctly exposed spectrum plate; all plates are then placed for that time in the developer and washed, fixed, and dried in the usual way.

It has been shown by Wood[3] that the exposure of a photographic plate for a short time to a very faint light materially increases its sensibility, so that it can be used for very weak objects, such as faint spectra. A small gas flame a few millimetres high is sufficient, but the time of exposure in order to give the best results must be found by trial.

This exposure to a weak light may be carried out either before or after the plate is used for the principal photograph. Wood remarks that he treats all his spectrum photographs in this way, and finds that it reduces the necessary time of exposure fully by one half. A very small electric lamp, illuminated by the current from a storage cell, is preferable to the gas flame.

It remains now to describe the special method employed by Schumann for the preparation of the plates for the photography of the extreme ultra-violet region to as far as $\lambda = 1200$ tenth metres. It has already been pointed out that Schumann discovered that gelatine exercises a very powerful absorptive influence upon the rays of short wave-length, a film of 0·00004 mm. producing a noticeable effect. He also found by experi-

[1] *Handbuch*, 1. 226.

[2] Obtained by passing SO_2 into a saturated solution of sodium sulphite.

[3] *Astrophys. Journ.*, 27. 379 (1908).

ment that a deposit of pure silver bromide was sensitive to the very short waves; and he therefore devised methods for the preparation of plates which contained either pure silver bromide or silver bromide with a very small trace of gelatine to bind it together, so small as not to exert any appreciable absorbing action upon the light.

Schumann has published two chapters on the methods of preparation of these plates. In the first paper[1] two alternative processes were described, according to the first of which, pure silver bromide is precipitated from mixed solutions of silver nitrate and potassium bromide (containing excess of the latter), and allowed to settle on plates placed at the bottom of the containing vessel. In the second method the precipitation of the silver bromide is carried out in the presence of a small quantity of gelatine in the solution. Some of the latter is carried down with the silver salt, sufficient to bind the silver salt to the plate, but not to destroy its sensitiveness to the extreme ultra-violet rays. The plates prepared by this method, however, are very slow, and require long exposures.

In his second paper[2] Schumann gives a very much improved method, and one which gives plates that are much more rapid, and at the same time more durable. The outline of the process is as follows:—A gelatine emulsion very rich in silver bromide is prepared, and allowed to set to a jelly. It is then washed in cold water and afterwards melted, and mixed with a large volume of water and filtered. The mixture is then poured over the plates which have been laid on a level surface, and allowed to stand. The silver bromide is then deposited on to the plate, and after this the supernatent emulsion is poured off, and the silver bromide film that is left behind is dried. On account of its importance the method may be described in detail.

Two solutions are made as follows:—

A	Potassium bromide	9·0 grms.
	Gelatine (Nelson's No. 1) . . .	4·5 grms.
	Distilled water	60 cc.

[1] *Wiener Berichte*, **102**. II. A, 994 (1893).
[2] *Ann. der Physik.*, **5**. 349 (1901).

B { Silver nitrate . . . . . 11·25 grms.
  { Distilled water . . . . . 60 cc.

After 20–30 minutes, when the gelatine[1] will be found to be properly swollen and softened, the flasks containing the solutions are both immersed in water at a temperature of 50–60° C., until the gelatine is completely dissolved. All the following operations must now, of course, be carried out in a brown or red light. The silver solution A is now poured, small portions at a time, into the gelatine solution B (not *vice versa*), the mixture being well shaken after each addition. After the addition of the whole of the solution B, the flask containing the mixture is closed and again thoroughly shaken. The flask is then placed in water at a temperature of 60° C., and allowed to stand quite quietly for half an hour. During this period some of the larger granules of silver bromide settle out. After the half-hour, therefore, the emulsion is poured off very carefully into a porcelain dish, so as not to disturb the precipitate. The dish is placed on ice or in a very cold place (not above 4° C.), and left for 2 to 3 hours, until the emulsion is completely set to a jelly; the firmer the jelly is the better. The jelly is now cut into small pieces with a horn spatula, and these are heaped together on a broad piece of fine muslin, which is then gathered up and tied together to form a bag. This bag is suspended for 2 or 3 hours in running water, or in a 2-litre vessel of water, which is changed ten times at quarter-hour intervals; the water must not be warmer than 14° C. This washing process is carried out to remove the soluble potassium bromide and nitrate. After the washing, the bag is taken out and gently squeezed to remove the adhering water; it is then suspended in a 1½-litre beaker, which contains 950 c.cs. freshly boiled water cooled to 55° C. The emulsion melts in a few minutes, and mixes with the water. It is carefully stirred with a glass rod, and twice filtered through glass wool. The glass wool plug should be sufficiently compact to allow the emulsion only to pass slowly. Great care must be taken in

[1] Schumann makes particular note of the fact that Nelson's No. 1 is the only brand of gelatine that is suitable.

the stirring and filtration to guard against the formation of bubbles. The exit tube of the funnel should touch the side of the vessel into which the emulsion runs, so that the stream does not break into drops. The emulsion may now be used at once, or it may once again be allowed to stand, so as to allow the coarser silver bromide to deposit. This makes for a great improvement in the plate, for these coarser particles give dark flecks in the finished picture. For this purpose the emulsion is filtered into a large flat bottomed dish, until the layer is about 4 to 5 mms. deep, when it is allowed to stand for three-quarters of an hour, after which it is carefully poured off, and used at once to coat the plates.

The glass plates require special treatment owing to the thinness of the emulsion, as it is quite impossible to pour a sufficient thickness on to an ordinary plate glass with sharp edges without some of it running off. A piece of emery cloth (not paper) is stretched and pinned down on a flat surface, and the glass plate, held at an angle of 30° to the flat surface, is rubbed backwards and forwards on the emery until the sharp angular edge is ground to a rough bevel about $\frac{1}{2}$ mm. wide. Schumann finds that this bevel greatly retards the tendency of the emulsion to run off the plate. The glass plates are then allowed to stand in strong nitric acid for half an hour, then washed with water and dried with a cloth. They are finally polished with a clean cloth, and all dust removed from them, but this should only be done just before the emulsion is poured over them.

When everything is ready for the coating, the plates are all laid on a long narrow piece of plate glass, which stands on feet about 8 to 10 cms. high, and is carefully levelled. Each plate should project 1 to 2 cms. over the edge of the plate glass. In coating large plates it is advisable to measure the emulsion for each plate, *e.g.* 50 to 60 c.cs. for a plate 13 × 18 cms., and 25 c.cs. for a plate 9 × 13 cms.; for small plates it does not matter. The emulsion is poured very carefully on to the plate, in order to avoid any bubbles being formed. The emulsion is poured on to the projecting edges of the plates, and if it only flows very slowly towards the other end of the plate, the plate may be lifted very gently by putting the finger under the

projecting portion. When the whole of the plates are covered, they are left to stand for 3 to 4 hours on the levelling table, in order to allow the silver bromide to settle out. The supernatant emulsion is then poured off, leaving the silver bromide deposit undisturbed, and this is the most delicate part of the process. Schumann's directions here are very precise. The first plate at the left-hand end of the plate-glass table is gently pushed along until it projects about $\frac{4}{10}$ths of its length; an evaporating basin is held underneath, and the plate is slowly lifted with the index finger of the left hand, and turned round the end of the plate-glass table, until the free end of the plate rests on the evaporating basin. The emulsion then runs off, and one can take hold of the plate by the edges at the two upper corners without disturbing the silver bromide deposit. The plate is slowly brought upright and inverted, so that the film side is downwards, and then it is placed on the drying board. This drying board is covered with filter paper, and is provided with a number of vertical wooden pegs, against which the plates are leaned. The plates, when being moved along the levelling table, must only be touched with a knife, the edge of which is pressed against the lower edge of the plate. Touching them with the finger will inevitably cause the emulsion to run on to the levelling table, and not only that particular plate, but the whole batch will be destroyed. In letting the emulsion drain off, great care must be taken not to let the emulsion which runs down the edges find its way over the plate again, or streaks will be produced which materially damage the value of the finished plate.

The drying may be allowed to take place in a dust-free room or preferably in a proper drying chamber, as otherwise zones of varying sensitiveness are liable to be produced. They dry very quickly, usually in about $\frac{1}{2}$ to $\frac{3}{4}$ hour. If time is a consideration, after the central portion is dry the still wet ring of emulsion round the edges may be wiped off with a slip of filter paper.

The dried plates may be packed face to face in pairs with very narrow strips of filter paper between them at the edges, in order to prevent the films coming into contact. Each pair

should be wrapped separately in black paper. Tinfoil must on no account be used as the plates are very sensitive to it and are quickly fogged. It must be remembered that the film is extremly sensitive to any pressure, so much so that they cannot even be brushed with a soft camel hair brush.

Cutting the plates, therefore, is a very delicate operation, but may be carried out as follows. The plate is laid film up on a table, and a very narrow strip of somewhat thick paper is put along each of the edges of the plate at right angles to the direction in which it is proposed to cut. A straight edge is then rested on these paper strips and the plate cut with a diamond through the film. The paper strips will be found to have damaged the film, and so care must be taken that these strips are so narrow that they will not extend over a part of the film which will be acted on by the light of the spectrum.

The plates prepared according to the above method are not very sensitive during the first few days after their manufacture, and also they do not give very good intensity of image. If, therefore, they are exposed in the spectrograph very soon after being made they must be treated with a very strong developer, one far too strong to be used for the ordinary dry plate without fogging it. On keeping the plates they gain in their sensitiveness and also in the intensity of the image. This is noticeable after 1 to 2 weeks, and after 1 to 2 months they give the best results. After three months a little fog begins to make its appearance. After two years they still give excellent results, but there is then to be noticed a falling off in the intensity.

As a developer Schumann has found nothing to equal Eder's pyrogallol formula, which is as follows:—[1]

A	Sodium sulphite	100 grms.
	Pyrogallol	14 grms.
	Distilled water	500 c.c.
	Conc. sulphuric acid . . .	6 drops.

The pyrogallol is to be added last of all.

[1] Eder's *Handbuch der Photographie*, 1. 225 (W. Knapp, Halle a.S., 1891).

B { Sodium carbonate crystals . 50 grms.
  { Distilled water . . . . . 500 c.c.
C { Potassium bromide . . . . 10 grms.
  { Distilled water . . . . . 100 c.c.

The usual strength of developer for gelatine dry plates is equal parts of A, B, and water, together with 4 to 6 drops of C to every 50 c.c. of the mixture. If the Schumann plates are freshly prepared then equal parts of A and B must be used, and if the intensity is still poor a 30 per cent. solution of potassium carbonate may be added drop by drop until, if necessary, as much as one quarter of the volume of the developer has been added. A few drops of C are recommended to keep the plate free from every trace of fog; this also helps to increase the intensity. Schumann also recommends using the developer very cold at the commencement and warming it by rubbing the hand under the dish as soon as the image begins to make its appearance (this is quite feasible since the plates actually exposed by Schumann were very small, viz. 13 × 37 mms.). With older plates one should use 1 part of A, 1 part of B, and 1 or 2 parts of water, with 1 to 3 drops of C for every c.c. of A used.

During all processes of development the plate should only be touched with a pair of forceps; it is convenient to leave these attached to the plate throughout the processes of development, fixation, and washing.

As fixing bath a 25 to 30 per cent. solution of sodium thiosulphate (hyposulphite) is used and the unchanged silver bromide dissolves in a few seconds. To wash the plates they should be held for about two minutes under a gentle stream of water, then after this a careful rinsing with distilled water is advisable. The plates are finally set aside in a dust-free place to dry, which in a warm atmosphere takes about 10 to 15 minutes. It must be remembered that the negative is very delicate, and may even be scratched when dusted with a soft brush unless the brush has been very carefully selected.

Generally speaking, these plates are less sensitive than the ordinary dry plate to the rays of longer wave-length than $\lambda = 2200$. They are less acted on, therefore, by the diffused light in the spectrograph.

CHAPTER XII

METHODS OF ILLUMINATION

SPECTROSCOPIC observations fall naturally into two main divisions, namely Emission spectra and Absorption spectra. The methods of production of emission spectra may be divided into four classes, flame, spark, electric arc spectra, and cathode streams (for the production of phosphorescence).

It is evident that the first three methods deal with the illumination of substances in the gaseous form and consequently they may well be grouped together; on the other hand, the subject of cathode streams producing illumination in solids and liquids, and absorption spectra which deal with the removal of certain definite rays from a light beam, may be treated separately. As the amount of work which has been done is very great and the methods which are involved are very numerous it will be found convenient to treat the whole subject in three chapters. In the present chapter, therefore, will be found an account of flame, spark, and arc spectra, and the electric discharge through gases under reduced pressure; while the two next chapters will treat of phosphorescence and absorption respectively.

Flame Spectra.—The Bunsen flame itself is a convenient method for the production of spectra, but under ordinary circumstances its use is restricted to a few more or less volatile metallic salts. The method of introduction of the salt into the flame is familiar enough to any one who has practised chemical analysis, where the colours given to a Bunsen flame by certain salts are made use of in the scheme of work. A platinum wire is taken, and a small loop is made on the end; the looped end of the wire is then heated to redness in the Bunsen flame to remove all traces

of deposit therefrom—notably sodium salts from the fingers. The wire is heated as long as any yellow tinge is given to the flame; it is best in the case of a wire which has been previously used to moisten the end with hydrochloric acid. When the wire is clean it may be dipped into a solution of the salt of the metal whose spectrum is required, and then put into the outer mantle of the Bunsen flame; at once the characteristic flame coloration will be produced, and this may be examined in the spectroscope in the ordinary way. It is best in these cases to use the chlorides of the metals, as these salts are volatile, and therefore give better results.

The metals which give the flame colorations in this simple way are, lithium, sodium, potassium, rubidium, and cæsium; barium, strontium, and calcium. Some other substances give flame colorations, but not of so decided a nature as to render this method feasible for the investigation of their flame spectra. It will readily be understood that the flame coloration as produced above is not very lasting, and so can hardly be used when one requires a continuous illumination. Under these circumstances the arrangement devised by Mitscherlich[1] may be employed, as shown in Fig. 139, in which the wick *c* consists of a bunch of very fine platinum wires or asbestos threads. The tube *a* is filled with a solution of the required salt, and, when the wick is put into the flame, a very constant coloration is produced. It is a great advantage to dissolve some ammonium acetate along with the required salt; this causes the solution to flow better along the wick. Mitscherlich recommends that 1 part of a concentrated salt solution be mixed with 20 parts of a 15 per cent. solution of ammonium acetate.



FIG. 139.

Another convenient apparatus has been used by Eder and Valenta;[2] two metal discs, about 6 to 8 inches in diameter, are mounted upon the same axle and screwed together with a ring of platinum gauze between their edges; this gauze projects about 1 inch all the way round.

[1] *Pogg. Ann.*, **116**. 499 (1862).
[2] *Wiener Denksch.*, **60**. 468 (1893).

The axle of the wheel is mounted at an inclination of 45°; the upper edge of the gauze projects into a powerful Bunsen burner, and the lower into a solution of the required metallic salt, placed in a shallow dish. When in use the disc is rotated at a uniform speed by means of clockwork; this apparatus will give an illumination which lasts as long as there is solution in the dish.

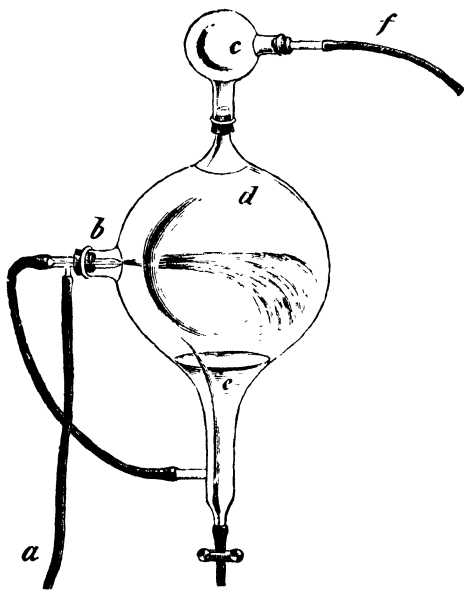


FIG. 140.

Several spraying apparatus have also been employed for this purpose, amongst which one may be described, namely, that used by Gouy.[1] In this type of apparatus the salt solution in a state of fine spray is carried along by a current of air and fed into the draught holes at the bottom of a Bunsen burner. A diagram of Gouy's apparatus is shown in Fig. 140, in which *b* represents the spraying apparatus; this consists of two tubes, one inside the other. A current of air is forced in through the tube *a*, and the spray is carried into the vessel *d*; the heavier

[1] *Ann. Chim. et Phys.*, **18**. 5 (1879).

drops fall to the bottom, while the air current passes through *c* and is conveyed by the tube *f* to the Bunsen burner. The liquid at *e* passes to the spraying apparatus through the connecting tube; the same liquid is therefore used over and over again, for it is only the finest particles which are carried away by the air stream.

With this apparatus de Watteville [1] has succeeded in obtaining the flame spectrum of mercury by using an aqueous solution of either the acetate or the cyanide. It is interesting to note that only one line is visible in this spectrum, viz. $\lambda = 2536{\cdot}72$, seeing that the other members of the second group of Mendeléeff's table, magnesium, calcium, zinc, strontium, cadmium and barium also possess one spectrum line which surpasses the others in intensity.

In cases where the Bunsen flame has not a sufficiently high temperature to give the spectrum of a metallic salt, the oxy-hydrogen blowpipe may be used. One of the methods of work with this blowpipe is as follows: A block of lime is bored as shown in Fig. 141, which represents it in sectional elevation. The mouth of the blowpipe is pushed into the lower hole, and the flame coming out of the top orifice is examined. The substance is put at the bottom of the boring, where the flame can play directly upon it. This apparatus was used by Lockyer and Roberts Austen,[2] and by Liveing and Dewar.[3] Hartley,[4] who has carried out a great number of investigations on flame spectra, has employed thin strips of cyanite as supports for the substance under

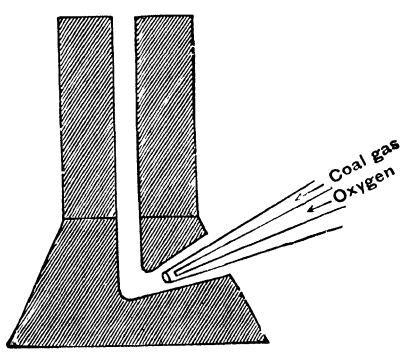


FIG. 141.

[1] *Comptes Rendus*, **142**. 269 (1906). [2] *Proc. Roy. Soc.*, **23**. 344 (1875).
[3] *Ibid.*, **28**. 352 (1879).
[4] *Phil. Trans.*, **185**. A, pp. 161 and 1047 (1894).

examination, which were simply held in the upright blowpipe flame; also, when possible, the substance is very finely powdered and made into small cylinders, which are held in the flame.

In a later paper Hartley[1] suggests the use of either strips of cyanite or strips of a mixture of carborundum and porcelain clay, which has been fired at a high temperature. Very good results are also obtained by the use of quartz fibres or rods. The best burner for the purpose is, in Hartley's opinion, the Mecke burner, with or without a blast. When it is required to obtain a lasting chloride spectrum he suggests the feeding of the burner with coal gas containing a little chloroform vapour.

Reference may also be made to the work on flame spectra by Hemsalech and de Watteville,[2] who in the course of their researches have made use of the oxy-acetylene flame. Amongst the very interesting results obtained by these experimenters may be mentioned the spectrum of calcium as given by this flame. It is very rich in the arc lines of this element and the distribution of the intensity is very much the same as that obtained by King with his electric resistance furnace (see p. 386).

It is interesting to note that in many cases banded spectra are obtained in the oxyhydrogen flame; this is most characteristically shown in the case of gold, silver, copper, magnesium, zinc, cadmium, aluminium, indium, and thallium. These banded spectra Hartley and Ramage[3] attribute to the metal itself, and not to the oxide, because metals which are (1) easily oxidisable to non-volatile oxides; (2) easily oxidisable to volatile oxides, and (3) not oxidisable at the temperature of the flame, all give banded spectra. It is also interesting to note that certain groups of elements give bands degraded towards the red, *e.g.* copper, silver, and gold; aluminium and indium; beryllium and lanthanum; while other groups give bands degraded towards the blue, *e.g.* magnesium, zinc, and cadmium. In connection with these banded flame spectra it is extremely interesting to compare some results obtained by Basquin[4] on the arc spectra of metals in an atmosphere of

[1] *Proc. Roy. Soc.* (Dublin), **11. 19.** 237 (1907).
[2] *Comptes Rendus*, **149.** 1112 and 1369 (1909).
[3] *Trans. Royal Soc.* (Dublin), II, **7.** 339 (1901).
[4] *Proc. Amer. Acad.*, **37.** 161 (1901).

hydrogen. Basquin photographed the arc spectra of several metals in hydrogen, and obtained the same flutings as Hartley and Ramage did; this was especially noticeable in the case of copper and aluminium.

Some further work upon these band spectra has been carried out by Fowler,[1] Olmsted[2] and Eagle.[3] The magnesium spectrum was examined by Fowler and a complete series of measurements of the bands made between the limits $\lambda = 5621$ and $\lambda = 4371$, the arc being made between magnesium poles in an atmosphere of hydrogen. Fowler concludes that the spectrum is due to magnesium hydride. Olmsted has also examined the spectrum of a calcium arc in the presence of hydrogen, and he finds that there are two main groups of bands extending from $\lambda = 6404$ to $\lambda = 6367$. Eagle has examined the similar banded spectra given by barium and strontium under the same conditions. As neither metallic barium nor strontium were obtainable in sufficient quantities, their chlorides were used on carbon poles.

Temperature Emission Spectra.—During the past three years a series of investigations have been carried out by King[4] on the spectra emitted by the vapours of substances heated to a high temperature in an atmosphere of hydrogen. The method briefly stated is to pass a heavy alternating electric current through a graphite tube placed in an air-tight chamber filled with pure hydrogen, thus heating the tube to incandescence and vaporising the metal or salt placed therein. It will be seen that this method of investigation has two distinctive characteristics. First, all electrical action such as occurs in the arc and spark is eliminated, and secondly any chemical action of unknown character and magnitude such as take place in the flame is avoided. Any spectrum, therefore, will be given at a temperature, which may be regulated quite easily, in the absence of oxygen and when the chemical action is very limited.

[1] *Phil. Trans.*, **209**. 447 (1909).
[2] *Astrophys. Journ.*, **27**. 66 (1908).
[3] *Ibid.* **30**. 231 (1909).
[4] *Ibid.* **27**. 353 (1908); **28**. 300 and 389 (1908); **30**. 190 and 381 (1909).

The apparatus as described in his first paper consisted of an outer air-tight chamber closed at each end, both the ends being fitted with a window through which observations could be made. This chamber, which contained the resistance tube, was a brass cylinder 10 cms. in diameter and 40 cms. long. The resistance tube was mounted in the centre of the cylinder, its axis being in a line with the windows so that observations of the internal incandescent resistance tube could be made from either end. The brass chamber was connected to an exhaust pump and also to a hydrogen generator. The resistance tube which was 20 cms. long and 4 mm. internal diameter was made of either carbon or Acheson graphite, the heating current being passed through the walls. This current was supplied from a 5 kilo-watt transformer. In the second paper a larger furnace was described with the outer chamber so constructed as to withstand an internal pressure of 200 atmospheres. The resistance tubes in this furnace are half an inch in diameter and 12 inches long, the heating current being supplied from a 50 kilo-watt transformer. The temperatures were measured with a Wanner pyrometer and during the work four different temperatures were employed, viz.:—1700°—1800° C, 2400°—2500° C, 2850°—2950° C, and 3015° C. Amongst the results may be mentioned the spectra of sodium, calcium, iron, titanium, and vanadium. It is exceedingly interesting to note that there is a great similarity between the spectra of these elements as obtained by King and those obtained by Hemsalech and de Watteville in the flame. In his later papers King has described his results on the investigations on the H and K lines of calcium.

Duffield and Rossi[1] have carried out similar experiments on heat emission spectrum in that they obtained the emission spectrum of silver by heating silver in a carbon tube resistance furnace.

It is important to notice that, generally speaking, the spectra of the burning gases cannot be obtained from a flame, those of the products of combustion being obtained. As exceptions to this may be mentioned the banded cyanogen

[1] *Astrophys. Journ.*, **28**. 371 (1908).

spectrum in the flame of cyanogen, the Swan spectrum in the inner cone of a Bunsen burner, and the banded flame spectrum of ammonia obtained when this gas is burnt with oxygen.

A very useful method of obtaining flame spectra has recently been devised by Hemsalech and de Watteville[1] for those cases where the substance is not volatile enough for the ordinary methods, or is especially valuable. The condensed electric spark is passed between electrodes of a metal which are enclosed in a small glass bulb. A current of dry air is passed through the bulb and then is fed into either a Bunsen burner or an oxyhydrogen flame, as the case may be. In a subsequent paper[2] they show that other substances than metals may be dealt with in a somewhat similar way. A carbon arc is used in place of the spark between metallic electrodes and the lower carbon, which is made the positive, is hollow, and into this hollow is packed the substance, together with some cement. If the ultra-violet region is to be examined, the authors recommend the following mixture:—three parts of boron trioxide and one part of the substance fused together and poured into the hollow carbon rod. In the case of the visible spectrum the following is preferred:—Two parts of the substance well mixed with one part of asbestos and sodium silicate cement and packed into the hollow carbon rod. The same method is used as before, namely the enclosing of the arc in a small glass bulb through which a stream of dry air is passed and then fed into the flame. Later publications[3] by the same authors deal with the flame spectrum of iron obtained in this way.

Arc Spectra.—The second means of producing illumination is by means of the electric arc, which brings undoubtedly a very much higher temperature to bear; in making the arc with carbon electrodes, either an automatic feed may be used or a simple hand-feed instrument. In the former the two carbon poles are kept in contact when the current is not passing, and

[1] *Comptes Rendus*, **144**. 1338, (1907).
[2] *Ibid.*, **145**. 1266, (1907).
[3] *Ibid.*, **146**. 859, (1908); **146**. 1389, (1908); **150**. 329, (1910).

on starting the current they are separated by the action of an electro-magnet, and kept at a distance depending on the current strength; these automatic instruments have certain disadvantages, and are rather inclined to get out of order. The hand-feed instrument is a simple mounting with a rack-work for moving the carbons forward. This hand-feed instrument naturally requires attention from time to time, as the poles are eaten away by the action of the arc, but, except in cases of the plain carbon arc, its use is to be recommended.

When the spectrum of the ordinary carbon arc is examined it is found to give a groundwork of a mass of fine lines, which belong to the Swan spectrum and to the cyanogen bands; furthermore, bright lines from the spectra of the various impurities in the carbons make their appearance, especially iron and calcium, with many others. These are a source of trouble, and render work on the arc spectra of substances, which must be produced with carbon poles, very difficult. There is no satisfactory method of removing these impurities, so that it is necessary, by careful comparison, to eliminate their particular lines.

The spectrum of a substance may be obtained by putting it into the arc between carbon poles; this may be done in two ways. The first and most satisfactory is to use cored carbons, *i.e.* carbons with a central hole bored along their length, and to pack the hole with the substance in question. Such a packed carbon is used as the positive pole, the negative pole being an ordinary solid carbon rod. The second method is to feed the substance, by small quantities at a time, into the arc; for this purpose it is best to make the positive pole the lower one, and to put the substance into the crater which is formed in this pole. This last method is very inclined to upset the stability of the burning arc, so that it flickers badly and jumps from one side to the other. If a metallic spectrum is being examined, then the arc may be made between poles of the metal itself, provided that the metal does not melt too easily. This method is most applicable to iron, and very excellent results can be obtained with the arc between poles of the best wrought iron; steel will be found to melt much too easily. In working with

such an arc it is necessary to adjust the current to the size of the poles used, because, if the current be too strong, the positive pole will melt.

Kayser[1] recommends about 10 to 15 amperes, with poles from 1 to 1·5 cm. in diameter. A carbon rod may also be used as the positive electrode, and as the negative electrode a rod of metal such as iron or copper. This method serves in the case of a metal which is too fusible for use for both poles. Again, one can use a cored carbon with a metal rod in the centre, as described above. On account of the incandescence of the poles of an arc, which produces a considerable amount of continuous spectrum, it is very advantageous to use the arc in a horizontal position; of course, this cannot be done when salts or such-like are to be fed into the crater of the positive pole, but when work is being done with the arc between cored poles or between two metal poles, it will be found to give much better spectroscopic results. I have used for a long time as a standard of measurement the spectrum of the iron arc as obtained between two horizontal iron poles; in certain experiments the necessarily heavy currents tend to melt the poles, so that they burn away unevenly, causing considerable jumping on the part of the arc. The method has been adopted, therefore, of rotating the two poles in opposite directions, which keeps the melted iron and iron oxide in a central position; in this way a perfectly steady arc is obtained with the heaviest currents. The apparatus is shown in Fig. 142.

Two exactly similar cast-iron pillars, *a* and *b*, are bolted upon the cast-iron bed-plate, *c*, a vulcanite sheet being interposed for purposes of insulation. At *d* and *e* these pillars are bored with 1-inch holes, into which brass cylinders accurately fit; the same is true at *f* and *g*, with this difference, that here a vulcanite insulation is inserted between the brasses and the cast-iron pillars. Each of these four brasses is bored with a $\frac{3}{8}$-inch hole, in which slip $\frac{3}{8}$-inch steel rods, which thus form the bearings. The steel rod *h*, which runs the whole length, is the driving-shaft of the instrument; small collars are mounted at *i* and *k* to prevent any lateral shifting. The two steel rods *l* and

[1] *Handbuch der Spectroscopie*, vol. i. p. 169.

m of the upper bearings also each carry two collars to prevent side shift, and on these rods are mounted the two wrought-iron poles *n* and *o*. These poles may be renewed at any time, as they are only brazed on to the steel rods; when new ones are put on they are turned up in a lathe so as to be perfectly true. In order to take up the wear caused by the burning of the poles during the working of the arc, the brass at *d* is made long, so that it can be slipped forward when required; it can be fixed in any position by the set-screw. Grooved pulley-wheels, 4 inches in diameter, are mounted on the steel rods, and of these *r* and *s*, *t* and *u* are connected by gut bands, one

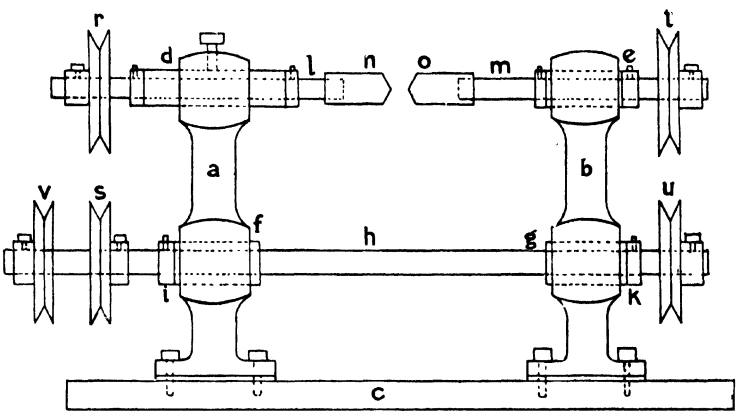


FIG. 142.

of which is crossed, in order to cause the poles to move in opposite directions. The pulley at *v* is connected by a gut band to a Henrici hot-air motor or some similar small engine. The current is supplied by wires to two binding screws on the pillars *a* and *b*. In order to start the arc the motor is set working, and then the brass at *d* is pushed forward until the arc starts, when it is slowly moved back until the arc works well. It is best to start the arc with a current of not more than 8 or 10 amperes, which is quite sufficient for all ordinary work, putting on a stronger one a short time after if required. The arc works best when the poles have got hot. A current of

25 amperes can be sent through the arc, using $\frac{5}{8}$-inch or $\frac{3}{4}$-inch poles, without any attention beyond occasional feeding. If the poles get too hot they will burn too fast, producing showers of sparks. This may be prevented to a great extent by dropping water upon the poles about an inch from their ends.

A modified and more convenient form of this apparatus has just been designed and made for me by Mr. W. H. Apthorpe, until recently the mechanician of the Muspratt

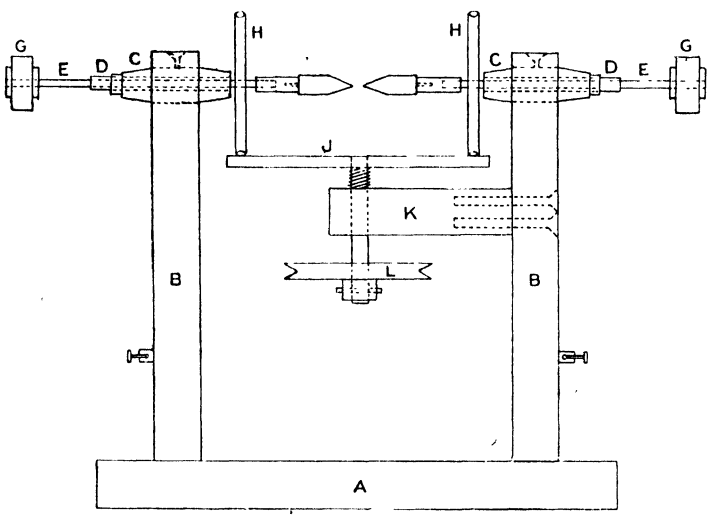


FIG. 143.

Laboratory of Physical and Electro-Chemistry, Liverpool. This is shown in Fig. 143, where A is a heavy wooden base to which are fastened two vertical brass uprights B, B, about $1\frac{1}{4}$ inches square and 10 inches high. C, C, are two brass bearings which are firmly fixed in the uprights, and are bored out so that the steel tubes D, D, work smoothly and truly in them. These steel tubes carry the steel rods E, E, which fit rather tightly, so that when the steel tubes are rotated these rods turn with them. On these rods are mounted the pole-pieces, and the distance between these can at any time be

regulated by moving the rods through the steel tubes. G, G, are two discs of vulcanite which enable this to be done when the machine is in use. The rotation in opposite directions is provided for by the two vulcanized fibre friction wheels H, H, which are mounted on the steel tubes D, D. Around the periphery of each wheel is stretched a small rubber ring, a small groove having been turned in the periphery to keep the ring in position. These two wheels, or rather the rubber rings, press up against the brass disc J, which is carried by the horizontal support K. The machine is driven by an electric motor, which is connected by a cord to the driving wheel L. In order to keep the brass disc up against the friction wheels, a small steel spring is put round the axle between the disc J and the horizontal support K.

The advantages possessed by this instrument are the increased velocity of rotation, and hence perfect steadiness of the arc, and further, any desired metal can be used for the pole pieces. It is not suited for very heavy currents, but for small currents it is excellent.

A method has been described by Pfund[1] of obtaining an arc which will burn with perfect steadiness, and without the least attention, for an hour or more. The arc is maintained in a vertical position, and the lower (positive) electrode consists of a rod of iron about 12 mm. in diameter. The upper end of this rod has a small cup-shaped bowl turned in it, in which are placed beads of the metal whose spectrum is desired. The upper (negative) electrode is a carbon rod about 1 cm. in diameter. On this rod is mounted a brass bush by means of a small set-screw, it being so arranged that the rod projects about 3 cms. through the bush, this brass bush being about 1 inch long. The arc burns best if supplied with 3·5 amperes at 220 volts, and the length of the arc should be limited to 6 mm. The bead of metal resting in the cup of the lower electrode should be about 3 mm. in diameter, and the condition essential to the proper behaviour of the arc is that the bead of molten metal or oxide be in the spheroidal state, and that it bulge out considerably above the edges of the cup in which it rests.

[1] *Astrophys. Journ.*, **27**. 296 (1908).

Having prepared beads of the different metals or their oxides, all that is necessary to change from, say, the copper arc to the iron arc, is to remove the copper bead by means of a pair of tweezers, and to replace it by an iron bead. If only the iron arc is required, then the upper electrode may be an iron rod 6 mm. in diameter. After burning for an hour or more in this case the upper electrode becomes incrusted with a layer of iron oxide. Before starting the arc anew, it is best to knock off this crust and readjust the brass bushing.

Liveing and Dewar[1] have used the arc enclosed in a block of lime or similar substance; a cubical block is taken with four horizontally bored holes at right angles to one another, and one vertical hole to the junction of the four horizontal borings. Through two opposite horizontal borings two carbon rods are pushed to form the arc, through a third any gas may be introduced, and the arc is examined through the fourth; down the vertical hole solids may be fed into the arc. An arrangement has been used by Crew and Tatnall[2] in which a rapidly revolving metal disc forms one electrode. This disc is mounted upon the armature of a small electric motor, and carries, fixed around its periphery, small pieces of the metal to be examined. The other electrode is a piece of the same metal mounted on a fine-cut screw, to allow its position to be accurately adjusted. In practice the motor is started and the current turned on, and then the second electrode is slowly pushed forward until it just touches the projecting pieces of the rotating disc. In this way the arc is spread out fan-wise in a very convenient manner for spectroscopic examination. An alternating current of 100 volts was used, and the current strength varied from 2 to 10 amperes.

Fabry and Perot, in their work on the absolute wave-length of certain metallic lines by means of interference methods, employed an apparatus which they called a "trembleur." This consisted of two metal pole pieces, one of which was fixed and the other mounted on a spring which was kept oscillating

[1] *Proc. Roy. Soc.*, **28**. 352 (1879).
[2] *Phil. Mag.* **38**. 379 (1894).
[3] *Comptes Rendus*, **130**. 406 (1900).

by means of an electro-magnet; every time the poles touched, the arc was started between them. The whole apparatus was placed in a vacuum.

Mention must also be made here of the Arons mercury lamp, as well as the cadmium lamp used by Hamy and by Michelson. Arons[1] has devised two forms of mercury arc lamps, the latter of which is shown in Fig. 144, which consists of an inverted U tube, B, with a platinum wire sealed in at each end at *m* and *n*. Two bulbs containing mercury are melted on outside the ends of the tube B, and the two connections are made with the mercury in the branch tubes as shown. The two limbs of B are filled with mercury, and when it is required to start the lamp the current is turned on and the lamp is shaken or tipped until the two mercury surfaces come momentarily into contact. It should be remarked that the tube B is completely exhausted. A large current should not be used, as the lamp becomes too hot; cooling it in water causes a condensation of mercury upon the walls of the tube so that no light can escape. Lummer has modified the apparatus so as to overcome this defect.

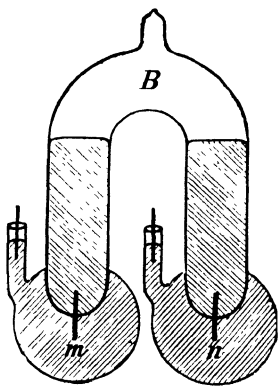


FIG. 144.

Barnes[2] has devised a very convenient form of lamp, which is shown in Fig. 145. Through the neck D of the globular vessel A, which is about 800 c.c. in volume, passes the iron tube E, of diameter 13 mm. Along the centre of this passes the porcelain tube F, 8 mm. in diameter. This porcelain tube is connected with a glass tube, which in turn is connected with a large rubber tube. Mercury fills the space between the porcelain and iron tubes, as well as the porcelain, glass, and rubber tubes attached. The electric wires are attached one to the iron tube E and the other to the mercury in the porcelain

[1] *Ann. der Phys.*, **47**. 767 (1892); and **58**. 73 (1896).
[2] *Astrophys. Journ.*, **19**. 190 (1904).

tube F. The opening B is closed by a glass plate, and the whole bulb is exhausted through C. By raising the mercury column until a drop flows over into E the arc is started, and any further adjustments are easily carried out by raising or lowering the mercury column. Barnes employed with this apparatus a current of 4 amperes at 110 volts, and found that, although mercury was deposited all over the walls of the apparatus, none reached the window at B.

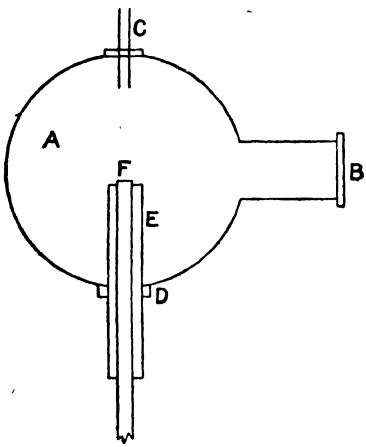


FIG. 145.

Hamy [1] employed a cadmium lamp, which consisted of a Plücker vacuum tube with outside electrodes, and contained a small quantity of cadmium. The tube was of glass, 20 mm. in diameter and 130 mm. long, with a centre capillary portion. A few centigrammes of cadmium were inserted, and the tube was then heated to about 300° C. and thoroughly exhausted; the tube was then sealed. Each end of the tube was covered by a brass cap packed with powdered graphite, which adhered to the glass and formed the electrodes. The whole was suspended in a copper tube somewhat larger than the vacuum tube, and outside the copper tube was a copper trough, which was heated by a row of Bunsen burners.

It has been pointed out by Arons that the mercury in the mercury lamp may be substituted by an amalgam of mercury, lead, bismuth, zinc, and cadmium, the spectrum of the light then given being very rich in lines.

A very simple form of mercury lamp has been described by Pfund,[2] which can easily be made by any one familiar with the elements of glass blowing. The lamp is shown in Fig. 146,

[1] *Comptes Rendus*, **124.** 749 (1897).
[2] *Astrophys. Journ.*, **27.** 299 (1908).

and consists of a piece of glass tubing, 7 cms. long and 1·2 cms. in diameter, to which there is sealed a larger tube 18 cms. long and 3 cms. in diameter. The upper end of this larger tube is ground flat, and a quartz plate is attached by means of sealing wax. A side tube is sealed on to the larger tube for the purposes of exhaustion. A platinum wire is sealed into the lower end of the smaller tube, which is then filled with mercury to a height of about 3 cms. The mercury forms the negative electrode while a hollow sheet-iron electrode forms the positive. This electrode is made by cutting out a piece of sheet iron to the shape shown in Fig. 147*a*, and this is subsequently bent into the form shown in Fig. 147*b*. It is important that the lower portion of this electrode be of smaller diameter than the

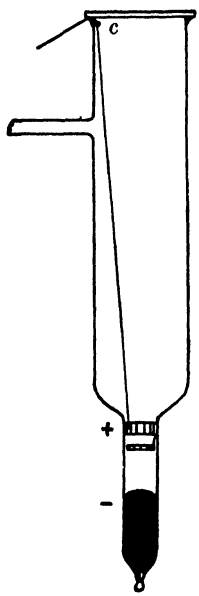


FIG. 146.

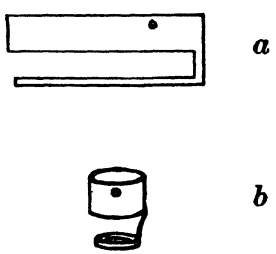


FIG. 147.

upper, so that it does not touch the glass tube at any point. This electrode is held in place by friction against the glass tube about 1 cm. above the mercury. An iron wire is attached to the electrode, and at the point *c* (Fig. 146), a piece of copper wire is fused to the iron, and the copper wire passes out of the tube through the sealing-wax junction. It is necessary that the copper wire be covered with shellac to guard against its being amalgamated by the mercury vapour. The lamp is used

in a vertical position, and takes from 1·4 to 1·6 amperes at 110 volts direct current. The lower, mercury filled portion is heated by means of a Bunsen burner, and the arc is started either by tilting the lamp or by jerking it so that momentary contact is made between the two electrodes. It is best to run the lamp for some time whilst it is still on the pump after the exhaustion has been carried as high as possible. In this way most of the water vapour and gases contained in the electrodes can be removed. Then, after carrying the exhaustion to as high a point as possible, the lamp is sealed off. It will generally be found after the lamp has been in use for some time that more gases are liberated, and the arc becomes so hot as to melt the glass. It is well to test this from time to time by holding a piece of paper against the glass. If the paper is charred the lamp should be re-exhausted.

Spark Spectra.—The third method of illumination is by means of the sparks from an induction coil. The sparks from the coil are caused to pass between small poles of the substance, and usually one or more Leyden jars are placed in parallel with the sparking apparatus in order to obtain a condensed discharge.

In using these induction coils it is perhaps not superfluous to point out that considerable damage may be effected by careless treatment. This refers in particular to the platinum contacts on the contact breaker or interrupter. In the larger size of coils there is always a tension screw provided, acting upon the lower end of the spring of the hammer. It is important that the adjustment of the sparking length should be made by means of this tension screw and not by the adjusting screw carrying the platinum contact. In starting a coil the tension screw should be screwed in so as entirely to free the spring, then the upper or adjusting screw should be so set that there is about $\frac{1}{32}$-inch clearance between the platinum contacts. When this has been once adjusted it should not on any account be altered, except when the platinum contacts require repairing. When using the coil it is only necessary to unscrew the tension screw until the required spark length is obtained.

The interrupter belonging to the coil may, of course, be

replaced by a mercury break or by a Wehnelt interrupter, or an alternating current may be directly employed.

The induction coil is used both for the production of the so-called spark spectra of substances, when the sparks are made to pass between two metal points or between a platinum point and a solution of a salt or some similar arrangement, and also for the discharge through gases which are usually under reduced pressure. In cases where it is necessary to use a very heavy discharge, it is preferable to substitute a step-up transformer fed with an alternating current for the induction coil. When required the Leyden jars are put into the secondary circuit in parallel with the discharge points; the effect of this is to reduce the electromotive force and increase the quantity of electricity in the discharge, and at the same time to make the discharge oscillatory. For the discharge points short pieces of pointed rods may be used which, if necessary, may be soldered on to stout copper wires; these rods or wires may be held in some form of stand so arranged that the spark length may be varied; the spark may be made to pass vertically or horizontally as one wishes. Generally speaking, in dealing with spark spectra it is necessary to use a Leyden jar or some other form of condenser, set up in parallel with the sparking apparatus. The size or capacity of this condenser most suitable for use depends largely on the induction coil or transformer used, and furthermore on the particular result required, for it has been found by various experimenters that very important changes in the character of the spark spectrum are produced by varying the capacity of the condenser. No general instructions can be given as to the size of condenser most suitable, yet it may not be out of place to describe a useful form of plate condenser that may very easily and cheaply be put together. Such a plate condenser is simply enough made by coating a piece of plate glass with tin-foil, taking care that the tin-foil sheets have a smaller area than that of the glass plate. Any number of such plates may be used with their alternate coatings connected together. In the case of one plate condenser used in my laboratory there are twelve pieces of plate glass each 18 ins. square and $\frac{3}{16}$ in.

thick. The tin-foil sheets are 12 ins. square, and are cut with a tongue projecting out from one side. In mounting the sheets on the glass plate, the plate is brushed over with a solution of shellac in methylated spirit, and then the tin-foil is carefully laid on to the glass and smoothed out. When the tin-foil is being mounted on the other side of the plate it is necessary that the tongue of foil projects towards the opposite end of the glass plate to that towards which the first tongue projects. The plates may be mounted in a grooved wooden frame, the grooves being about one inch apart. It is convenient so to arrange the plates in their grooves that the tin-foil tongues of every alternate pair of coatings project towards the same end of the wooden frame. A slotted binding screw is fastened to the glass plate over each tongue, and this forms a convenient connection to each coating. In connecting up a series of such plates it is only necessary therefore to connect together every alternate pair of binding screws.

It may, perhaps, not be out of place to give the formula by means of which the capacity of a condenser may be calculated. This is given by—

$$\frac{KA}{4\pi d}$$

where A is the area of the tin-foil, d the distance between the coatings, and K is the dielectric constant of glass. Both A and d must be expressed in centimetres, and for ordinary glass K may be taken as 6. In order to reduce the value so obtained to microfarads it must be divided by 100,000.

When the spark spectra of metallic salts are required, these may be obtained by passing sparks between carefully purified porous charcoal points which have been boiled in an aqueous solution of the salt. These were first used by Bunsen,[1] who took small cones of wood charcoal; these were purified by first of all heating to whiteness when surrounded with powdered charcoal, and then by boiling successively with hydrofluoric, nitric, and hydrochloric acids, care being taken thoroughly to wash them between each boiling. The cones were allowed

[1] *Phil. Mag.* **50.** 417, and 527 (1875).

to dry, and then boiled in an aqueous solution of the salt required.

Another way is to cause sparks to pass between a platinum wire and a solution of the required salt. Two apparatus designed for this are shown in Fig. 148 at *a* and *b*; the design *a* is due to E. Becquerel,[1] and the other, *b*, to Delachanal and Mermet.[2] In both cases platinum wires are used, and the solution is put in connection with the negative pole; in the apparatus *b* the platinum wire is surrounded by a glass cone, and the solution does not reach up to the wire, but ascends by capillary attraction. Still a third way has been used by Hartley,[3] which is shown in Fig. 149; the two electrodes are made out of graphite, and are cut to a chisel shape. The lower electrode has grooves cut in it, and is placed in a U-shaped tube filled with the salt solution, which then mounts up the grooves by capillary attrac tion. Both electrodes are connected by means of platinum wires to the current leads, and are set with the chisel edges parallel to one another and to the axis of the collimator tube, so that any wandering of the spark along the edges of the electrodes produces no displacement in the image thrown upon the slit.

It must be remembered that under ordinary circumstances the air spectrum lines will be obtained mixed with the lines of the metallic spectrum when the spark passes between metal poles in air. The relative brilliancy of the air and metallic lines obtained in this way depends entirely upon the volatility of the metal; with platinum poles the air lines are very much stronger in relation to the metallic lines than they are in the case of zinc and such metals. It is necessary, of course, to eliminate these lines in working with the spark spectra, and this may be done very readily by taking a photograph of the platinum or silver spark spectrum (when the air lines are strong) and comparing it with the photographs taken of the metal in question; the lines common to the two will be the air lines, and these can thus be eliminated. In the measurement of

[1] *Comptes Rendus*, **65**. 1097 (1867); **66**. 121 (1868).
[2] *Ibid.*, **81**. 766 (1875).
[3] *Phil. Trans.*, **175**. 49 (1884).

wave-lengths the air lines often prove of considerable advantage; their wave-lengths have been accurately determined by several observers, and thus they may be used as test lines in

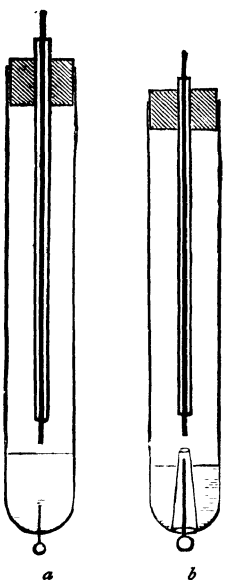


FIG. 148.

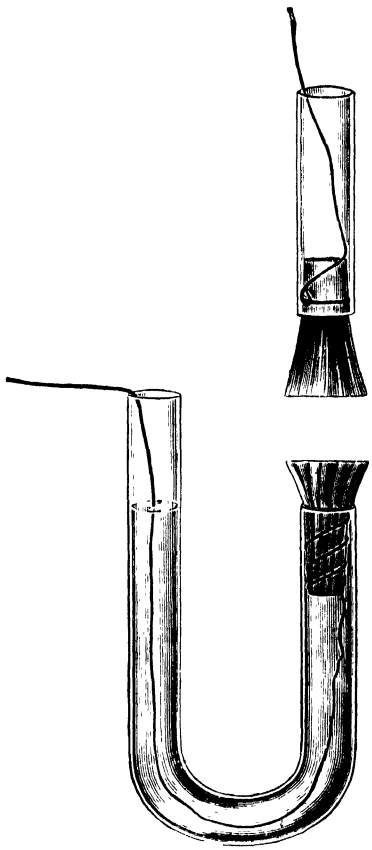


FIG. 149.

the comparison of the standard spectrum, and the spectrum to be measured; the air lines are picked out and their wave-lengths determined by measurements from the standard spectrum, and if they are found to be correct, then one can

assume that the two spectra are correctly placed in relation to one another (*vide* p. 148).

Two simple pieces of apparatus have been designed by Krulla[1] for obtaining the spark spectra of salts in solution. In every apparatus which has hitherto been used the electric sparks are made to pass between a metallic electrode and the solution of the salt so that the spectra are always more or less contaminated by the lines due to the metallic electrode. Krulla overcomes this difficulty by causing the spark to pass between two surfaces of the solution. In the first form (Fig. 150) there is a double U-tube, the lower limb of which is filled with the solution of the salt in question. An ordinary tap funnel is also filled with the solution, and the stop-cock is opened sufficiently to allow the stream of solution to break into drops just above the surface of the liquid. Two platinum wires are sealed through the glass as shown, and these are connected to an induction coil or to a transformer. The discharge passes between the dropping stream and the lower liquid surface, and though it flickers considerably, the source of light is very intense. The second form is more advantageous in many respects, but it requires a larger volume of solution. The arrangement is shown in Fig. 151, where there are two funnels, the lower tubes of which are bent as shown and drawn out so as to deliver small jets of liquid. Both funnels have an electrode sealed in, and these are connected with an induction coil or transformer. Both funnels are filled with the salt solution, and so arranged that the two jets pass within 2 mm. of one another at some point, care being taken that the jets do not break up into drops before this point. The discharge will pass at this point, and will be found to be very brilliant and perfectly steady.

We are indebted to Hartley[2] for an exhaustive study of the spark spectra of substances, and his conclusions upon the spark spectra of the metals and of their salts may well be quoted.

In the case of carbon or metallic electrodes, when these are moistened with water the short lines are lengthened.[3]

[1] *Zeitschr. phys. Chem.*, **66**. 78 (1909). [2] *Phil. Trans.*, **175**. 49 (1884).
[3] See Chapter XV., p. 514.

With very few exceptions the non-metallic constituents of salts do not affect the spark spectra of solutions.

Insoluble and non-volatile compounds do not yield spark spectra.

Solutions of metallic chlorides give spectrum lines which are identical in number and position with the principal lines of the metals.

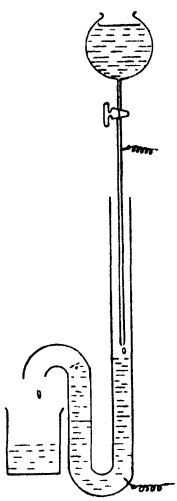


FIG. 150.

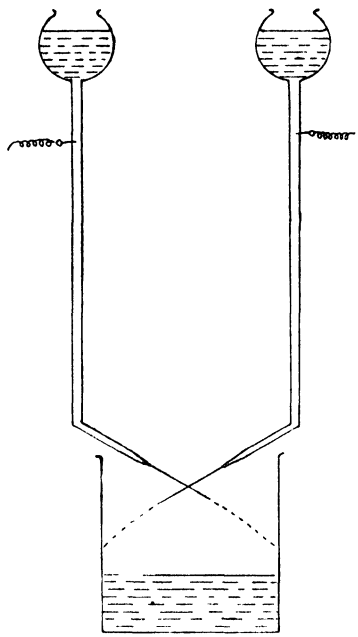


FIG. 151.

Short lines become long, but otherwise their character is identical whether the spectra are produced by metallic electrodes or solutions.

The effect of diluting solutions of metallic salts is first to weaken and attenuate the lines, then with further dilution to shorten them, the length of the longest and strongest lines generally decreasing until they finally disappear.

A considerable amount of work has recently been carried

out upon the persistence of the various lines in the spectrum of a metal as the solution of one of its salts is increasingly diluted. The lines in any given spectrum vary very considerably as to their persistence, and, as Hartley has shown, it is not necessarily the strongest lines that persist the longest. The investigation of these persistencies has been carried out by de Gramont[1] and by Pollok,[2] both of whom show that a quantitative method of estimation can be based on these investigations. To those rays which persist the longest de Gramont has given the name of "ultimate rays." The study of the relative persistence of all the rays in a number of spectra has formed the basis of a very laborious and exact research by Pollok, who, partly alone and partly with Leonard, has published many of his results. For complete details on this special and important branch of spectroscopy reference must be made to the companion volume in this series.[3]

Two very interesting papers have been published by Goldstein[4] on a method of obtaining the spark spectra of both metals and non-metals. A vertical glass tube is taken which has an electrode at each end, and a quantity of a well-powdered and perfectly dry alkali metal halogen salt is put into it. Sufficient of the salt is taken completely to cover the bottom electrode, which is made the anode. The tube is then exhausted, and when the discharge is passed it always follows a path between the salt and the glass walls of the tube. The discharge is intensely brilliant, and if no condenser is used in parallel with the tube, the spectrum is always that of the alkali metal, while if a condenser is used the spectrum of the halogen (chlorine, bromine, or iodine) is seen. Goldstein has also succeeded in this way in observing the spectra of sulphur, arsenic, phosphorus, antimony, and silicon.

[1] *Comptes Rendus*, **144.** 1101 (1907); **146.** 1260 (1908); **147.** 307 (1908); **150.** 37 and 154 (1910); **151.** 308 (1910); **153.** 318 (1911). *Journ. de Physique*, March, 1911.

[2] *Proc. Roy. Soc.*, (Dublin), **11.** 217. (1907); **11.** 229 (1907); and **11.** 257 (1908).

[3] *Practical Spectrographic Analysis*, by J. H. Pollok, D.Sc.

[4] *Ann. der Phys.*, **27.** 773 (1908); *Verh. d. Deutsch. Phys. Gesell.*, **10.** 426 (1910), and also *Phys. Zeitschr.*, **11.** 560 (1910).

If potassium fluoride is used with the condensed spark a new spectrum of potassium is obtained, the spectrum of fluorine being too weak to have any influence. The corresponding new spectra of caesium and rubidium have also been obtained in the same way, and Goldstein calls them the fundamental spectra of these three metals. He afterwards found that the same spectra are given with the condensed spark through the vapours of the metals themselves.

In Fig. 152 are shown the arc and spark spectra of copper which have been photographed with the quartz spectrograph illustrated on p. 133. The remarkable difference between the two spectra is well shown; this spectrum was taken with the spark between two copper wires, the spark being given by a large coil (14-inch spark in air) with a condenser of twelve plates, each plate being made of $\frac{3}{16}$-inch plate glass with one square foot of tin-foil on each side.

The Mechanism of the Spark.—Before leaving the subject of spark spectra, a few words may be said upon some recent work in this direction; a full description would be far beyond the scope of this book, but it is necessary that mention be made of present time researches so that it may be seen in which directions they are proceeding. Three of these especially may be briefly described: 1st, The study of the mechanism of the spark; 2nd, the spark under liquids; and 3rd, Lockyer's enhanced lines. The first work in connection with the mechanism of the spark that concerns us is by Schuster and Hemsalech,[1] "On the Constitution of the Electric Spark," who studied the mechanism in the following way: Instead of a stationary photographic plate they employed a film which was moving at the rate of from 90 to 100 metres per second in a direction perpendicular to the spectrum lines; in this way it became possible to detect how the spark passes. It was then found on taking such a photograph of a spark that the air lines appeared perfectly straight, showing that the duration of this portion of the discharge was very rapid compared with the motion of the moving plate. They further found that the metal lines were due to oscillatory discharges, and were all

[1] *Phils. Trans.*, 193. A, 189 (1900).

PLATE II.

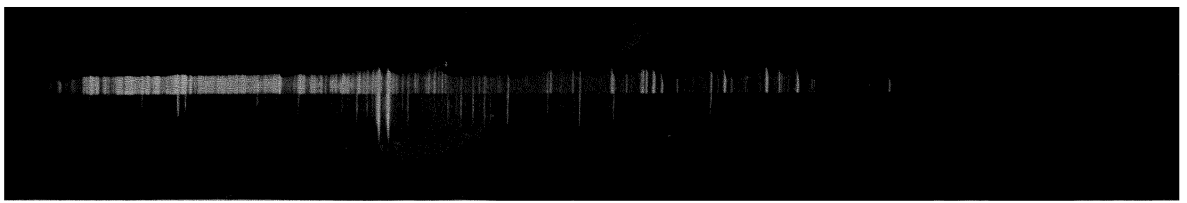


FIG. 152.

[*To face p.* 406.

curved so that they must start from the electrodes and travel with decreasing velocity towards the centre, the speed being calculable from the curvature of the lines; also it was noticed that this metallic discharge takes place after the discharge through the air. The mechanism thus is evidently as follows: The spark first passes extremely rapidly through the air, a single discharge; this vaporises the metal, which then spreads across the spark gap, conveying the current. The velocity of travel of the metallic vapour varies with different metals from 1300 to 400 metres a second, and appears to be quicker with metals of low atomic weight, but it varies for different lines of the same metal.

Schuster and Hemsalech also investigated the effect of introducing self-induction into the circuit, and they found that the air lines then disappeared from the spectrum, if the self-induction were great enough. This part of the work has been continued by Hemsalech,[1] who found that, in addition to removing the air lines from the spectrum of the spark, the self-induction also caused certain new lines to appear, and rendered the spectrum lines generally much narrower; he was able, for instance, in the case of hydrogen under atmospheric pressure, to obtain the spectrum lines as sharp as they are obtained in a vacuum tube. This narrowing of the lines produced by the introduction of self-induction in the circuit is of considerable use in certain cases, especially in work upon the Zeeman effect, when, of course, for the best resolution it is necessary to have the spectrum lines as fine and narrow as possible (see p. 536). A self-induction coil may be made quite readily by winding wire round a bobbin, the coil being put direct in the circuit. Hemsalech in some of his experiments used a coil 50 cm. long, 5 cm. internal diameter, containing eight layers of wire each consisting of one hundred and fifty turns.

Schuster and Hemsalech's work on the mechanism of the spark was taken up again by Schenck,[2] who obtained some very interesting results, but which are at present rather inexplicable. Schenck investigated the action of self-induction,

[1] *Comptes Rendus*, **128**. 285 (1899).
[2] *Astrophys. Journ.*, **14**. 116 (1901).

particularly in the case of the spark spectrum of cadmium. The apparatus consisted of a large induction coil fed with an alternating current, and a spark length was obtained of from 6 to 8 mm. with six one-gallon Leyden jars in the circuit. The period of the condenser was found to be $1{\cdot}3 \times 10^{-6}$ secs., and each spark consisted of ten or twelve complete oscillations. A large size Rowland grating was employed for the spectrum photographs. The cadmium spectrum was examined between the limits of $\lambda = 3700$ and $\lambda = 2100$, and it was found that the lines may be divided into three groups: A, B, and C. Group C consists of one hundred and forty lines about 0·3 A.U. wide with hazy edges; they resemble air lines, but are absent from other spark spectra. They extend only about 2 mm. from the poles, while the remaining lines extend right across the spark gap. They disappeared when the condenser period was raised to 17×10^{-6} secs. by throwing in self-induction. Lastly, they are not present in the arc spectrum, and are not reversed. A similar group was found in the spectrum of zinc.

Group B contains most of the remainder of the lines known as "spark lines," that is, lines prominent in the spark and weak in or absent from the arc. They are not reversed; when the condenser period is increased to 75×10^{-6} secs. some of these lines disappear and the others shorten up to the poles, while the rest of the metallic lines extend uniformly across the spark gap.

The lines of group A are the so-called "arc lines," that is, those lines common to the arc and spark, their intensity being generally greater in the arc. They thus form a spectrum simpler than that of the arc, and the effect of self-induction is to make the spectrum of this group more complicated and approach that of the arc. The greater the period of the condenser the nearer is the approach to the arc spectrum. These lines extend right across the spark gap when the condenser period is great enough to shorten the lines of group B close up to the poles. They undoubtedly are due to luminous metallic vapours extending across the entire spark gap.

Schenck also investigated the appearance of the spark in

a rapidly revolving mirror. The appearance of the spark under these conditions presents three general features. First, a brilliant white straight line due to the first discharge, sometimes followed by one or two weaker straight lines at intervals of half the complete condenser period. Second, curved lines of light which shoot out from the poles towards the centre with a continually diminishing velocity; when a streamer advances from one pole, the other pole is quite dark. Third, a faint light, generally of a different colour from the streamers, which fills up the spark gap and persists for a certain length of time after the oscillations die out. Now, the air lines are produced by the first straight line discharge, as Schuster and Hemsalech have already shown; the origin of the other lines (groups A and B) Schenck discovered by observing the spark in a rotating mirror, set at one time with its axis perpendicular to the spectrum lines and at another time parallel to them. From measurements of the plates the following times of duration of certain lines were calculated:—

	Wave-length.	Character.	Duration.
Magnesium	4481	Strong spark line	24×10^{-6} secs.
,,	3838	Strong arc triplet	45×10^{-6} ,,
,,	3832		
,,	3830		
Zinc	4925	Strong spark lines	14×10^{-6} secs.
,,	4912		
,,	4811	Strong arc lines	24×10^{-6} ,,
,,	4722		
Cadmium	4800	Strong arc lines	36×10^{-6} secs.
,,	4678		
,,	4416	Strong in spark	18×10^{-6} ,,

If anything, in this table the duration of the arc lines are underestimated; it is clearly shown how much longer the arc lines last than the spark lines. Schenck further found that the spark lines or those belonging to group B are due entirely to the curved streamers in the spark, but some of the spark lines are only to be found in the first few streamers. The lines of

group A or the arc lines are partly due to the streamers, but a large part of their luminosity is due to the glow which persists throughout the spark gap after the streamers cease. This glow is undoubtedly due to metallic vapour distributed over the spark gap. Schenck is of the opinion that the curved streamers do not carry the current, because an examination of the photographs shows that the streamers travel with a continually diminishing velocity, and that before they have reached halfway across the spark gap the whole discharge has passed and the return oscillation is beginning. It is also of importance to note that these streamers start from the negative electrode. For the velocity of the streamers Schenck obtained an initial value of 2·5 km. per second, in the case of the magnesium line at $\lambda = 4481$, which falls to about 1·7 km., about a millimetre out from the pole.

A simple method for the study of the spark has been devised by Hemsalech,[1] who employs wedge-shaped electrodes set up in the same vertical plane, and at a slight angle to one another. On the top of each is fastened a small platinum wire, which just projects beyond the edge of the electrode in each case. From 3 to 6 mm. above the electrodes is mounted a glass tube 3 mm. in diameter, which directs a current of air through the space between the wedge-shaped edges of the electrodes. A steady current of air is maintained through this tube, and it is found that the several oscillations in each spark become separated, and appear at different distances below the two platinum points. The initial discharge passes between the two points, so that the appearance of the discharge is a very fine, bright, straight spark between them. Below this will be seen a series of large, curved sparks. Hemsalech has been able to obtain as many as sixteen different oscillations, of which six to ten are quite fixed and regular. The velocity of the air in one of Hemsalech's experiments was 36 metres per second.

In a later paper Hemsalech[2] describes the spectra of the initial spark and the subsequent oscillations, and as the former

[1] *Comptes Rendus*, **140**. 1103 (1905).
[2] *Ibid.*, **141**. 1227 (1905).

shows the line spectrum of air, and the subsequent discharge the band spectrum, he concluded that the initial discharge passes through non-ionised air, and the oscillations through ionised air.

Some further work has been carried out on this subject by Milner[1] and by Royds.[2] Part of Milner's work was concerned with the nature of the streamers. In order to find out whether these streamers consist of charged particles or not, he observed by means of a rotating mirror the spark which was made to pass across a powerful magnetic field. The displacement of the streamers that were then observed proved conclusively that the particles composing these streamers must be electrically charged. Royds dealt more especially with the velocity of these streamers and the variation in intensity and velocity caused by self-inductance. All the lines of the same spectrum do not indicate the same velocity but they may be divided into two classes, long lines indicating normal velocity and short lines indicating a larger velocity. The velocity of the lines of the first type is probably due to diffusion but that of the second type is too large to be explained in this way. Some of Royds' observations are given on the next page.

Mohler[3] has photographed the spectrum of the spark looking at it end on, in order to see if the rapidly moving particles in the streamers caused any displacement in the position of the lines in the spectrum on what is known as the Doppler effect. The electrodes were of different metals, and a photograph was taken looking along the spark in one direction, and then without disturbing the plate the spark was rotated through 180° and a second photograph taken. In this way the effect, if any, would be doubled, as at the one time the particles would be moving towards the slit, and at the other time away from the slit. The actual effect that was observed was very small, corresponding to a velocity of 0·37 km. per second for the lines of aluminium at $\lambda = 3961$ and $\lambda = 3944$; an actual displacement of the lines of 0·1 A.U. was observed

[1] *Phil. Trans.* **209.** 71 (1908).
[2] *Ibid.*, **208.** 333 (1908); and *Phil. Mag.*, **19.** 285 (1910).
[3] *Astrophys. Journ.*, **15.** 125 (1902).

VELOCITIES OF THE METALLIC VAPOUR IN METRES PER SEC. CAPACITY = 0·0306 M.F.D.

Self-inductance (calculated).	0·000014 henry.	0·00025	0·00073	0·0025	0·0043	0·0068	0·0124
Period . .	$0·388 \times 10^{-5}$ sec.	$1·65 \times 10^{-5}$.	$2·98 \times 10^{-5}$.	$5·5 \times 10^{-5}$.	$7·2 \times 10^{-5}$.	$9·05 \times 10^{-5}$.	$12·25 \times 10^{-5}$.
Magnesium . .	930 m./sec.	416	390	—	378	381	226
Calcium . . .	551 165	590 102	582	376 139	400 108	— 121	— 97
Mercury . . .	936 1155	594	616	518	—	—	—
Lead	345	.....	282	280	—	—	—
Bismuth . . .	303	534	224	—	—	—	—
λ 4260 . .		615 for the same					
λ 4561 . . .		1170 distances from the electrodes.					

on the plates. The displacements of certain iron lines were slightly smaller, as also were those of some magnesium lines. The cadmium lines at $\lambda = 4078$ and $\lambda = 4800$ gave a slightly greater velocity. The line which gave Schenck a velocity of 2·5 km. per second could not be measured properly, as it was too wide and shaded. Doubtless, however, only an average velocity was observed, since according to Schenck the velocity falls to two-thirds of its initial value at 1 mm. from the electrode, it being extremely difficult only to photograph the spectrum of the very commencement of the spark. Mohler noticed a very interesting result in the fact that when the particles were leaving the slit the lines of magnesium at $\lambda = 2795$, $\lambda = 2802$, and $\lambda = 2852$ were strongly reversed, just as the last line is reversed in the arc; this was not observed when the particles were approaching the slit.

The Arc and Spark Discharge in Liquids.—A second direction in which important and interesting work has been carried out is in the way of electric discharges under the surfaces of liquids, both arc and spark discharge having been investigated. That the electric arc could be made to burn under water was first noticed by Humphry Davy[1] in 1802; Masson,[2] in 1851, experimented with the arc under different liquids, but only found a continuous spectrum. Liveing and Dewar,[3] using carbon poles under water, observed the bands of the Swan spectrum, but none of the cyanogen bands, even though the water contained ammonia or potassium nitrate. An investigation has been carried out by Konen[4] on the spectra obtained by burning the arc with poles of various substances under various liquids. For the maintenance of the arc a continuous current was used of 60 amperes at 72 volts, or 20 amperes at 220 volts, and the electrodes were placed in a deep glass basin with a quartz window. A quartz lens focussed the rays upon the slit of a spectroscope with a grating of 1 metre focus. For the electrodes copper, iron, brass, or

[1] *Journ. Roy. Inst.*, **1.** 165 (1802).
[2] *Ann. Chim. et Phys.* **31.** 295 (1851).
[3] *Proc. Roy. Soc.*, **34.** 123 (1882).
[4] *Ann. der Phys.* **4.** 742 (1902).

carbon was used, and a great many liquids were tried. A great deal of trouble was met with, because the electrodes rapidly disintegrated, except in the cases of organic liquids, when graphitic carbon was deposited upon them. The liquid was in this way rendered muddy very quickly, but this difficulty was overcome by having a tube, open at both ends, reaching from the arc to the quartz window; into this tube by a side branch fresh liquid was continuously supplied. In all cases a continuous background to the spectrum was obtained, reaching to $\lambda = 3600$, while certain metallic lines were seen, namely, the calcium lines at $\lambda = 3634$ and 3969, and also the aluminium lines at $\lambda = 3944$ and 3962; the D lines of sodium were also present, but always as absorption lines. The following metallic spectra were examined: iron, copper, and brass, also calcium, barium, sodium, potassium, lithium, and thallium, and these all gave bright line spectra. In no case were any banded spectra seen. The lines generally were sharper than in the case of the arc in air, their intensity less, and there were fewer self-reversals, so that this method is to be recommended for the study of metallic spectra. The nature of the surrounding liquid has no influence upon metallic spectra, except in cases of certain concentrated salt solutions of the metals barium and calcium, when the strongest lines of the dissolved metals make their appearance. The metallic spectra can, however, be obtained if cored carbons containing metallic salts be used.

In the case of carbon electrodes the surrounding liquid has of course a great influence. Under ordinary circumstances, in the carbon arc the four cyanogen bands are obtained, with their heads at $\lambda = 4606{\cdot}33$, $4216{\cdot}12$, $3883{\cdot}55$, and $3590{\cdot}48$, but if the carbon rods are well heated first and then the arc is made in water which has been previously well boiled, these four bands are invisible, and only the Swan bands can be seen. A very small quantity of air blown into the water at once gives the cyanogen bands; their invariable absence when no nitrogen is present in the liquid and their appearance in the presence of nitrogen conclusively proves the origin of these bands to be cyanogen. Konen endeavoured to settle the disputed question

of the carbon bands [1] in the same way; he heated the carbon rods *in vacuo* to remove every trace of air, and then made the arc under the surface of well-dried liquids containing no oxygen. In all cases, however, were the Swan bands seen. These last experiments do not seem to me to be in the least conclusive, because, although the carbon electrodes were deprived of their oxygen *in vacuo*, they were, after cooling, taken out into the air and then put into the liquid. In the time taken by the transference quite sufficient air would have accumulated to give rise to a small quantity of carbon monoxide in the arc. The readiness with which carbon absorbs oxygen compared with the absorption of nitrogen would account for the fact that it is more easy to get rid of the cyanogen bands than the Swan bands (always, of course, supposing that the latter are due to carbon monoxide). Konen, in his paper, states that the entire absence of oxygen could not be proved.

As regards the spark of discharge in liquids, Wilsing [2] was the first who obtained any practical results in this direction; he employed electrodes of different metals, and made the spark from a large induction coil to pass between them under water. A spark gap with electrodes of the same metal was placed in series, and photographs of the two spectra were simultaneously taken upon the same plate. He found that in the case of the spark under water considerable broadening and shifting of the lines to the red took place, also a considerable number of reversals. Wilsing explained the shifting of the lines as being due to the pressure effect as investigated by Humphreys and Mohler [3] (see p. 634); the actual effects he obtained varied from 6 A.U. with zinc to 1 A.U. with iron, and nothing with platinum.

Hale,[4] in 1902, investigated the particular case of iron electrodes in water and salt solutions, and found that a part of

[1] Whether they are due to the element carbon or to carbon monoxide, see p. 522.

[2] *Berl. Ber.* (1899), 426; and *Astrophys. Journ.*, **10.** 113 (1899).

[3] *Astrophys. Journ.*, **3.** 114 (1896).

[4] *Ibid.*, **15.** 132 (1902).

the iron spectrum was reversed; further, that the reversals tend to increase in number and intensity with (1) the length of the auxiliary spark gap in air (placed in series with the spark in water); (2) the diameter of the electrodes; (3) the capacity of the condenser; (4) the pressure of the water; (5) the strength of the solution in salt solutions. With a 9·5 per cent. solution of barium chloride almost all the spectrum can be reversed; certain shiftings of the lines were observed also in certain groups. Lockyer[1] also has made investigations in the same field, using various metals as electrodes in pure water. Iron, zinc, magnesium, silver, lead, and copper electrodes were tried, but only the first three showed any reversals. The phenomena noticed may be divided into three classes: (1) broadened bright lines, well shown in the copper spectrum, the lines being stronger on the blue side and hazy towards the red; (2) broadened bright lines, with central absorption well shown by line at $\lambda = 4063{\cdot}76$ in the iron spectrum; (3) broadened bright lines, with non-symmetrical absorption (maximum of emission towards the red), also best shown by several iron lines.

Konen[2] in his paper gives the results of a series of observations he has made with many metals in a great number of liquids. He investigated the brush discharge and also the condensed and uncondensed spark discharge, using a coil capable of giving a spark of one metre long in air. The brush discharge was found to be too faint to be spectroscopically investigated, while the uncondensed spark gave weak lines upon a continuous background; the latter gave the Swan spectrum in carbon containing liquids. When a condenser is intercalated in the secondary circuit the whole effect is altered; the intensity of the continuous spectrum is increased, it being possible with two carbon electrodes to get it absolutely continuous. The surrounding liquid has just as little influence as in the case of the fluid-enclosed arc. As regards reversals, Konen was not able to repeat Hale's results with the solutions of salts, and in the case of a 9·5 per cent. barium chloride

[1] *Proc. Roy. Soc.* **70**. 31 (1902); and *Astrophys. Journ.*, **15**. 190 (1902).
[2] *Loc. cit.*

solution no reversal was seen; there is thus a considerable difference between the effect of the discharge produced by an alternating current as in Hale's case, and one from an induction coil. Konen, however, agrees with Wilsing's results, for he found bright and dark lines together, and was not able to obtain all the lines bright or all reversed. Konen considers that Lockyer's reversals were nearly all self-reversals, as they were dark lines on a bright ground, while the truly reversed line is black upon a faint continuous background; Lockyer's results, therefore, must be due to a different phenomenon. Konen also observed a shifting of the lines towards the red comparable with that found by Wilsing; in the ultra-violet from $\lambda = 2755$ to $\lambda = 2606$ the lines were displaced about 2 A.U. towards the red; with lines of greater wave-length the shift was less.

Some further very important work has been carried out on this subject by Konen[1] and by Finger,[2] who have examined the spark spectra of more than 17 metals under water, and the results given by a comparison of the water-spark spectra and the air-spark spectra are very complex. Certain differences between the two were noted which may be mentioned. In the first place, the change from the spark in air to the spark in water does not give the same results as an increase of pressure does on the spark in air (see p. 507). The following changes in the character of the various spectrum lines on passing from air to water were recognised :—reversal, broadening, strengthening, weakening, loss of definition, change in wave-length, and entire disappearance. The most important result obtained in this work is that all the lines belonging to the same series in any one spectrum undergo the same change. Besides the lines which unmistakably belong to the series, there are other lines which are usually grouped together for some definite reason, as, for example, the enhanced lines. The behaviour of these lines is of considerable interest, but very few irregularities could be detected amongst them as

[1] *Zeitschr. Elektrochem.*, **15**. 165 (1909). *Verh. d. Deutsch. Phys. Gesell.*, **11**. 369 (1909).

[2] *Zeitschr. wiss Phot.*, **7**. 329 and 369 (1909).

regards their behaviour when the spark is changed from air to water. For example, it would appear that the enhanced lines in any one spectrum do not necessarily behave in exactly the same way. In many cases an increase in the intensity is to be noticed, but no general regularity in this increase is evident. The authors come to the conclusion that the difference in the behaviour of the enhanced lines in a spectrum under the same conditions of emission justifies them in concluding that these lines have not one common origin, but that they arise from different conditions. For this reason they feel that it is not possible to attribute, with Lockyer, such lines to one special line spectrum.

Lockyer's Enhanced Lines.—A third very important field of work which has been opened up is that of the enhancement of certain lines in the spectra of certain elements when passing from the arc to the spark discharge. It has long been known that the spark spectrum is generally simpler than the arc spectrum of an element, and there are generally lines in the spark spectrum which are brighter than they are in the arc spectrum. If the spark is increased in intensity, these lines are still more enhanced relatively to the others, so that a final result is conceivable of a spectrum containing only these enhanced lines. We are entirely indebted to Lockyer for the investigation of these lines and for the discovery of their coincidence with many of the lines in the spectra of the stars. In 1879[1] and 1881[2] Lockyer observed the effect of high tension discharge upon the line spectra of metals, and noted certain lines which were brightened in passing sparks through a flame charged with the vapour of a metallic salt, and also the lines brightened on passing from the arc to the spark as a means of producing spectra. Two iron lines, of wavelengths $\lambda = 4924{\cdot}1$ and $\lambda = 5018{\cdot}6$ respectively, are especially enhanced in this way. Lockyer has generally considered that the passage from the arc to the spark discharge means a great increase of temperature, and that these enhanced lines are due to an enormous temperature developed in the

[1] *Proc. Roy. Soc.*, **30**. 22 (1879).
[2] *Ibid.*, **32**. 204 (1881).

spark, although more recently[1] he points out that he has always included the action of electricity in the term "temperature."

In a later paper[2] he gives seven enhanced iron lines, and feels justified in concluding that these would constitute the spectrum of iron in a space heated to the temperature of the spark and shielded from a lower temperature. Lockyer thus distinguishes between four different types of spectra[3] as follows, iron being quoted as an example:—

(1) The flame spectrum, consisting of a few lines only, including the well-known triplets, and many strong lines in the ultra-violet.

(2) The arc spectrum, consisting of some thousand lines.

(3) The spark spectrum, differing from the arc spectrum in the enhancement of some of the short lines and the reduced brightness of others.

(4) A spectrum consisting only of the lines which are intensified in the spark, and which would only be seen at the highest temperature.

A great number of substances have been investigated for their enhanced lines, and the wave-lengths of some few have been published. The apparatus used in the earlier work consisted of a 10-inch spark Apps coil with large Leyden jars, the spectra being photographed with a prism apparatus; the enhanced lines of iron, calcium, and magnesium were obtained in this way. In a later paper[4] are given the results obtained with much larger apparatus; the Spottiswoode coil was used, giving a 42-inch spark, and a condenser of a single gallon jar to twelve 15-gallon jars was used; later a plate-glass condenser of 30 square feet surface was substituted. The spectra were photographed with a large Rowland grating, and the wave-lengths are given of the enhanced lines of aluminium, bismuth, chromium, copper, iron, magnesium, manganese, titanium, and vanadium. Some additions to the list of enhanced lines

[1] *Proc. Roy. Soc.*, **76**. 145 (1906).
[2] *Ibid.*, **60**. 475 (1897).
[3] *Ibid.*, **61**. 148 (1897).
[4] *Ibid.*, **65**. 452 (1899).

of copper have been given by King,[1] and also to those of titanium, iron, and nickel by Reese.[2]

Complete lists of the wave-lengths of enhanced lines measured at the Solar Physics Observatory at South Kensington have been published under the auspices of the Solar Physics Committee.[3]

It is difficult to see why the temperature of the spark should be considered to be so enormously hotter than that of the arc. Apart from any other reason, the spark has by no means such a powerful heating action upon the electrodes as has the arc. That the simpler spectrum of the spark may be due to a simpler form of matter, as assumed by Lockyer, is very probable, but it by no means follows that temperature is the factor which aids this dissociation. It seems not improbable that we may seek the origin in the enormously rapid change of electric stress, if one may so speak, known to occur in the spark discharge. Modern theories attribute spectrum lines to the vibrations of single electrons or single groups of electrons belonging to the atoms. Radioactive phenomena show that electronic motions are probably independent of temperature, which is a molecular or atomic phenomenon. If, therefore, a change of condition produces a change in a line spectrum, this change must be due to other causes than temperature; possibly it may be due to different exciting causes in the spark. Still, the evidence seems in favour of an actual dissociation, and we must take this into consideration.

Up to the present, all the radioactive substances have been those of high atomic weight, and therefore possibly might be expected to be more unstable. It is by no means impossible that elements of lower atomic weight should become radioactive, if only by the application of some external force they were made unstable. Can it not, therefore, be imagined that,

[1] *Astrophys. Journ.*, **20**. 21 (1904).

[2] *Ibid.*, **19**. 322 (1904).

[3] "Tables of wave-lengths of enhanced lines" (1906); "Researches on the chemical origin of various lines in solar and stellar spectra" (1910). H.M. Stationery Office.

under the great stress undergone in the spark, an element, usually quite stable, should become radioactive, and break down in similar ways to radium and the others? Can we not have a condition of "assisted radioactivity"? Certainly on these lines we may explain several very curious phenomena. First, we may attribute Lockyer's enhanced lines to the products of radioactive degradation of the elements; thus his protocalcium is one of the products from calcium, produced not by enormous temperature but by a simple radioactive change. The beautiful results obtained by Lockyer in the application of this work to the stars are in no way altered, except his conclusions as to stellar temperature.

The stars considered by Lockyer to be extraordinarily hot may or may not be so; all we can say is, that they consist of protocalcium, etc., as the case may be. Whether these substances in the star have actually been derived from calcium, etc., or whether they have not arrived so far in their life history is another matter. Second, the extraordinary results obtained by Schenck may be explained on this hypothesis; in his work he found evidence of particles[1] shot out with great velocity from the electrodes, when the spark was passing. Here we have perhaps a visible sign of the radioactive process, corresponding to the α particles in the case of radium. It is true that the velocity noted by Schenck is very much lower than the α radium particle, it apparently being about 2·5 km. per second, but this does not necessarily condemn the hypothesis. Lastly, perhaps herein lies the explanation of the results obtained upon the passage of the spark through oxygen, when it was found that light and heavy fractions of this gas could be obtained.[2]

It is hoped very shortly to publish some results of experiments undertaken with the object of putting this view to the test.

The Spectra of Gases.—The production of luminescence in gases is very different from the previously described methods, and is a process requiring very careful handling on account of

[1] See page 407.

[2] Baly, *Proc. Roy. Soc.*, **57**. 468 (1895).

the fact that the presence of but small quantities of impurities may entirely disturb the result. As a general rule gases are illuminated by the passage of the discharge from an induction coil through them, when under reduced pressure. The preparing and filling of the vacuum tubes must necessarily be coupled with certain precautions for the removal of contaminating influences, because the quantity of gas in each tube is so small that minute amounts of impurities have a great relative importance. Certain investigations have been made upon the spectra of gases at ordinary atmospheric pressures; sparks from an induction coil are passed between platinum wires in the gas, some form of tube being used as is shown in Fig. 153. The gas is enclosed over mercury in the tube *a*, which has two platinum wires sealed into the glass, between which the sparks pass. As will be explained more fully later, certain gases give different spectra according to whether or no a Leyden jar is put in the circuit; the condensed or uncondensed spark is therefore employed as may be required, but in the latter case the discharge should not be sufficiently strong to heat the electrodes red hot.

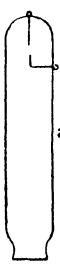


FIG. 153.

By far the most general method is to submit the gases under reduced pressure to the action of the discharge. Various shapes of tubes have been employed, of which the most useful are shown in Fig. 154 at *a*, *b*, and *c*.

The tube shown at *a* was first designed by Plücker, who found that when a capillary tube is placed between two wider portions the brilliancy of the illumination is enormously increased in the narrow portion. The forms *b* and *c* are arranged that the glowing gas may be observed through a quartz plate so that the ultra-violet rays may not be absorbed; in *b* the capillary portion is viewed "end on," and *c* is used in investigations of the glow round the electrodes. Many other designs have been produced according to the especial character of the work, but it will be found that for all ordinary investigations one of the above forms will suffice. Each of the tubes is shown provided with two electrodes; in certain cases these cannot be used, and then it is necessary to wrap the ends

of the tubes with tin-foil, which is put in connection with the secondary poles of the induction coil. It is not, I think, advisable to employ electrodeless tubes unless circumstances render it necessary, for although they are easier to make they are not so easy to fill; and further, they are rather inclined to give the Leyden jar spectrum of the gas when one exists. A further objection to them is that they are liable to become pierced if the discharge is too powerful.[1]

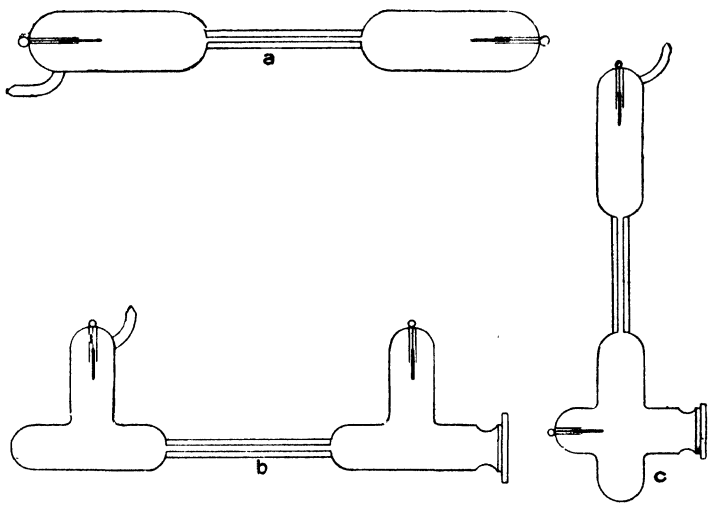


FIG. 154.

The following directions may be given for the making of a vacuum tube. The most important part of a vacuum tube is the electrode. Unless this is properly made it may, and generally does, become a never-ending source of trouble; it breaks to pieces, melts up, and then often cracks the tube. Except for special purposes, the electrodes themselves are usually made of aluminium wire; this is the most satisfactory, as, on account of its good conductivity, it does not readily become hot, and

[1] Hamy has used metal covers fitting over the ends of the tubes, which are packed with powdered graphite. This prevents the piercing of the tube by the discharge.

therefore is less inclined to melt. Platinum is sometimes used, but this always gets very hot, and, further, "evaporates" very considerably; a mirror is deposited upon the walls of the tube immediately surrounding the electrode, this being particularly noticeable at the negative pole. When an aluminium electrode is used, it must be joined to a piece of platinum wire which can be sealed into the glass; the two wires can be quite easily fused together by heating the extreme end of the aluminium in a fine-pointed blow-pipe flame and gently pressing the platinum against it until it melts, when the platinum will just penetrate the aluminium. The junction is at once removed from the flame, and will be found to be quite strong. Before carrying out the operation it is advisable to cut both the aluminium and platinum wires to the required length; each of them may then be held in a pair of tweezers or small pliers, and will be found much easier to manipulate. After the junction has been made, it is necessary to protect the platinum wire by a glass cover, so that no discharge can take place from any portion of its surface. A piece of fine quill tubing is made in the blowpipe with a bore sufficiently large just to pass over the aluminium wire; if, at the junction of the platinum and aluminium, there are any lumps which prevent this cover from slipping over it, they may be removed by filing. The electrode with its cover is shown in Fig. 155 at *a*; the next step is to melt down the glass cover on to the platinum, as shown in *b*, using a fine-pointed flame. A small quantity of blue enamel glass is then melted round the end of the platinum, as shown at *c*, care being taken that the enamel and the ordinary glass are well fused together, and that the enamel portion is larger than the rest. The use of the enamel lies in the fact that it is not possible to seal platinum into ordinary German glass without the joint cracking on cooling, owing to the great difference between the coefficients of expansion of the platinum and glass. The enamel glass has a coefficient of expansion midway between the two, and platinum can thus be sealed in quite safely with its aid. English lead

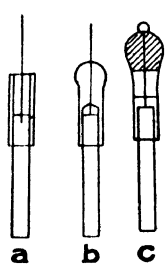


FIG. 155.

glass, on the other hand, needs no enamel, but it is very much more difficult to work, owing to the liability of the lead oxide to be reduced to lead. Some enamels are made of lead glass, but in my opinion they are not so satisfactory as the blue soda variety.

The electrode is now ready for sealing into the tube. The previously rounded end of the tube has a small hole blown in it, which is then filled with enamel, and the whole melted down and blown out until quite even and round. A hole is then made in the enamel end of the tube, into which the electrode is placed, and the enamel lump on the latter is carefully melted to the edges of the hole, and then the seal is several times melted down and blown out until a good junction is obtained. The three stages are shown in Fig. 156; *a* is the tube with the

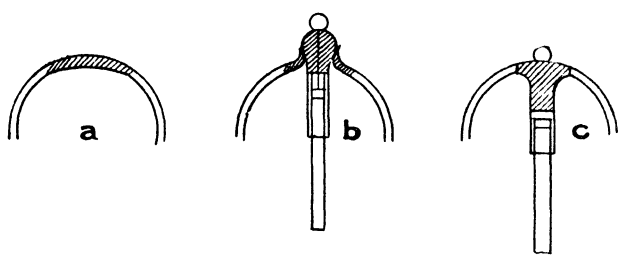


FIG. 156.

enamel melted into the end; *b*, the same with a hole blown in the enamel end, and the electrode resting on the edges; and *c*, the finished junction. In all three the enamel is represented by the shaded portion; the preparing of the end of the tube by melting in a little enamel previous to the sealing of the electrode is a very necessary proceeding, a better joint being always obtained in this way.

It will be found that electrodes prepared in this way will answer perfectly satisfactorily for all ordinary gases; if they are to be used with very strong currents, the aluminium wire should be rather thick; Nos. 16–18 S.W.G. are very convenient sizes.

The monatomic gases, neon, krypton, etc., require a little alteration in the electrode if one wishes to pass the current

continuously for long periods. For some reason even aluminium electrodes get very hot with these gases, and therefore they must be more carefully made, to prevent their rapid disintegration.[1] Stout aluminium wire of at least No. 12 S.W.G. is taken, and from one end along the axis a fine hole is bored for a short distance. Into this the platinum wire is placed, and the aluminium pressed on to it with a pair of pliers; the platinum is held quite firmly in this way. The glass cover-

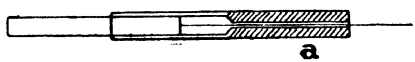


FIG. 157.

piece is made by making some capillary tubing out of the enamel glass and joining it on to a piece of ordinary glass tubing, as shown in Fig. 157, with the electrode lying in its place. The enamel is melted on to the platinum at the extreme end, *a*, which must be at least half an inch from the aluminium, after which the electrode is finished off in the usual way.

A very important precaution that must be taken is the thorough cleansing of the glass of the vacuum tube; this must, of course, be seen to before the electrodes are sealed in, and should be done by filling the tube full of hot chromic acid (potassium bichromate and strong sulphuric acid) and allowing it to stand for a short time; after which it is thoroughly rinsed with distilled water and dried. The tubing from which the vacuum tube is made should also be cleaned before it is used.

The process of filling a vacuum tube with a gas may be carried out by means of the apparatus diagrammatically shown in Fig. 158, where A is a mercury air-pump which is connected to the apparatus for filling through the drying tube *a*, containing phosphorus pentoxide, and the stopcock *b*. The apparatus for filling is shown at B, and the vacuum tube at C. The former consists of a bulb, *c*, with four branch tubes, one of which leads to the stopcock [2] and inverted syphon *d*; a second connects

[1] Baly, *Phil. Trans.*, **202**. A, 183 (1903).

[2] It may not be out of place to give a good lubricant for stopcocks, which may be made as follows: 2 parts of soft rubber and 1 part of vaseline are melted together, and then $\frac{1}{8}$th part of paraffin wax is added and the whole well stirred. The mixture is then allowed to cool.

through the drying tube *e* (phosphorus pentoxide) to the stop-

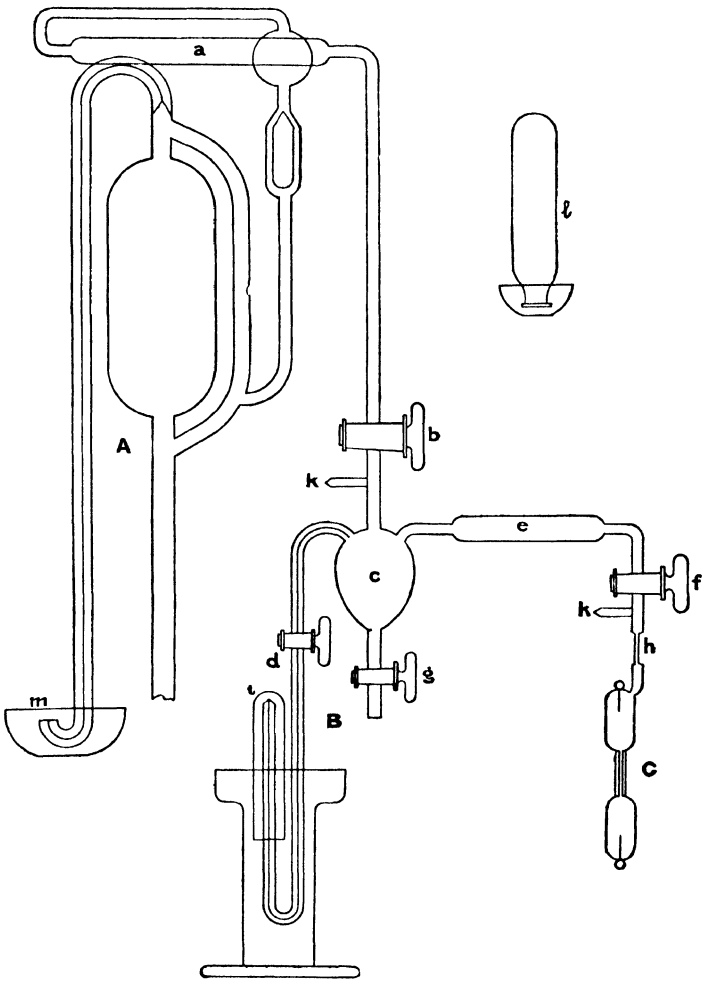


FIG. 158.

cock *f*; the third and fourth respectively lead to the stopcocks *b* and *g*. The vacuum tube C is joined through a constricted

portion, *h*, to the stopcock *f*; the inverted syphon *d* dips into mercury in a glass trough as shown. It is far preferable that in an apparatus such as this all the joints should be sealed with the help of a hand blowpipe to ensure the absence of any leaks; the side branches at *k*, *k* are for the purpose of blowing in during such sealings. Over the end of the inverted syphon *d* is placed a tube, *i*, containing the gas required for the experiment; such tubes of gas are conveniently kept standing in mercury in a porcelain crucible, as shown at *l*.[1] This gas can thus be admitted into the exhausted apparatus by depressing the tube *i* until the end of the syphon is in the gas, and then opening the stopcock *d*. It is necessary, therefore, for the inverted syphon to be full of mercury before the gas is admitted, and this is the first step to be taken in the process of filling a vacuum tube. When the apparatus has been partially exhausted, the stopcock *d* is slowly opened with the end of the syphon under the mercury; the mercury runs in, and is allowed just to rise above the stopcock, when it is again closed. The whole apparatus is now thoroughly exhausted, and the current from the secondary of an induction coil (the same size as will be afterwards used in connection with the tube) is passed through the vacuum tube. There are certain sources of contamination in every vacuum tube which must be removed if a pure spectrum be desired, before the gas can be admitted; these are, moisture on the glass walls and on the electrode, a small quantity of hydrogen apparently occluded in the aluminium electrodes, and sometimes dirty glass surfaces. The first two are almost entirely sources of hydrogen, and the last of carbon dioxide.

It is the last which gives the greatest trouble, but it may be entirely got rid of by carefully cleaning the tube with chromic acid during its making, as previously directed. We need, therefore, only concern ourselves with the first two sources of trouble; these may be removed by continuing the exhaustion while the discharge is passing until the hydrogen ceases to be evolved. This, as a rule, does not take long, and is considerably hastened by passing a strong current and by carefully heating the tube

[1] For a full description of the modern methods of gas manipulation, see *The Study of Gases*, M. W. Travers. Macmillan & Co., 1901.

with a Bunsen flame. The exhaustion should be carried to as high a degree as possible; that is to say, until the tube shows brilliant green phosphorescence or until the discharge refuses to pass. The spectrum of the discharge at any time may be examined with one of the plain direct-vision prisms described on p. 66. If the carbon banded spectra become visible, owing to there being carbon dioxide present, it will generally be found rather more troublesome to reach a sufficiently high exhaustion. Under these circumstances the tube should be heated as hot as possible, and, after the admission of a small quantity of air, re-exhausted; this being repeated until the carbon bands disappear. If they prove very obstinate, it will often prove of considerable help to close the stopcock *b*, and then fill the vacuum tube with air by carefully opening the stopcock *g*. If the tube be again exhausted, it will frequently be found that the carbon bands have disappeared.

Attention may also be drawn to the necessity of using perfectly pure phosphorus pentoxide in the drying tubes *a* and *e;* this substance must be free from lower oxides of phosphorus, which are very detrimental. A sample of the substance, when allowed to stand in the air, should be converted into a quite colourless mass of metaphosphoric acid, without any red or yellow spots.

When the vacuum tube has been exhausted, a small quantity of the required gas may be admitted; the stopcock *b* is closed, and the tube *i* is well pressed down over the inverted syphon; the stopcock *d* is then slowly opened, until the mercury just runs through. When a volume of mercury has passed equal in volume to the amount of gas required (which should be less than the total volume of the syphon), the tube *i* is raised so as to cover the end of the syphon with mercury. The gas then enters the apparatus, and is followed by a column of mercury; the stopcock *d* is closed when this second column of mercury begins to pass through it. It will generally be found that a volume of gas occupying two or three inches of the capillary is sufficient; it is best to admit a little too much gas, and then slowly reduce the pressure, by opening *b*, until the best illumination is obtained in the vacuum tube.

The tube may now be sealed off by carefully melting the constricted portion at *h* with a fine-pointed blowpipe flame. If the gas is very valuable, it may be exhausted out of the residual apparatus through *b*, and collected at the end of the delivery tube of the pump at *m*.

When the vacuum tube spectra are required of the vapours of substances solid at ordinary temperatures, the special apparatus for filling is not necessary; some of the solid in question is put into the vacuum tube before sealing to the apparatus, and the tube is then sealed on in a horizontal position. When the tube has been completely exhausted, the substance is heated until it vaporises, and its spectrum is obtained; the exhaustion is continued for a short time to remove any gas which may have been occluded in the substance, and the tube is sealed off.

Certain substances necessitate special precautions being taken in obtaining their spectra; amongst these the following examples may be quoted. The new gases—helium, neon, argon, krypton, and xenon—have, as mentioned above, the curious property of heating the electrodes very considerably in vacuum tubes, and this gives rise to the evolution of a second quantity of hydrogen.[1] If into a tube, which has been carefully exhausted in the manner described above, all the hydrogen possible having been removed, a small quantity of one of these gases be admitted, at once a further quantity of hydrogen is evolved in quite sufficient amount absolutely to mask the new gas spectrum. It is therefore necessary that this hydrogen be removed before the new gas spectrum can be obtained pure; this can only be done by the repeated admission of small quantities of argon and re-exhaustion, the process being repeated until the hydrogen lines disappear from the spectrum. Any one of the new gases would answer the purpose, but argon is at present the only one that we can afford to waste in this way. It is curious that this effect does not take place when the gases are not quite pure—that is to say, when they contain diatomic impurities; a further point of interest is that the process known as electrical evaporation of the electrodes

[1] Baly, *Phil. Trans.*, **202.** A, 183 (1903).

takes place very rapidly with these gases when pure, the aluminium subliming and depositing a mirror on the glass walls immediately surrounding it. Again, these gases carry mercury vapour with them into the vacuum tube with great ease, so that its spectrum is very strong, sometimes even masking that of the other gas present. This, however, can be removed by keeping the discharge passing for some minutes through the tube, when apparently the mercury is absorbed by the electrodes.

Chlorine and bromine cannot be kept over mercury, and therefore these substances require special treatment. The simplest method is to use a metallic chloride or bromide which can be decomposed by the action of heat, a small quantity of the salt being placed in a side tube joined to the vacuum tube. When the vacuum tube is exhausted, the salt may be heated, and the halogen evolved; the gold salts may be used, as the chloride readily decomposes at about 250° C., and the bromide at about 120° C. On cooling, the halogen is slowly absorbed again, so that the tube must be heated whenever it is required. In these cases the ordinary aluminium electrode must not be used, as the stable halogen salts of this metal will be formed; as an alternative, platinum electrodes may be used, which are protected by an enamel coating, so as to leave only a very short piece exposed, or, better still, electrodeless tubes may be employed.

A further trouble sometimes met with in vacuum tube work is the gradual disappearance of the gas in the tube, owing to absorption, decomposition, polymerisation, or some such cause. The new monatomic gases are very liable to be slowly absorbed, but as this takes a long time, the simplest way is to open and fill the tube anew when the pressure has become too reduced. Cyanogen is a very good example of a gas which polymerises under the action of the discharge; this takes place so rapidly when the gas is pure that the current will only pass for a few minutes after admission of the gas. In such cases it is very convenient so to arrange the apparatus that the vacuum tube is fixed opposite the spectroscope slit, and to fill it in that position, and then as fast as the gas disappears more may be

admitted. The spectrum can in this way be photographed without sealing off the vacuum tube.

In the case of cyanogen,[1] the product of polymerisation is a brown solid (paracyanogen), and therefore in some experiments on the spectrum of this gas an end-on vacuum tube was employed, which was placed facing the slit, and thus the deposit of paracyanogen on the capillary walls did not interfere with the illumination. Silicon tetrafluoride is another example of a gas which requires to be treated in exactly the same way.

Among the directions given above for filling a vacuum tube, it was briefly stated that the pressure exerted by the gas therein should be adjusted until the best result is obtained. The pressure of the gas often exercises a very considerable influence on the definition of its spectrum lines, and, further, on the relative visibility of the components of a gaseous mixture. An example of the first effect may be drawn from the new monatomic gases, for unless the pressure lies within certain small limits the radiations become very ill defined; this is true for krypton in the orange region, and particularly for xenon over the whole spectrum.[2] It was found in filling tubes with xenon that, unless the pressure was below a certain limit (which was not measured, but probably about 1 to 2 mm.), the lines, especially of the spectrum obtained with the Leyden jar in the circuit, were hopelessly confused, having in many cases a width of 6 to 8 A.U., and were seen upon a continuous background. When the pressure was slowly reduced, the continuous background disappeared, and the lines became in the end absolutely sharp. It will often be found in working with gases under reduced pressures that there is a definite pressure at which the best effect is produced.

The second effect of pressure, namely the effect on the relative visibility of the components of a mixture of gases, is well shown by some results obtained by Collie and Ramsay with a mixture of helium and hydrogen.[3] With a mixture of two parts of hydrogen and one of helium, the latter was

[1] Baly and Syers, *Phil. Mag.* **2**. 386 (1901).
[2] Baly, *Phil. Trans.*, **202**. A, 183 (1903).
[3] *Proc Roy. Soc.*, **59**. 257 (1896).

invisible at a pressure of 2·61 mm., but at a pressure of 0·43 mm. the helium spectrum was strong, and as the pressure was reduced it became stronger, until at 0·072 mm. the red line was as bright as the red hydrogen line; at 0·012 the helium spectrum was stronger than the hydrogen throughout. The same was true of other mixtures of the same gases, it being found that the less helium in the mixture, the lower was the pressure necessary to make it visible. Generally speaking, therefore, the pressure is an all-important factor in spectroscopically testing a mixture of gases. Some interesting qualitative observations upon the spectra of mixed gases have been published by Nutting.[1] It has also been found that, when the discharge is passed through a mixture of two gases, they are separated, one appearing in the negative glow and the other in the positive column.[2]

Some important experiments have been carried out by Soddy[3] on the method of producing high vacua by means of the absorbent power of metallic calcium. The calcium is placed in a small porcelain test tube which is heated in an electric resistance furnace, the whole being surrounded by a shield tube of porcelain. The complete apparatus is enclosed in a glass tube which is directly connected to the vacuum tube which has to be exhausted. As a result of many experiments Soddy was able to prove that metallic calcium when heated will absorb every chemically valent gas, but that helium, argon, and the other monatomic gases are not absorbed. He has also shown that the apparatus is very simple to put together and easy to use; although the optimum temperature of the calcium is well above the softening point of ordinary glass, yet there is no danger of the glass walls being sucked in owing to their being protected from the heat by the porcelain shield tube.

The absorption is rapid, so that this method of exhaustion is exceedingly convenient. Care must be taken, however, not

[1] *Astrophys. Journ.*, **19**. 105 (1904).

[2] Baly, *Phil. Mag.*, **35**. 200 (1893); J. J. Thomson, *Nature*, **52**. 454 (1895).

[3] *Proc. Roy. Soc.*, **78**. 429 (1907).

to heat the calcium to too high a temperature, because some of the substances which are formed, *e.g.* calcium hydride, will be liable to dissociate and evolve the gases which were absorbed at a lower temperature. The actual absorption takes place in a very short time, and if in practice it be found that the absorption when once started does not complete itself, it will be advisable to allow the temperature to fall and not to rise, so as to increase the stability of the dissociating compound. The natural tendency on finding that the gas is not entirely absorbed would be to increase the temperature, but Soddy points out that incomplete absorption is usually due to the temperature being too high. The great advantage of this method is that the tube containing the calcium and the furnace may be connected to the vacuum tube, there being no need for any drying tubes, so that the total volume of the apparatus is reduced to a minimum.

Some very interesting results were found by Soddy in the course of his experiments with the furnace owing to the fact, as stated above, that argon and its companions are not absorbed by the calcium. It follows that if air is admitted to heated calcium the argon is left behind in a state of great purity. In the course of his investigations he constructed a vacuum tube and calcium apparatus of known volume, and admitted successively known amounts of air, the oxygen and nitrogen being absorbed between each admission with the result that a definite and known amount of argon accumulated in the apparatus. In one experiment the volume of the apparatus was 123 c.c., and it was possible to admit a measured amount of 0·13 c.c. at one time. This quantity of air therefore corresponded to a pressure of argon of 0·0075 mm. It was found that after absorption of the oxygen and nitrogen no discharge would pass through the vacuum tube until three quantities of air had been admitted and absorbed. In other words a discharge would only just pass through argon under a pressure of 0·0225 mm. In a second experiment the volume of the apparatus was 100 c.c. and 12 c.c. of air were admitted after the calcium had been heated to the absorbing temperature. This quantity was absorbed without difficulty, and the

residual argon must have exerted about 1 mm. pressure, yet the tube showed brilliant green phosphorescence.

It follows from these experiments that below a pressure of one-fiftieth of a millimetre, no discharge can be sent through a tube containing argon. At 0·5 mm. the resistance of the tube is greater than that of an air gap 5 mm. long, while at a pressure of 1 mm. the tube is brightly phosphorescent. It is evident from this that the generally accepted idea of high vacua must be modified, for it is usually assumed that when the electric discharge will not pass through a vacuum tube the pressure inside is vanishingly small; owing to the fact that monatomic gases such as argon, etc., refuse to allow the discharge to pass at so high a pressure as one-fiftieth of a millimetre, the non-conductance of a vacuum tube cannot be accepted as a criterion of the smallness of the gaseous pressure therein. It was stated on p. 431, that one of the troubles met with in vacuum tube work with the rare gases, argon, etc., is their gradual absorption by the electrodes. Soddy has now shown that the fact that tubes filled with these gases become non-conducting is not due to the absorption of the gases by the electrodes, but simply due to the absorption of small traces of the diatomic gases so that the monatomic gases become then perfectly pure and therefore offer abnormal resistance to the electric discharge.

Soddy points out that similar considerations apply to the method of producing vacua by the use of charcoal cooled in liquid air. This method is now very largely used in scientific work, and was first employed by Dewar.[1] Dewar found that charcoal, when cooled in liquid air, absorbs gases with extreme readiness, and the vapour pressure of the gases thus condensed is extraordinarily small, so that this method may be used for a rapid and effective exhaustion of any apparatus, such as vacuum tubes. The best charcoal for the purpose is that made from cocoa-nut shells. The shells may be charred in the following manner. They are first broken into small pieces, which are put into a crucible and covered with silver sand. The crucible is put into a furnace, and heated until no further distillation

[1] *Proc. Roy. Soc.*, **74**. 122 (1904).

products are evolved. The crucible is then taken out of the furnace and allowed to get quite cold before the charcoal is taken out of the sand. The charcoal thus produced is then placed in a glass tube, which is sealed to the apparatus to be exhausted. This tube is then immersed in liquid air, and it will be found that the gases are rapidly absorbed with the production of a very high vacuum. It will be found advisable between each experiment to drive off all the gases condensed in the pores of the charcoal if the maximum absorbing power is to be exerted. This is simply enough carried out by heating the tube containing the charcoal with a Bunsen burner, and exhausting it with some form of air-pump. In order to protect the charcoal from exposure to the atmosphere when not in use, it is advisable to fit a stop-cock to the tube containing it, which may be closed when the tube is not in use. Just as in the case of the metallic calcium in Soddy's method, so in the case of the charcoal, it happens that the monatomic gases helium, argon, etc., remain very largely unabsorbed at the liquid air temperature, so that vacua are obtained which are non-conducting to the discharge, yet still may contain quite appreciable quantities of the rare gases.

A few words may be said before leaving the subject of the discharge through gases under reduced pressure about the apparatus used to supply the necessary electrical energy. For this purpose either an induction coil or a step-up transformer may be used, very excellent forms of both of which are on the market. It must be remarked, of course, that the discharge from these two types of instrument is intermittent, and to a certain extent alternating; and, therefore, if a continuous direct current is required, a high potential system of batteries must be used. The difficulty with vacuum tubes and a continuous current from a battery is the initial resistance offered by the gas to the passage of the current. As is well known, if this resistance is once broken down by some suitable means, quite a low potential difference will be sufficient to drive a current through the vacuum tube. Many methods have been used at various times for overcoming this difficulty, but perhaps the best and most convenient is the so-called Wehnelt cathode,

as described by Wiedemann and Wehnelt.[1] These authors pointed out that if a piece of platinum foil covered with calcium, strontium, or barium oxide be used for the cathode in a vacuum tube, and be heated to redness, a current of several amperes, at 110 to 220 volts, may readily be made to pass through the tube. It was shown also that, under these cir-

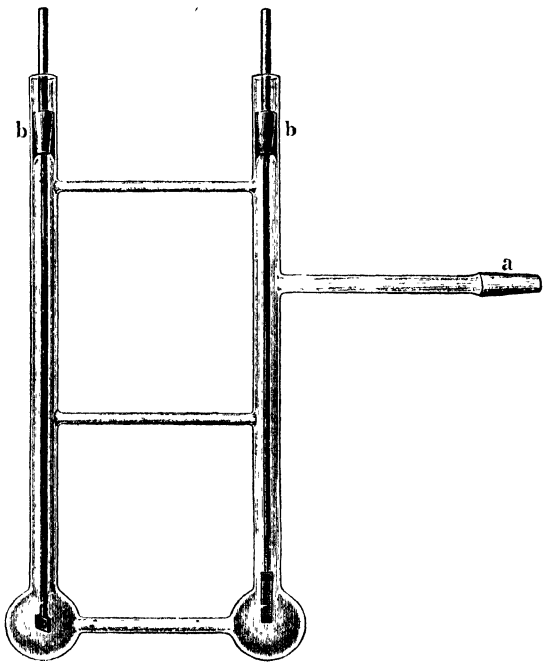


FIG. 159.

cumstances, the anode melts and volatilises, and the vapour from it is brilliantly illuminated by the discharge.

This is a most convenient method of examining metallic spectra. Konen and Jungjohann[2] have devised a special form of vacuum tube for this particular purpose of direct-current discharge. It is shown in Fig. 159. The two bulbs at

[1] *Phys. Zeitschr.*, **6**. 690 (1905).
[2] *Verh. d. Deutsch. Phys. Gesell.*, **12**. 145 (1910).

the bottom of the tube are three centimetres in diameter; the capillary tubing has a two-millimetre bore, and is about 66 mms. long. The electrodes are made of nickelled steel, and are ground in at *b*, *b*. It is advisable to cover this ground joint with a little mercury to guard against any leakage of air. The lower ends of these electrodes consist of aluminium cylinders, and the particular one to be used as cathode has a narrow slit cut in it, in which is fastened a small piece of platinum foil. This platinum is about 0·25 cm. square and 0·01 mm. thick, which has previously been dipped in an aqueous solution of barium and calcium nitrate, and then heated to redness in a Bunsen flame, so that it becomes covered with a thin layer of oxide. The authors, in using this tube, have employed a battery of 420 cells, which gives a potential difference of about 840 volts and a current of 1·2 amperes. It is not at all difficult to start the discharge passing in the tube, this being done simply by warming it with a Bunsen burner. The tube is most conveniently made of quartz, and may be joined to the glass apparatus necessary for exhaustion by means of the ground end at *a*.

CHAPTER XIII

PHOSPHORESCENCE AND FLUORESCENCE

It is well known that many substances may be made to give out light under certain influences, such as cathode streams in a vacuum tube or ultra-violet light. This fact was first noticed by Crookes and others about the year 1878, whilst investigating the effects of electric discharges passing through glass tubes exhausted to high vacua. Crookes found certain minerals when subjected to cathode streams in a vacuum tube glowed with extraordinary brilliance. For example, specimens of diamond were found which glowed with each of the colours bright-blue, pale-blue, apricot, red, yellowish green, orange, and light green. Again, alumina in its various forms was found to be strikingly phosphorescent, in nearly all cases glowing with a rich full red, the spectrum showing a faint, continuous light, ending in the red near the B line, after which comes a black space and then a very brilliant and sharp red line. Emeralds phosphoresce with a crimson colour, sapphires with a bluish grey, and certain specimens of tinstone were found which glowed with a yellow light. Spodumene also has a golden yellow phosphorescence under the same conditions, but shows no distinctive spectrum lines. Glucina, when prepared with special care, was found to phosphoresce with a continuous spectrum, showing a bright blue colour. Besides these natural minerals, certain artificially prepared sulphides and sulphates were found to glow in a vacuum tube under the action of the cathode streams, with light giving either a continuous or a discontinuous spectrum. The latter is especially noticeable in the sulphates of the rare earth elements.

In addition to the above-mentioned substances, the

following minerals give very characteristic colours when phosphorescing. Lepidolite gives a deep crimson, willemite a magnificent green, calcite a red, strontianite a blue colour respectively. Again, it has been shown by Jackson that it is possible to prepare samples of lime which glow with different colours. A very beautiful effect can be produced by carefully calcining a sea-shell, such as a cockle-shell, and exposing it to the cathode rays. The lime thus produced glows with a variety of colours.

To these phenomena the names have been given of phosphorescence and fluorescence, and at times these names have been used more or less indiscriminately to describe the various phenomena. Grouped under these names there lies a large branch of investigation which is of profound and fundamental importance, for it is in this direction as well as that of the phenomenon of absorption that we must look for the foundation of a theory of chemical reaction and reactivity.

It appears from the modern work on these lines that the whole of the phenomena grouped under the names phosphorescence and fluorescence are very closely allied in spite of the fact that they have frequently been considered as distinct. The reason for this distinction may be readily understood when one compares the luminescence of a solid substance such as lime, or a rare earth oxide under the influence of the cathode discharge and that of an organic compound such as fluorescein under the influence of ultra-violet light. In the former case the luminosity generally, if not always, persists an appreciable period after the exciting influence has been stopped, while in the latter case the luminescence does not so persist. The name phosphorescence has generally been accepted as applying only to the first class, while the name fluorescence has been applied to the second class. Kayser in his "Handbuch der Spectroscopie" adopts this nomenclature, but Urbain, on the other hand, owing to his conviction that all the phenomena are due to the same cause, groups them under the common name of phosphorescence, and uses the word "persistence" to define the continuance of the light emission after the exciting influence has been removed.

Although perhaps Urbain's definition is more consistent with facts, still, owing to the more general use of the terms in the sense as accepted by Kayser, it will perhaps be preferable to follow his lead.

There is another phenomenon of light emission closely connected with phosphorescence, viz. thermoluminescence. Many minerals have been found to emit light when heated, and, generally speaking, the radiations emitted are characteristic of the substance concerned. One of the most striking examples of this phenomena is chlorophane, which gives out a characteristic green light when it is heated. It is fairly evident that every phenomena of light emission, with the exception of those directly connected with a chemical reaction, are produced by the absorption of radiant energy in some form or another. This energy is subsequently emitted by the substance. In certain cases the emission takes place entirely during the period of excitation, but in other cases it persists for a definite period after the excitation has been cut off. It appears that the question depends partly upon the temperature and partly upon the condition in which the luminescent molecules exist. Generally, for example, when the substance is dissolved in some liquid solvent, the emission does not persist after the excitation has been cut off. On the other hand, this persistence frequently occurs in the case of solid substances. Owing to the fact that the emission of the light in the case of solid substances frequently persists after the excitation has been cut off, it is evident that the velocity of absorption must be greater than the velocity of emission. Experiment shows that it is possible by reducing the temperature to decrease the velocity of emission in relation to the velocity of absorption. Granted a sufficiently low temperature it is possible so much to reduce the velocity of emission that the substance can store up the exciting radiation without any appreciable amount being emitted in a reasonable time. Such substances when the temperature is raised will then emit the stored up energy and so become thermoluminescent.

On this theory it is clear that the three phenomena phosphorescence, fluorescence, and thermoluminescence are closely

connected. Fluorescence embraces those phenomena in which the velocity of emission is equal to the velocity of absorption, thermoluminescence occurs with those substances in which it is possible by the effect of low temperature or otherwise to reduce the velocity of emission to a minimum, whilst phosphorescence embraces those phenomena lying between these two extremes.

In speaking of the lower limit of temperature below which the velocity of emission is vanishingly small, it must be pointed out that this is a function of the substance and differs very materially for different substances; for example, it is quite possible that this limit of temperature may be above the ordinary temperature of the earth, so that minerals may exist which stored up radiant energy in a previous geological epoch, and which will become luminescent when warmed. In forming any theory to explain these phenomena it is of course necessary to take account of the molecular conditions of the substance in question. Although perhaps it will be advisable to postpone the theoretical consideration until an account has been given of known experimental facts, yet it may be accepted that the freer the molecular and atomic motions are, the more closely similar will be the velocity of absorption and emission. Conversely it may be expected that the more restrained the molecular motions are, the slower will be their capability of returning to their initial state after this has been disturbed by the absorption of the radiant energy. The substances therefore most likely to be capable of thermoluminescence, or in other words those most capable of storing the radiant energy will be those in which the molecular motions are the most restrained. It is not improbable that this restraint is greater in the case of crystals than it is in the case of amorphous solids. Consequently it is not surprising that the most strikingly thermoluminescent substances are crystalline minerals.

It is hardly necessary to give a description here of the older methods of observation. The first systematic work in this direction was carried out by Crookes, and we are mainly indebted to him, to Lecoq de Boisbaudran, and to Urbain for

accurate investigations into this subject. Crookes has mainly devoted himself to the phosphorescence of minerals and the rare earths as excited by cathode streams. In his earlier work in which he was dealing with visible phosphorescence he employed a tube as shown in Fig. 160. It will be remembered that the cathode streams are driven from the negative pole normal to its surface, and travel in straight lines. The thin flat electrodes shown in the figure are therefore particularly adapted to direct the streams upon the substance lying in the lower portion of the tube. The methods of preparation and exhaustion of these tubes are sufficiently similar to those already described for the ordinary vacuum tubes, that there is

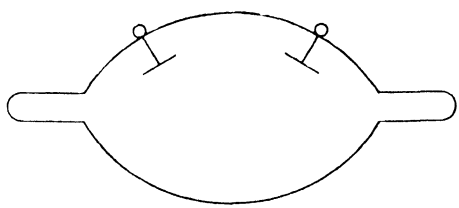


FIG. 160.

no reason minutely to describe them. The most important point in connection with them is the necessity for a very high exhaustion. It is advisable during the exhaustion carefully to heat the tube with a Bunsen burner in order to drive off the gas which is occluded upon the walls and in the substance to be excited. It will generally be found, if the exhaustion be carried first of all to a high point and the discharge made to pass, that a considerable quantity of carbon dioxide and hydrogen will at once be given up by the various parts of the tube. It is clearly necessary that all of this be removed before the tube is finished. This can be done with patience, by continually heating the tube and re-exhausting, this being repeated until no more gas is evolved. This can readily be tested by watching the effect of further heating upon the appearance of the discharge; no effect, of course, should be produced. As regards the extent to which these tubes must be exhausted, this must be judged for each separate tube. It

will be found that the phosphorescent effect will during the exhaustion steadily improve until a maximum is reached, after which it will begin to decline; the degree of exhaustion at which the maximum occurs differs with different tubes. In connection with the use of these tubes, it must not be forgotten that many minerals tend to give up gases under the influence of the rays, due to the heating, etc. Care should in such cases be taken only to run the discharge for a very short time; if, however, it is required to make a lengthy observation, or take a photograph of the spectrum, it is advisable to leave the tube in connection with a mercury pump, so that any gas which is evolved can at once be removed.

In his later work Crookes found it necessary to examine the phosphorescent emission in the ultra-violet region of the

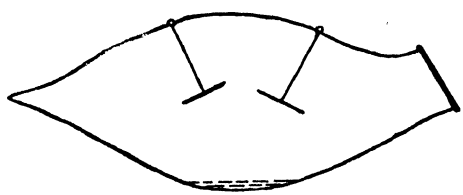


FIG. 161.

spectrum, and therefore it became necessary to alter the design of the vacuum tube so that the phosphorescent material may be viewed through a quartz window. A diagram of such a tube is shown in Fig. 161.

Urbain[1] has devised forms of tubes which are excellently suited for the observation of these phosphorescent spectra. When it is not required to examine the ultra-violet phosphorescence, the form of tube is used as shown in Fig. 162, in which a ground glass joint connects the lower portion of the tube containing the substance to be examined. The anode is made in the form of a ring, while a slightly concave surface of aluminium forms the cathode. Owing to the fact that the cathode streams pass through the annular anode, they are very closely bunched together, and therefore the ground

[1] *Ann. de Chim. et Phys.*, **18**. 222 (1909).

joint is protected from their bombardment, and they strike the substance which is placed in the bottom of the lower tube. The great convenience of this apparatus is that the lower tube can readily be removed, cleaned and primed with a fresh substance. Urbain has introduced a slight modification for use when the ultra-violet phosphorescence is to be examined. The lower tube is then made in the shape shown in Fig. 163, the substance being heaped up in the angle of the tube, and the phosphorescence examined through the end of the tube, which is closed by a quartz plate. Urbain has also

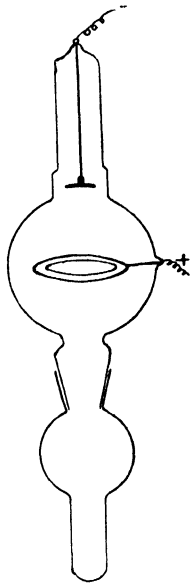


FIG. 162.

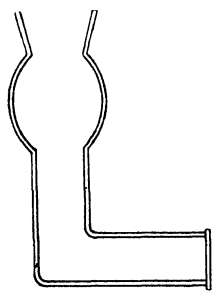


FIG. 163

devised an arrangement in which a number of these tubes are united together in one apparatus. This is shown in Fig.

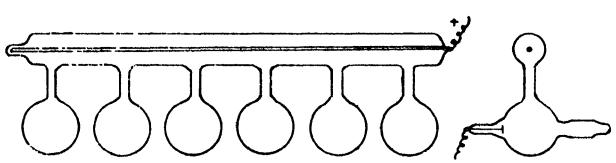


FIG. 164.

164, which is shown in plan and also end elevation. In this apparatus the anode is a long wire passing the complete length of the upper glass tube, whilst each observation tube

carries its own cathode. When in use all the cathodes are joined together, so that the apparatus is exceedingly well suited for a comparison between the phosphorescence of different substances such as occur during the fractionation of the rare earths, when it is necessary to follow the fractionation process with spectroscopic observations in order to see how it is progressing. The advantage of the arrangement lies in the fact that each of the materials are made to phosphoresce under as nearly as possible the same conditions.

Lecoq de Boisbaudran[1] has devoted himself to the study of fluorescence of metallic salts in solution, and the apparatus which he used is shown in Fig. 165. As may be seen, it rather resembles the apparatus in which the spark spectra of solutions are obtained, but whereas in the latter case the liquid is made the negative and the sparking wire the positive pole, Lecoq de Boisbaudran reversed this arrangement, making the liquid the positive and the wire the negative. Under these circumstances, the under surface of the liquid meniscus below the region where the sparks are passing becomes fluorescent, this fluorescence, of course, being due to the salts dissolved therein. Owing to the reversal of the direction of the spark, Lecoq de Boisbaudran gave the name *spectres de renversement.* By the use of this apparatus he has succeeded in observing the spectra of the rare earths and also of manganese and bismuth.



FIG. 165.

While there is no question of giving anything approaching a full account of the work which has been done upon the phosphorescence of solid substances, certain facts have been observed by Lecoq de Boisbaudran, Lenard and Klatt, and Urbain which stand out as being of fundamental importance, and which it is impossible to pass by. Perhaps the most important of these is the discovery made by these physicists that a pure substance does not phosphoresce, and that the phosphorescent effect is always due to a solution of one substance in another either solid or otherwise. This was emphatically shown by

[1] *Comptes Rendus*, **100**. 1437 (1885).

Urbain and Bruninghaus,[1] who give the following conclusions based on their experiments. (1) Pure bodies do not show any phosphorescence at all. (2) Phosphorescence always results from a mixture of at least two bodies. (3) Phosphorescence is more especially a property of diluted matter. (4) In all cases of a mixture of two substances which phosphoresce one acts as the diluant for the other, which is the active principle. This has been called the phosphorogene (Bruninghaus). (5) In such a binary phosphorescing mixture there always exists an optimum of phosphorescence which corresponds to a very small quantity of the phosphorogene; for example, in the case of the rare earths mixed with lime, the optimum corresponds to about one per cent. of rare earth. (6) This law of optimum is quite general, being applicable to all phosphorescing substances.

These conclusions resulting from Lecoq de Boisbaudran, Lenard and Klatt, and Urbain's work naturally throw an entirely new light on Crookes' well-known investigations. During the course of his work, which has extended over a very large number of years, Crookes has investigated the phosphorescent spectra of the rare earths and the manner in which these change as the mixtures of rare earths are fractionally crystallized or precipitated according to the usual chemical methods for the separation of the rare earths. During the course of these experiments he observed that certain bands and lines in the phosphorescent spectra became intensified, which led him to the view that each band or line is to be attributed to a separate element. It is evident, from the later results described above, that these intensifications were simply due to Crookes obtaining the optimum of phosphorescence for the particular mixture he was dealing with. It is hardly necessary to point out what a profound modification must be made in the conclusions which Crookes himself drew from his investigations.

In forming any theory of phosphorescence it is evident that some relation must be considered to exist between phosphorescence and absorption. It is unfortunate that as long as cathode streams, canal rays, or Rontgen rays are employed as exciters the vibration period of the chemical molecules, when

[1] *Ann. Chim. et Phys.*, **18**. 293 (1909).

absorbing, cannot be arrived at. Certain observations, however, have been made which go to prove in a very conclusive way that there is a close connection between phosphorescence and absorption. It was shown by J. Becquerel [1] that certain crystals, for example, xenotime and tysonite, which possess absorption bands, when cooled in liquid air, gave absorption more comparable with that of a gas. The absorption bands were found to sub-divide themselves into groups of fine lines. H. Becquerel,[2] arguing on a probable close relation between phosphorescence and absorption, concluded that the phosphorescent bands should also at low temperatures resolve themselves into groups of lines. This he showed to be the case with uranyl nitrate, the double sulphates of uranium and potassium, and of uranium and ammonium, and also the double chlorides of uranium and potassium. In all these cases the bands are resolvable into fine lines at low temperatures, and they are shifted towards the shorter wave lengths.

Some interesting observations have been made by Kowalski [3] who has also examined, at the temperature of liquid air, the phosphorescence of alcoholic solutions of the nitrates of the rare earths excited by ultra-violet light from a mercury lamp. He found that the phosphorescence of these solutions lasted about five minutes after the exciting light was cut off. This result seems to bear out what was said above, about the effect of temperature reducing the velocity of emission in relation to the velocity of absorption. Solutions of phosphorescent substances do not at ordinary temperatures as a rule emit phosphorescent light after the excitation has ceased.

Recently some very remarkable experiments have been carried out by Goldstein [4] on the phosphorescent emission spectra of solid aromatic compounds. He finds that when aromatic substances cooled in liquid air are subjected to the

[1] *Comptes Rendus*, **144.** 420 (1907).

[2] *Ibid.*, **144.** 459 & 671 (1907).

[3] *Ibid.*, **145.** 1270 (1907).

[4] *Verh. d. Deutsch. Phys. Gesell.*, **6.** 156 and 185 (1904), and **12.** 376 (1910), and **13.** 378 (1911). Also *Phil. Mag.*, **20.** 619 (1910).

action of the cathode rays they always evidence three spectra in succession. Goldstein has named these respectively the initial spectrum, the chief spectrum, and the solution spectrum. All three of these spectra are highly characteristic of any particular substance, but the second is more especially so, and it is possible to recognize at sight this chief spectrum of many compounds. Goldstein further points out that the solution spectrum, which is a true phosphorescent effect, *i.e.* it persists after the excitation is cut off, is due to the presence of impurities. This spectrum forms the most delicate test imaginable for the presence of an impurity. For example, he has been able to show the presence of less than 0·001 per cent. of naphthalene in a sample of methyl benzoate. Indeed, it has not been found possible to prepare a substance so pure that it does not show the solution spectrum of an impurity of some kind.

There is no doubt that these observations of Goldstein and the phenomena which he has observed belong to the same group as all those phenomena in which light is emitted under suitable excitation. It is generally known that the colour of phosphorescent substances depends very much upon the temperature as well as upon the degree of dilution of the active substance. This effect of temperature is especially noticeable in the case of strontium sulphide which was studied by E. Becquerel.[1] This substance at 200° C. gives an orange phosphorescence, and as the temperature falls the colour passes through yellow, green and blue, until at −20° C. it is dark violet. The explanation of this change is to be found in the fact that the complete phosphorescent spectrum of a substance such as strontium sulphide consists of many bands, and that the relative intensity of these bands varies very considerably with the temperature. This has been more extensively examined by Lenard and Klatt[2] who compared the colours and intensities of the phosphorescence of a number of substances at −180° C., −45° C., 17° C., 200° C., 300° C., and 400° C. They found that some bands reached a maximum

[1] *Ann. Chim. et Phys.*, **55**. 5 (1859).

[2] *Ann. der Phys.*, **15**. 225, 425 and 633 (1904).

at low temperatures, others at high temperatures, while some showed a maximum at mean temperatures.

A still closer relation between phosphorescent and absorption bands has been shown by H. and J. Becquerel and Kamerlingh Onnes[1] and later by J. Becquerel,[2] for these authors have shown that it is possible to reverse the emission bands of a phosphorescent spectrum and make them into absorption bands. J. Becquerel in his paper describes how a crystal of a uranyl salt may be set up with its face turned towards the observer and the phosphorescence produced by a beam of exciting radiation directed at an angle upon it. On directing a beam of light, which does not contain the exciting radiation, through the crystal from behind, the phosphorescent bands previously seen as bright emission bands will then be seen as dark absorption bands.

In dealing with the fluorescence of substances in solution such as organic compounds under the influence of ultra-violet light, it is necessary to employ a special form of apparatus. Since the region of fluorescence is usually restricted to the surface of the liquid where the exciting light enters, several forms of apparatus have been devised for this, and a very convenient form is shown in Fig. 166. It consists of a tube, B, into which is fitted another, A, by means of a ground joint. C and D are two quartz plates, which are cemented on with some suitable cement. The solution of the substance to be examined is placed in B, and a beam of exciting light is passed through A and brought to a focus at C. The fluorescence is produced in the immediate neighbourhood of the quartz plate and may be photographed through the tube D. The bulb and side tube F serve for filling the tube. The adjustment of this apparatus in front of the slit of the spectrograph is easy enough when the fluorescent light is visible, but a little difficulty may arise if the emitted light is invisible.

The simplest way is to set up a permanent stand to hold the apparatus in front of the slit. This adjustment may very easily be done when the cell contains some solution such as

[1] *Konink. Akad. Wetensch. Amsterdam, Proc.*, **12**. 761 (1909).

[2] *Comptes Rendus*, **151**. 981 (1910).

fluorescein, which fluoresces strongly in the visible region of the spectrum. The adjustment can be made by the eye, and if the stand and the spectrograph be now fixed relatively to one another, there will then be no difficulty with the invisible fluorescence, for the whole apparatus will always be in perfect adjustment. The phenomena of fluorescence amongst carbon compounds is familiar enough to any one who has worked in organic chemistry, but of course only those substances will be recognized as fluorescent which happen to emit light in the visible region. It has been shown by Stark, Ley, and others that an enormous number of carbon compounds emit ultra-violet fluorescent light. In these cases, of course, it is absolutely essential that the observations be made photographically, and such an apparatus as that described above may be used. As will be shown in the following chapter, it is a very simple matter to observe the absorption exerted by organic compounds, and as we are, therefore, able to make accurate observations of both the absorption of light which is acting as the exciter of fluorescence and of the fluorescent light itself, it would seem that in these cases there is considerable hope that the real connection between the wave-length of the two will be discovered. Unfortunately, however, the absorption bands of organic compounds in solution are, as a rule, very broad, and so, although observations have been made of the fluorescence and absorption of the compounds, yet no direct relation between the two is yet forthcoming. Now, however, that monochromatic illumination apparatus with quartz optical parts are obtainable, there is a great opening

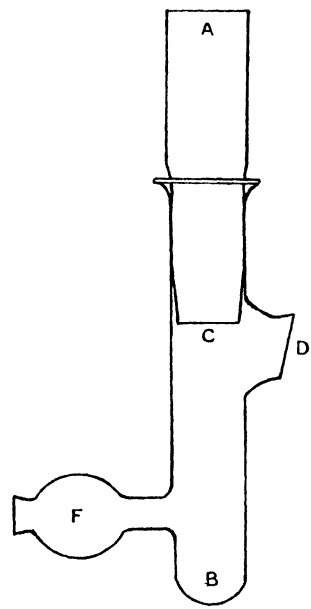


FIG. 166.

for very valuable work in this direction. Each fluorescent substance should be excited in turn by a series of monochromatic illuminations each lying within the region of the absorption band and the fluorescent spectrum observed in each case.

The intimate connection that exists between phosphorescence, thermo-luminescence, fluorescence, and absorption leads one to hope for a satisfactory theory of their origin which is based upon chemical properties and structure. During the past few years a certain amount of knowledge has been gained of the absorption spectra of organic compounds and their relation to chemical constitution, and it certainly seems possible to formulate a theory connecting these two which also seems able satisfactorily to account for all the emission phenomena dealt with in this chapter. The discussion of this theory may well be reserved until the results of absorption spectra have been detailed in the next chapter.

CHAPTER XIV

ABSORPTION SPECTRA

It is found that when a beam of light passes through certain substances definite rays of light are absorbed, and when the emergent light is analysed in a spectroscope it will be found that certain rays are missing. Such a spectrum is termed an absorption spectrum.

The earliest absorption spectra were observed by Brewster, who observed those of certain coloured solutions, and also of nitrogen peroxide gas,[1] finding in the first cases certain more or less broad absorption bands, and in the latter a very great number of fine lines. Similar investigations were made by Miller and Daniell[2] on the absorption spectra of iodine bromide and euchlorine (a mixture of chlorine with oxides of chlorine). The methods of experimentation varied in these investigations to a certain extent, but consisted in the main of the spectroscopic examination of the light from a source emitting a continuous spectrum, after its passage through a vessel containing the substance.

In these experiments a spectrometer was used to measure the position of the absorption bands.

A certain amount of visual work has been done upon the absorption spectra of metallic salts in solution. In these cases we have absorption bands of various widths which are not sharply defined at the edges, and generally they cannot be resolved into lines. The scope of this work in general has been limited to the measurements more or less accurately of the bands, and it cannot be said that any success has attended the attempts to interpret the meaning of the bands.

[1] *Phil. Mag.* **2**. 360 (1833); **8**. 384 (1836); **7**. 436 (1835).
[2] *Pogg. Ann*, **28**. 386 (1833); *Phil. Mag.* **27**. 81 (1845).

They have been utilised in certain cases in important works upon constitution of compounds, of which an excellent example may be given of Ostwald's [1] work upon the spectra of the various permanganates in which he showed by the similarity of the absorption spectra that the electro-negative ions must be the same in them all. Further, a considerable amount of work has been done by Krüss and Nilson,[2] Crookes,[3] Auer v. Welsbach,[4] and many others, upon the absorption spectra of the salts of the rare earths. The first-named consider that more than twenty elements are really existent in place of the six so-called elements, praseodymium, neodymium, erbium, holmium, samarium, and thulium, basing their conclusions upon the assumption that each absorption band is characteristic of one element. Into the arguments for and against this I cannot enter here.

A great deal of quite valueless work has been done upon the absorption bands of solutions; many of the measurements have been based upon purely arbitrary scales, and further, insufficient attention has been paid to the position of the maximum of absorption of a band. A measurement of a band simply stating the wave-lengths of the edges is of no use, because very often the middle is not the darkest part. Several ways have been suggested of accurately arriving at the wave-length of the maximum of absorption, among which the following may be mentioned:—

1. Krüss and Oeconomides [5] employ solutions the dilution of which is increased until the band almost disappears. At each dilution as the band narrows itself its limits are measured; and finally, just before the band disappears, two very close readings are obtained. Evidently the absorption maximum must lie between these points, and may be found by taking the arithmetical mean or by setting the cross wires of the eye-piece upon the region of greatest darkness.

[1] *Berichte*, **20.** 2134 (1887).
[2] *Chem. News*, **57.** 27 (1888).
[3] *Wiener Ber.*, **92.** (1885).
[4] *Berichte*, **16.** 2054 (1883); and **18.** 1426 (1885).
[5] *Zeits. Phys. Chem.*, **3.** 601 (1889); **9.** 579 (1892); and **9.** 226 (1892).

2. By means of a spectrophotometer the actual intensity of the band is compared with a standard light; where the greatest difference between the two is found, there lies the absorption maximum. This comparison is usually carried out in an instrument in which the spectrum containing the absorption band is seen contiguous to a continuous spectrum. The brightness of this continuous spectrum can be altered at will by various means; only a very small portion of each spectrum is observed, the rest being cut off by shutters in the eye-piece. In an actual observation comparison is made at various portions of the absorption band, the continuous spectrum being reduced in brightness until the two are equal. The point of maximum absorption is where the continuous spectrum has to be most darkened in order to produce equality. This method was bettered by Camichel and Bayrac,[1] who employed a Crova spectrophotometer. In this instrument the slit is divided into two parts, one being illuminated by a beam of intensity I_1, which passes through two Nicols, and the other by a beam, I, which passes through the absorbing substance. The two spectra are equalised, and then $I_1 \sin^2 \alpha = KI_2$ where $\frac{\pi}{2} - \alpha$ is the angle between the Nicols, and K is a constant. In practice the extremity of a band is observed and the two spectra made of equal brightness, care being taken to limit the amount of spectrum observed. The angle α is read, and so is the scale reading of the telescope; the telescope is then turned slowly towards the other side of the band until the spectra become equal again, when a second scale reading is obtained for the same value of α. Several pairs of points of equal brightness are thus obtained in the band, each pair giving a different value of α. The scale readings for each pair of points are then plotted on squared paper against $\sin^2\alpha$. A curve is drawn through these points, and a line drawn through the means of all the pairs of scale readings; this line, which is usually straight, will cut the curve at the point of maximum absorption. A very similar method was used by Laubenthal.[2]

[1] *Journ. de Physique*, 1. 148 (1902).
[2] *Ann. der. Phys.*, 7. 851 (1901).

None of these methods seem, however, to have been applied, except in one or two cases, to the study of absorption spectra, and beyond the fact that certain metallic salts have characteristic absorption spectra, there is but little known. (For a complete description of absorption spectra, see Kayser's *Handbuch der Spectroscopie*, vols. iii. and iv.; and Urbain's *Introduction a l'Etude de Spectrochimie.*)

Some interesting work has been done by Formánek[1] upon the absorption spectra of the lakes produced by certain metallic salts with alkannin. A great many chlorides of metals, such as the alkali metals and those of the alkaline earths which have no absorption spectra, form lakes with this dye, which are soluble in water and have characteristic absorption spectra. These absorption bands Formánek has measured, and has based upon them a qualitative spectroscopic analysis.[2] The alkannin is soluble in 95 per cent. alcohol to a red solution, and this is diluted down (with 95 per cent. alcohol) until when placed in a cell 10 to 12 mm. thick the absorption bands are seen to be quite separated. About 5 c.c. of this solution are put into the cell, and two or three drops of a neutral solution of the chloride of the metal are added. If no colour or spectrum change is produced, a small drop of dilute ammonia (20 per cent. solution of ammonia of 0·96 sp. gr.) is allowed to run down the side of the absorption vessel; a characteristic absorption spectrum will then be developed.

A further investigation into these absorption bands of Formánek's has been made by Laubenthal[3] in the case of the alkali metals and those of the alkaline earths. The position of the bands were more accurately measured by method (2) above, and certain regularities were found. For example, the bands shift towards the red in both groups with increasing atomic weight, and the shifts are proportional, so that the ratio between the wave-lengths of the two bands of each spectrum

[1] *Zeits. für anal. Chemie*, **39**. 409.

[2] *Die Qualitative Spectralanalyse anorganische Körper.* Mückenber, Berlin (1900), and *Die Qualitative Spectralanalyse anorganischen und organischen Körper* (1905).

[3] *Ann. der Phys.*, **7**. 851 (1902).

is constant for each group of metals (see, further, Chapter XVII.)

In dealing with absorption spectra the first problem which confronts us is the source of light to use. Generally speaking, the rays from some convenient source are passed first through the material, the absorption of which is to be investigated, and then into the spectroscope. It is evident that a visual comparison of the light before and after absorption cannot be satisfactory. In the first place, it is quite impossible to attain to any reasonable accuracy with visual measurements; and secondly, the visual measurements cannot extend into the ultra-violet. It follows that photographic methods must be used in these observations, and the absorption spectra determined by a simple comparison of the photographs taken of the spectrum of the selected source with and without the interposition of the absorbing material. At first sight it would seem most advisable to employ a source of light for this purpose which gives a completely continuous spectrum of equal intensity throughout, but it must be remembered that the wave-lengths of the rays that are absorbed must be determined. Naturally this cannot be done unless some method is at hand adapted to the purpose. If a continuous spectrum is employed it becomes necessary to use a Rowland grating or some similarly accurate method of determining the wave-length of the absorbed rays. The use of a grating will, of course, increase the time of exposure, and since, as will be seen from what follows, it is advisable to make observations of the absorption exerted by the material in question at many different concentrations, the increased time of exposure makes the whole examination very lengthy and tedious. A very large number of investigations in this direction have been made with a source of light containing a very great number of radiations, that is, a source the spectrum of which contains a great complexity of lines.

In this case it is merely necessary to observe the rays which have been absorbed, when the wave-length of the absorbing region can at once be arrived at; for example, the spark between electrodes of iron has been used in this

connection. It is a fairly simple matter to take a photograph of this source of light and calibrate it by marking the wave-length or oscillation-frequency of as many lines as possible upon the plate. Such a plate can then serve as a standard of comparison, and if the spectrum be again photographed after the absorbing material has been interposed, the two spectra can be matched by placing one against the other, and then the limits of the region absorbed can at once be read off. In a very long and important series of investigations Hartley has employed as his source of light the spark between electrodes either of an alloy of tin, lead, cadmium, and bismuth, or simply of pure cadmium. Although the number of lines present in these spectra are relatively few in number, there is the advantage that the region between the lines is filled with a continuous spectrum, and this Hartley finds exceedingly convenient in his measurements of absorption, especially where the absorption lines are very narrow. The wave-length of the absorption band or bands may readily be found in this case by measuring their position in relation to known metallic lines in the spectrum on either side. Purvis, in his investigations on the relation between the absorption exerted by organic substances in the liquid and gaseous states and in solution, also uses the cadmium light as his source. On the other hand, the excessive intensity of the cadmium lines compared with the continuous spectrum between them presents several serious disadvantages, as may at once be expected to occur if the wave-lengths of an absorption band and of a cadmium line happen to fall very near together. Such an absorption band, if narrow, would very probably be missed altogether, unless some steps be taken to guard against this; for example, in some experiments on the absorption spectrum of chlorobenzene it was found that an absorption band occurred at $\frac{1}{\lambda} = 3878$.[1] Now, there is a strong cadmium line at $\frac{1}{\lambda} = 3885$. Had not this absorption spectrum been examined with the help of another source of light, this particular band would have been

[1] Baly, *Trans. Chem. Soc.*, **99**. 856 (1911).

missed. Again, Jones in his work uses as the source of light the spark between carbon poles thoroughly coated with the oxides of uranium and molybdenum. The spectrum of this spark is intensely rich in lines which are very evenly distributed and do not vary very greatly in their intensities. The method of preparing these electrodes is as follows. Two electric light carbon rods are filed to a wedge shape at the ends, and these are then boiled in a strong solution of uranium nitrate, after which they are dried and heated to dull redness. This process is repeated three times. They are then boiled in a strong solution of ammonium molybdate and again heated to dull redness, this also being done three times. When used, the electrodes are mounted so that the wedges are parallel to one another and also to the axis of the collimator tube.

In some investigations on the absorption of organic substances I have used as sources of light the iron arc and the spark between a nickel wire and an iron wire. Although the latter is preferable to the former, owing to the failure of lines in the extreme ultra-violet, and to certain gaps in the main body of the spectrum, yet neither is as satisfactory as the spark between Jones' electrodes. Theoretically, of course, no discontinuous emission spectrum is perfect for absorption observations, especially where fine line absorption is being dealt with, but owing to the enormous convenience gained, it is generally preferable to use one as the source of light. Perhaps the most satisfactory method is to make use of two sources, such as the cadmium spark and the uranium and molybdenum spark, and make absorption observations with each in turn.

In some observations on the absorption of chlorine, Mrs. Laird employed sunlight, and determined the absorption by means of the Fraünhofer lines, but it would seem that, apart from the experimental difficulties of using sunlight, the reduction of the absorption photographs in the case of fine-line absorption will be too great to allow of this method being generally used. Grebe[1] has used the spark between aluminium electrodes under water as his source, and points out that this

[1] *Zeit. wiss. Phot.*, **3**. 376 (1905).

gives a completely continuous spectrum over the whole range with the aluminium lines reversed, and also one band which is probably due to water vapour. He used a grating apparatus in order to determine the wave-length of the absorption bands. His method is as follows: Two aluminium wires, each two millimetres in diameter, mounted on two stoppers ground into a flask, were used as the electrodes; the flask was filled with water, and was provided with a quartz window to enable the passage of the ultra-violet light. The distance between the two electrodes was about 0·25 mm., and the apparatus was connected with an induction coil giving a 30 cm. spark in air. An air spark gap was placed in series with the apparatus, and a condenser was also employed. It was found that, owing to the rapid disintegration of the aluminium, the water soon became cloudy, but this difficulty, of course, may be got rid of by having a steady stream of water flowing through the apparatus.

It must be remembered that, generally speaking, all emission spectra are inclined to fail as regards spectrum lines in the orange and red regions, and that therefore the above methods are not suitable for observations and measurements of absorption in these longer wave-length regions. In some investigations of blue organic compounds with absorption bands in the red and orange,[1] it was seen to be necessary to use some different method, and it was found that interference bands are admirably suited. These interference bands may be produced according to the method described by Edser and Butler, based on Fabry and Perot's investigations, and the method is described on page 164 of making such an interference apparatus. When these interference plates are mounted in front of the slit of the spectroscope, and the image of a source such as a Nernst lamp is focussed by a lens upon the air layer between the plates, the spectrum obtained is seen to be crossed by a number of interference bands. These bands may readily be used for the determination of the wave-length of the absorption bands. As was pointed out on page 166, the oscillation-frequencies of the bands are a linear function of the scale readings. It is only necessary,

[1] Baly and Desch, *Trans. Chem. Soc.*, **93**. 1747 (1908).

therefore, to take a photograph of some simple spectrum, such as that of hydrogen superposed upon the interference bands, and then read off the position of the hydrogen lines upon the interference fringes, using these as a simple linear scale. If the reading of each hydrogen line be then plotted against the oscillation-frequency of the line, it will be found that all these points lie on a straight line. From this it will be seen that the oscillation-frequency of any individual fringe may be read off. This, of course, need not be done more than once with any one interference apparatus, and the above calibration will serve for all photographs taken with it, as long as the interference plate does not change in any way. As a source of light, either of the following may be used: a Nernst lamp, Welsbach burner, or the positive pole of an electric arc between carbon poles. The same objections mentioned above as regards discontinuous emission spectra apply to this method of interference fringes. They may, however, be entirely got over by means of two pairs of interference plates. It would seem that this method is capable of extension into the blue and ultra-violet regions, provided that a source of light can be obtained with an unbroken continuous spectrum over the whole range of wave-lengths. Such a source of light is provided by Grebe's method of the aluminium spark under water. It would be necessary in this case to use quartz plates for the interference apparatus, with a nickel film cathodically deposited in place of the half-silvering, in order to eliminate both the absorption of the glass and the want of reflecting power of the silver for the ultra-violet rays.

In dealing with the work on absorption spectra which has been carried out in recent years, it is quite impossible to treat of it in detail. There is so much variety in its scope and character that no useful purpose would be served in describing all the separate investigations. The more is this true because up to the present there has been found no true co-ordination between the observed facts, and no satisfactory theory has been put forward to explain the many phenomena. Especially is this the case for the investigation of the absorption of light by inorganic compounds, where, beyond the accurate measurement

of the absorption bands, and in some cases the arrangement of these in series, nothing has really been effected. It has been found possible in certain cases to connect the absorption of organic compounds with their constitution, but notwithstanding this, it must be recognised that the whole subject of absorption spectra is still in its infancy. The work which has been done, however, is sufficient to show that there is a very great field opened here, and one which well deserves to be tilled, for it would seem certain that we may hope therefrom for great advances in our knowledge of both chemical structure and reactivity.

It will be convenient, in describing some of the modern work on absorption spectra, to treat of inorganic and organic compounds separately, owing to the special work which has been carried out upon the latter. Amongst the former may especially be mentioned the absorption exerted by the halogens.

Bromine and iodine have been investigated by Hasselberg,[1] who has also observed nitrogen peroxide. This brief reference to these must suffice. The banded absorption of chlorine was first noticed by Morrere in 1869,[2] who also found a band of complete absorption in the extreme violet. Liveing and Dewar[3] also investigated this absorption band, making use of the spark between iron electrodes as the source of light. Mrs. Laird[4] has carried out a complete examination of the absorption spectrum of chlorine, which may be shortly described as a good example of modern methods. The apparatus used consisted of a full-size Rowland grating; and as the source of light, sunlight and the electric arc were used. To contain the chlorine several tubes of various sizes were employed; one of these was of glass tubing 80 cm. long, and 5·3 cm. internal diameter, provided with glass ends, which were afterwards replaced by quartz plates mounted in lead; another of the

[1] Bromine, *K. Svensk. Akad. Handl.*, **24**. No. 3 (1891); *Mém. de l'Acad. de St. Petersb.*, **26**. No. 4 (1878); Iodine, *Mém. de l'Akad. de St. Petersb.* (7), **36**. (1888).

[2] *Comptes Rendus*, **68**. 376 (1869), and *Pogg. Ann.*, **137**. 165 (1869).

[3] *Chem. News*, **47**. 121 (1883).

[4] *Astrophys. Journ.*, **14**. 85 (1901).

tubes was 137 cm. long, and a third of steel 33·2 cm. long, for working with the chlorine at other than atmospheric pressures. A certain amount of trouble was encountered in recognising the chlorine absorption lines amongst the solar ones, but this could be done by careful compensation between plain solar and arc photographs, and those taken of the same through the absorbing layer of chlorine.

Measurements were made of the absorption lines, which extended from $\lambda = 4800$ to $\lambda = 5350$ at atmospheric pressure; under 2·5 atmospheres pressure they could be traced as far as $\lambda = 5450$. Observations were also made upon the general absorption band in the ultra-violet, but it was not found possible to resolve it into lines, even when the pressure of the chlorine was as low as 5 cm. This absorption band was found to vary much in extent with change of pressure or length of chlorine traversed by the light, and at the greater pressures it extends even over the absorption lines, reaching $\lambda = 4990$ at a pressure of $2\frac{1}{2}$ atmospheres. The line spectrum with change of pressure hardly altered in character at all, only becoming blacker with increase of pressure, but new lines are added towards the red. The general absorption band and the line absorption thus appear to be due to quite different causes.

The absorption spectrum of iodine has been similarly investigated by Konen,[1] who made use of a Rowland grating of one metre focus, and the positive crater of the electric arc as his light source. Both Hasselberg[2] and Konen have noticed that the effect of increasing the pressure on the iodine spectrum is to increase the intensity and width of the lines, and further to originate a general absorption, which begins at the violet end of each band of lines, and, extending towards the red, becomes finally total. Konen has also compared the emission spectra of iodine with the absorption spectrum, and found that the latter corresponds to the vacuum tube spectrum (band spectrum), the flame spectrum and the phosphorescent spectrum obtained by heating iodine vapour in a closed space. On the other hand, the absorption spectrum of chlorine does

[1] *Ann. der Phys.*, **65**. 285 (1898).
[2] *Loc. cit.*

not agree with the emission spectrum. An interesting comparison may be drawn between the three halogens; the absorption lines shift nearer the red with increasing atomic weight, similarly also do they increase in number and sharpness, and further, the thickness of gas layer required to render the absorption lines visible decreases with increase of atomic weight.

The work on iodine has been further extended by Friederichs,[1] Fredenhagen,[2] and by Evans.[3] This later work is chiefly concerned with the effect of temperature on iodine, it being noted, for example, by Friederichs that the absorption bands weakened as the temperature rose, and finally disappeared at 900° C. Evans confirmed these observations, and found further that the temperature of disappearance of the absorption increases as the pressure increases. He points out that the degree of dissociation of the vapour when the absorption spectrum vanishes is high, and suggests that it may be possible to account for the disappearance of this spectrum on the assumption that the monatomic molecules produced by dissociation show no absorption within the limits of the visual spectrum. Evans[4] has also carried out a similar investigation with bromine vapour, and comes to the same conclusion as in the case of iodine, for he finds that the disappearance of the absorption lines is closely connected with the dissociation of the diatomic molecules, and can be explained on the hypothesis that the monatomic molecules give no absorption spectra within the limits $\lambda = 3500$ and $\lambda = 6800$.

An important investigation on the absorption of the oxides of nitrogen in the infra-red has been carried out by Warburg and Leithaüser.[5] These authors show that all the oxides of nitrogen as well as ozone show characteristic absorption bands between 2μ and 7μ which were determined by means of a spectrometer with a fluorite prism and a bolometer. Perhaps

[1] *Zeit. wiss. Phot.*, **3**. 154 (1905).
[2] *Phys. Zeitschr.*, **8**. 89 (1907).
[3] *Astrophys. Journ.*, **32**. 1 (1910).
[4] *Ibid.*, **32**. 291 (1910).
[5] *Berlin Ber.*, (1908) 148, and *Ann. der Phys.*, **28**. 313 (1909).

the most interesting part of these authors' work is that they have applied their measurements to the quantitative determination of these gases in a given mixture. They also found that when submitted to the silent electric discharge air gives ozone, nitric anhydride, and nitrous oxide, but that under the influence of the arc discharge obtained with a 2000 volt alternating current only nitrogen peroxide is produced.

Some exceedingly interesting results have been obtained recently upon the influence of a foreign gas on the absorption exerted by certain gases and vapours. Dufour[1] found that the absorption bands of bromine vapour tend to shift towards the red with an admixture of other gases, such as, for example, air, hydrogen, and carbon dioxide. Some of the bands do not appear to shift, but the majority of them do. For example, the absorption line at $\lambda = 5535{\cdot}4$ shifts about 0·028 Ångström for each atmosphere increase of pressure of the foreign gas. A similar phenomenon was observed by Wood[2] with mercury vapour, which possesses an absorption band at $\lambda = 2536$. If the quartz bulb containing the mercury is thoroughly exhausted before being sealed and then heated, this band is found to broaden asymmetrically towards the longer wave-lengths. If now air, hydrogen, or helium be present in the bulb the band will broaden symmetrically at first, and at a higher temperature the asymmetrical broadening towards the red sets in. This would seem to argue that the band tends to shift towards the shorter wave-lengths in the presence of a foreign gas.

In a later paper Wood[3] has described similar experiments with cadmium and thallium vapour, using mercury vapour as the foreign gas. In both cases it was evident that the mercury tends to shift the absorption towards the longer wave-length, thus agreeing with Dufour's observations. Some work has also been done by Clinkscales[4] on the banded absorption of sodium vapour. He found that many of the lines shift their position as much as 0·15 Ångström in the presence of hydrogen

[1] *Comptes Rendus*, **145**. 757 (1907).
[2] *Astrophys. Journ.*, **26**. 41 (1907).
[3] *Ibid.*, **29**. 211 (1909).
[4] *Phys. Rev.*, **30**. 594 (1910).

or nitrogen at one atmosphere pressure. He also found that the character of the spectrum is changed to a great extent when either of these gases is admitted into the vessel containing the sodium vapour.

On the absorption of inorganic salts in solution in various solvents a very great deal of work has been done recently, but it must be remembered that in these cases the influence of the solvent itself must come into play. In this branch of the subject we must include all the metals which give coloured salts, such as, for example, copper, cobalt, nickel, and the rare earths, and also the coloured salts of inorganic acids, including permanganates, chromates, bichromates, nitrites, and nitrates, the last of which only gives absorption in the ultra-violet.

On the absorption spectra of the salts of the rare earths in the solid crystalline state and in solution a very large amount of work has been done in recent years, and, moreover, the observations have in general been conducted with very great accuracy. It is out of the question that any approach to a detailed account can be given of these or of any of the work on the absorption exerted by inorganic salts. Attention might be drawn, however, to the characteristic absorption spectra of the rare earth metals and the uses to which these are put in the fractional separation of these metals from one another. For example, the old "element" didymium was resolved into the two elements praseodymium and neodymium, it having been noticed that the absorption bands were found to vary in their relative intensities when certain salts of didymium were fractionally crystallised. When this fractional crystallisation is carried to the highest possible limit it was found that salts were obtained giving entirely different spectra. The separation of all the rare earths from one another always partakes of a fractional crystallisation or precipitation, and as the salts of praseodymium, neodymium, samarium, europium, holmium, thulium, erbium, and dysprosium have characteristic absorption spectra, so the separation may easily be followed and checked by the spectroscope.

As was stated above, there is no doubt whatever that the solvent plays a very important part in the production of the

absorption bands, and although this has been recognised by some experimenters, yet the fundamental importance of this influence does not seem to have been realised. Perhaps one of the most striking evidences is given by potassium permanganate, the absorption spectrum of which has been examined in different solutions by Merton.[1] The permanganates of potassium, calcium, barium, and zinc were investigated in solution in water and various organic solvents, and the wave-length of the maxima of three of the bands were observed in each case. As it was found that the atomic weight of the metal makes very little difference, the means of the values for the four salts for each solvent may be given, and are set forth in the following table :—

Water	5719	5477	5255	
Acetone	5736	5494	5275	
Methyl acetate . .	5720	5479	5258	
Acetic anhydride. .	5719	5480	5260	Potassium salt only.
Pyridine	5735	5492	5274	
Methyl cyanide . .	5719	5477	5257	
Methyl alcohol . .	5747	5505	5282	
Ethyl alcohol . .	5747	5503	5282	
Ethylene glycol . .	5730	5484	5267	Potassium salt only.
Ethyl alcohol and amyl alcohol, equal volumes	5747	5504	5280	Potassium salt only.
Potassium perchlorate	5577	5345	5135	Potassium salt only.

The last named was a solid solution, and presumably the salt is not very much dissociated, and, as may be seen, gives the smallest values for the wave-length of the bands amongst all the above solvents. On the other hand, water gives the highest degree of dissociation of those mentioned, and yet the absorption bands in this case lie midway between those given by pyridine, acetone, and the alcohols and those given by potassium perchlorate. This shift, therefore, cannot be connected directly with the dissociation, nor does it depend on the nature of the metallic radical. Clearly the solvent must be responsible for the change, and it would seem that it is the chemical character of the solvent in relation to the potassium permanganate which must be taken into account. It is well known that the nature

[1] *Trans. Chem. Soc.*, 99. 637 (1911).

of the solvent has a very great influence on the position of the absorption bands of many substances, and the view has been put forward that the phenomena are due to "solvates" or definite compounds of the solvent with the salt. Whether this be true or not it does not give us very much help, for if we ask why the absorption bands vary from solvent to solvent, the formation of solvates is by no means a complete and satisfactory answer. The original question may merely be altered to, Why do the different solvates have different absorption?

An important theory was put forward by Kundt[1] that there is a direct connection between the index of refraction and the dispersion of a solvent and the position of the absorption bands of a salt dissolved in that solvent. Kundt's so-called rule was stated as follows: If one colourless solvent has a distinctly greater refractive and dispersive power than a second solvent, then on dissolving an absorbing substance in the two the absorption bands will lie nearer to the red in the case of the first solvent than they do in the case of the second. There is no doubt, however, that the greater number of observed facts do not obey this rule, and it must, therefore, be considered as untenable, at all events in its present form.

An important point in connection with the absorption of solutions arises from a comparison of the absorption of two different concentrations of the same salt in a given solvent. It follows from the general laws of absorption that if two solutions of the same salt be made in the same solvent, one of which is, say, twice the concentration of the other, the absorption of a given thickness of the first solution should be equal to that of twice the thickness of the second. This is known as Beer's law.[2] As a matter of fact, many cases are known when this law does not hold, and therefore still more striking evidence is thereby gained of the fundamental influence of the solvent on the salt dissolved.

Amongst the work which has been done upon the absorption spectra of acid radicals may perhaps be mentioned the work on the spectra of the metallic nitrates. This was first done by

[1] *Ann. der Phys.*, **4**. 34 (1878).
[2] *Pogg. Ann.*, **86**. 78 (1852).

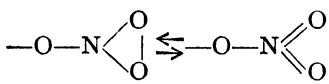
Hartley.[1] In these experiments he has employed the same methods as in the case of organic compounds, which will be described below. The aqueous solutions of a number of metallic nitrates were observed, and absorption bands were found to occur; the nitrates of the metals which give colourless solutions show one absorption band, and in the case of coloured salts the absorption bands due to the metal were of course also obtained. In the case of the fatty esters of nitric acid, *e.g.* ethyl nitrate, there is no trace of the absorption band. Hartley reasons from his results that the metallic nitrates are not entirely separated into ions when dissolved in water, but that each molecule is separated into two parts in such a way that the movements of one part are influenced by the movements of the other; he views the compound as being in a condition of molecular tension. The conclusion is based upon the fact that the characteristic absorption is considerably modified in the case of the nitrate of a heavy molecule, just in the same way as the absorption spectrum of an organic compound is modified by weighting the molecule. If the absorption were due entirely to the NO_3 ion, then the mass of the metallic ion would have no influence.

In conjunction with Miss Burke and Miss Marsden, I have made some further observations of the absorption spectra of the nitrates[2] of silver, ammonium, and lithium in solution in alcohol, water, and in various mixtures of the two. A connection was found to exist between the persistence of the absorption bands and the water content of the solvent. It is interesting to note that the dissociation of the salts in the various solvents appears to be influenced in a similar way to the absorption spectra, *i.e.* a decrease in the persistence of the absorption band was accompanied by a decrease in the dissociation and *vice versa*.

A very exhaustive paper has also been published on the absorption spectra of the nitrates by Schaefer,[3] who concludes that the absorption is not dependent on the amount of

[1] *Chem. Soc. Trans.*, **81**. 556 (1902); and **83**. 221 (1903).
[2] *Ibid.*, **95**. 1096 (1909).
[3] *Zeit. wiss. Phot.*, **8**. 212 and 257 (1910).

dissociation, because the decrease in the latter produced by the addition of another salt of the same metal does not alter the absorption. Again, the absorption is the same whether the substance is undissociated or whether it is ionised. In conclusion, he puts forward the suggestion that the absorption is due to the reversible process as expressed by—



Speaking generally of absorption spectra, since we have seen what a profound influence the solvent has, the question arises as to what would happen if the absorbing substance were examined in a state of absolute purity without any solvent being present. It has already been stated in the last chapter that the rare earths give no phosphorescence when in a state of perfect purity, and so the question may reasonably be asked as to whether the absorption spectrum of a substance might not vanish, or at all events change very considerably, in the absence of any impurity. Certain experiments recently performed in my laboratory would seem to show that in the case of certain organic compounds the absorption tends to diminish when the substances are examined in a gaseous state and in complete freedom from any impurity. This matter will be dealt with more fully in the next section, but it raises the question as to the value of much of the work which has been done on the absorption of inorganic substances.

Absorption Spectra of Organic Compounds.—A considerable amount of work has been done upon the absorption spectra of organic compounds in the visible region by various experimenters, amongst whom may again be mentioned Ostwald in support of the electrolytic dissociation hypothesis, and also Krüss, Vogel, Schütze, and others who have studied the absorption spectra with the hope of finding some connection between the constitution of a body and its absorption spectrum. Although certain empirical rules have been found, it can hardly be said that anything in the way of a definite connection has been observed. By far the most valuable work in this direction has been carried out by Hartley in his investigations upon

ultra-violet absorption spectra; here, undoubtedly, have been discovered certain most important facts connecting chemical constitution and absorption spectra; and, further, it appears that we possess, thanks to Hartley, a most searching method of studying generally the whole question of constitution. The constitution of many bodies, when chemical methods have failed, have been undoubtedly established by this means, and it is not too much to hope that the whole question of molecular structure of organic compounds may be solved in this way.

The beauty of Hartley's method chiefly lies in the method of expressing the results obtained; he has not merely examined the position of the absorption bands or the limits of absorption, at some definite concentration of solution, but has measured the absorption limits at a great many concentrations, always increasing the dilution step by step until complete transmission is obtained. The oscillation frequencies of the edges of the regions of absorption are then plotted against the corresponding strengths of solution, and a curve drawn through the points so obtained. It is the shape of these curves which have been connected with the chemical constitution.

The first paper upon this subject was by Hartley and Huntington in 1879,[1] which contained the absorption curves for a great many substances. The method of experiment consists in photographing the spark spectrum of an alloy of tin, lead, cadmium, and bismuth, through a solution of the required substance by means of a quartz spectrograph. The spectrum of this alloy contains a considerable number of lines fairly equally distributed over the blue and ultra-violet, and consequently it is easy to detect the presence of absorption and measure its limits by observing whether any lines or groups of lines are missing. Hartley and Huntington investigated in this way water, methyl, and ethyl alcohols, and these were found to be quite diactinic, as they transmit all the rays as far as $\lambda = 2000$ A.U. They have been, therefore, used as solvents for many organic compounds whose absorption spectra have been put upon record. In this paper Hartley and Huntington plotted their results as follows: the oscillation frequencies were

[1] *Phil. Trans.*, 170. 257 (1879).

the abscissæ, and the ordinates were the volumes in which a definite quantity of the substance was dissolved. An example

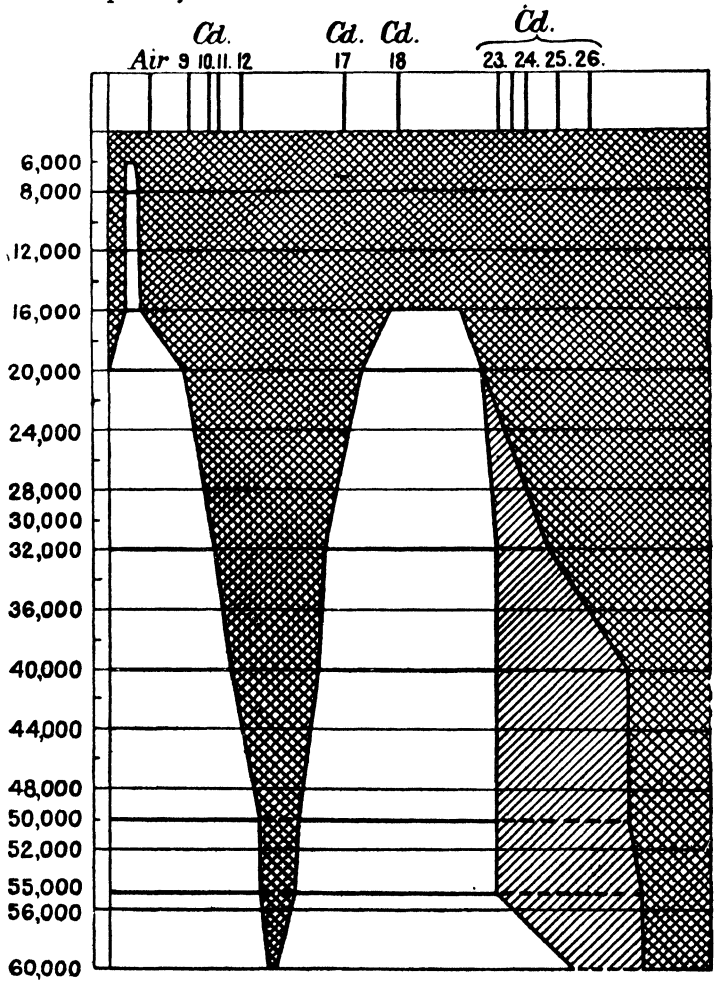


FIG. 167.

of this form of diagram is shown in Fig. 167, which represents the absorption curve obtained with paranitrophenol.

In later papers, instead of putting the volumes of the solutions upon the ordinates, Hartley substituted the equivalent thicknesses of solution. As an example of this, let us consider that a solution of a particular substance is made up of $\frac{N}{100}$ strength (1 milligramme-molecule dissolved in 100 c.c.), and that the spark spectrum is photographed through 30, 20, 15, 10, 5 and 4 mm. thicknesses respectively; the solution is then diluted to ten times its bulk, and again photographed through the same thicknesses.

Let us imagine now that complete transmission occurs at the 4 mm. length of this diluted solution, so that further dilution is unnecessary. The results may be thus considered to have been obtained with 300, 200, 150, 100, 50, 40, 30, 20, 15, 10, 5 and 4 mm. thicknesses of the last dilution $\left(\frac{N}{1000}\right)$, and may be so plotted. These actual thicknesses might not be all that would be required in practice; they serve, however, as an example of the method. Fig. 168 shows copies of absorption curves drawn in this way.[1] It will be seen that there is a considerable difference between the two ways of expressing the amount of matter acting on the light, because in the first case the effect of a small dilution change is more marked with the weaker strengths than with the stronger, while in the second case the opposite is true. All Hartley's later results up to 1904 have been expressed by the second method, and he names his curves "curves of molecular vibrations." In these experiments quartz cells were used for holding the solutions, several of different sizes being used in order to allow different thicknesses of solution to be used.

Hartley, both alone and also in conjunction with Dobbie, Lauder, and others, has continued these investigations, and a very great number of substances have been observed. A complete list of all that had been previously done is to be found in Kayser's *Handbuch der Spectroscopie*, vol. iii.

In certain experiments upon the same subject Dr. Desch and I made an improvement on Hartley's series of absorption cells

[1] *Chem. Soc. Trans.*, **81**. 929 (1902).

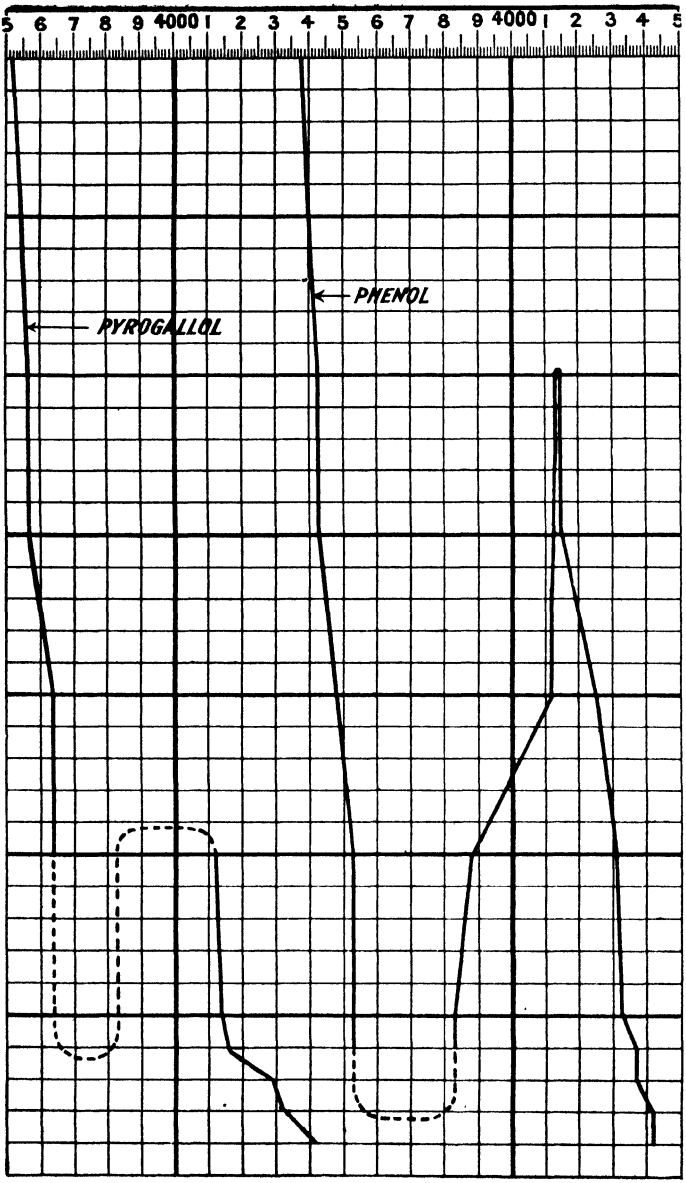


FIG. 168.

of fixed sizes.[1] This apparatus consists of an adjustable cell with quartz plates and a diagram of one of these cells is shown in Fig. 169; it consists of two glass tubes which fit loosely one inside the other. Both of these tubes have a flange at one end which is ground flat and square to the axis; upon this flange is cemented a quartz plate in each case as shown at A and B. C is a bulb tube sealed to the side of the outer tube, as drawn, and serves to take up the solution when the thickness of layer is decreased by pushing in the inner tube. At D a broad india-rubber band is slipped over the junction in order to keep it water-tight; the rubber band may be cut off a piece of rubber tubing about 1 inch in diameter and 1 inch broad. The dimensions of the outer tube are about 1 inch wide and 5 inches long. The outer tube has a millimetre scale etched upon it; this scale is so ruled that its zero division coincides with the inner side of the quartz plate A, and thus the reading of the inner side of the plate B upon the scale gives the thickness of the solution.

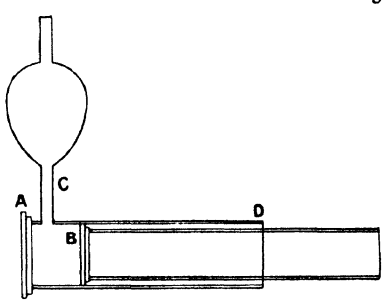


FIG. 169.

As regards the cementing of the quartz plates in position, either sealing-wax or a cement made by dissolving gelatine in hot glacial acetic acid is used; the former in the case of cells employed for aqueous solutions, and the latter for alcohol and similar solvents. A very good cement is also made by making a strong solution of hard gelatine in hot water and then adding a little potassium bichromate. If this be used and the joint exposed to ultra-violet light an exceedingly good result will be obtained owing to the well-known action of the bichromate in rendering the gelatine insoluble when exposed to light.

The inner tube of the cell is preferably lined with black paper so as to stop as far as possible the reflections of the light from the glass walls.

[1] Baly and Desch, *Chem. Soc. Trans.*, **85**. 1039 (1904).

A different method has been adopted, also, of plotting the results. It was pointed out above that Hartley in his earliest researches plotted the equivalent volumes of solution containing a fixed quantity of the substance, and later the equivalent thickness of a solution of fixed concentration. In the first case the effect of a given relative change in the amount of substance was more marked in the curves at smaller concentrations than at greater concentrations, and in the second case exactly the opposite is true. It is preferable that some method be adopted by means of which a given relative change in dilution or thickness can be represented by the same shift whatever be the actual strength of the solution. This will be at once gained by the use of the logarithms of the concentrations or relative thicknesses in place of the values themselves.

In Fig. 170 are shown three absorption curves. They all refer to the same substance, and are drawn respectively according to the three methods described. The full curve is drawn according to Hartley's second method, the dot and dash curve according to his first method, while the dotted curve is drawn with the logarithms of the thicknesses of solution of constant concentration. The two absorption bands persist approximately during the reduction of the molecular concentration to one quarter, a fact which is clearly best expressed by the logarithmic curve.[1] From the absorption curves plotted by this method it is very much easier to compare the relative persistence of the absorption bands; that is to say, the change of concentration over which the band lasts. This persistence is a very characteristic function of a band, and upon it important deductions can often be made as to the nature of the structure of the molecule.

As regards the results obtained with the absorption spectra of organic compounds, there are, broadly speaking, two types of spectra, namely that in which the absorption is perfectly general, with no evidence of any absorption band, and that in which one or more distinct absorption bands are shown. To the first class, generally speaking, belong the spectra of

[1] This method of plotting spectroscopic results had already been suggested by Lord Rayleigh: *Nature*, **27**. 559 (1883).

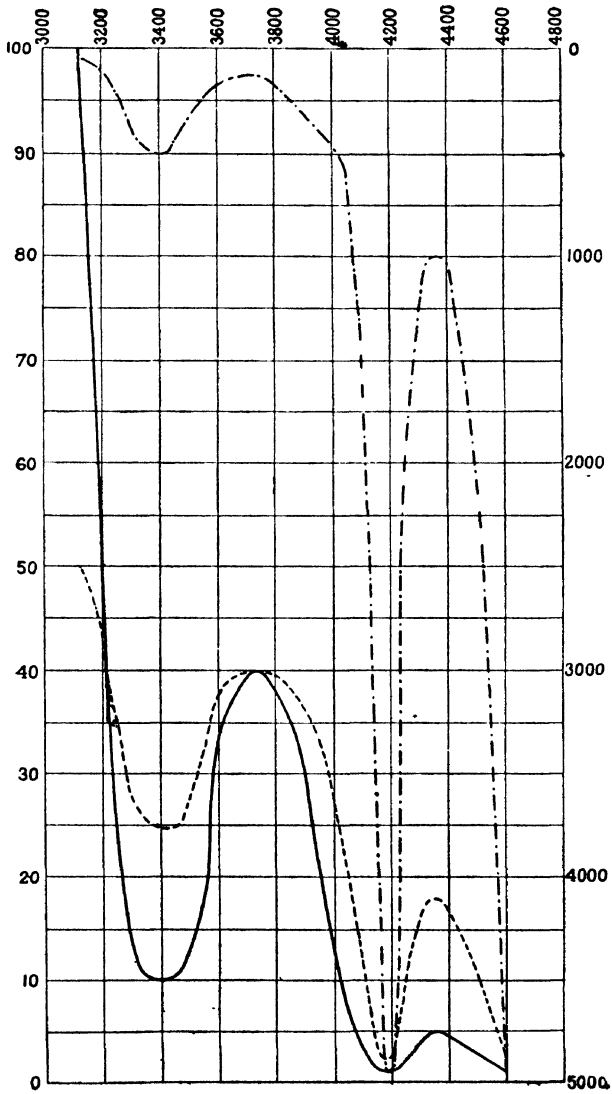
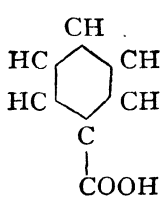
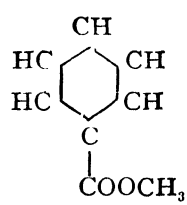

3000
3200
3400
3600
3800
4000
4200
4400
4600
4800
100
90
80
70
60
50
40
30
20
10
0
0
1000
2000
3000
4000
5000

FIG. 170.

the fatty compounds, while the second class contains the spectra of the aromatic or benzene compounds. It must be understood at once that this is a very rough distinction, and that it is quite possible to obtain compounds in the fatty series which show an absorption band, and on the other hand to introduce groups into the benzene ring so that the bands disappear and the absorption becomes continuous. This distinction, however, serves to show the difference in character between the compounds which show banded absorption and those which do not. The whole question of interpretation of the different spectra lies in the true meaning of the absorption band, what it is due to, and why some compounds give it and not others. Before dealing with this, however, some of Hartley's work may be quoted, in order to show what use can be, and has been, made of this method in the determination of the molecular constitution of chemical compounds. In order to understand the facts, it is necessary that the results of some of Hartley's earlier work be mentioned. For example, the introduction of a methyl group into the molecule does not influence its absorption. Thus the spectra of benzoic acid and methyl benzoate are absolutely identical; the formulæ of the two compounds are—



Benzoic acid.

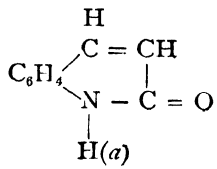


Methyl benzoate.

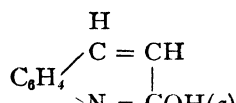
In the latter case we have the acid hydrogen replaced by the methyl group $-CH_3$. Several examples of the same might be given. It follows from this that if we find the spectra given by a compound and its methyl derivative to be the same, we are quite justified in assuming the molecular constitution of the two compounds to be absolutely similar.

Such a case as this is the constitution of carbostyril. From

its chemical behaviour it is not possible to say for certain whether this substance has the ketonic structure as shown in I., or the enolic structure shown in II.

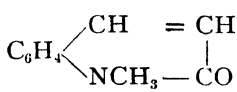


I.

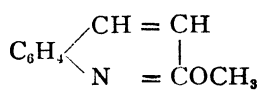


II.

This substance gives in certain cases reactions which favour the first formula, and in other cases reactions which favour the second formula; one cannot decide from its chemical behaviour whether the hydrogen atom (*a*) is linked to the nitrogen or to the oxygen atom. The methyl derivatives of both substances are known, however, which can be easily proved to have the formulæ—



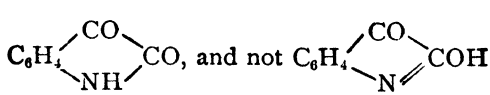
Methylpseudocarbostyril.



Methylcarbostyril.

Hartley and Dobbie[1] have examined the absorption spectra of the three substances, and find that the absorption curve of carbostyril agrees almost exactly with that of the methylpseudocarbostyril, but not with that of methylcarbostyril. They therefore conclude that carbostyril has the ketonic structure as shown in formula I.

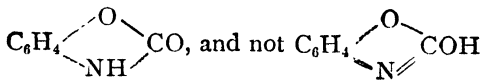
In exactly the same way they proved that isatin has the structure—



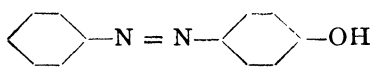
Hartley, Dobbie, and Paliatseas[2] have also examined the

[1] *Chem. Soc. Trans.*, **75**. 640 (1899).
[2] *Ibid.*, **77**. 839 (1900).

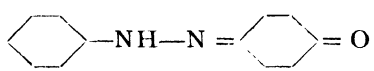
absorption spectrum of *ortho*-oxycarbanil, and by comparing it with the spectra of the two ethyl derivatives conclude that it has the formula—



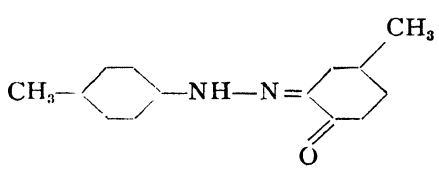
Two important papers have been published by Tuck [1] in which he deals with the constitution of the hydroxyazo-compounds, and makes use of similar methods to those used by Hartley and Dobbie. For example, by a comparison of the absorption spectra of the *para*-hydroxyazo compounds with those of the two possible methyl derivatives, he proves that these compounds exist in the true azo form. Thus he finds that benzeneazophenol has the formula expressed by—



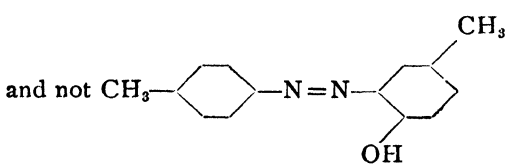
and not



Similarly he showed that the *ortho* compounds exist in the form of true quinone hydrazones. Thus *para*-tolueneazo-*para*-cresol has the formula—



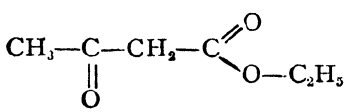
and not



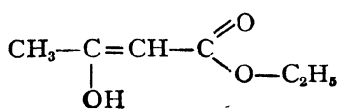
[1] *Chem. Soc. Trans.*, **91.** 449 (1907), and **95.** 1809 (1909).

Some light, however, appears to be thrown upon the absorption spectra of tautomers, and at the same time upon the meaning of the bands by some investigations upon the ethyl acetoacetate and acetylacetone compounds.[1] These compounds show banded absorption, and are, therefore, exceptions to the broad distinction laid down at the beginning o this description, because they belong to the fatty series of compounds. They are, therefore, peculiarly interesting, as it is possible to investigate the bands without any fear of complication from the presence of a benzenoid nucleus. Ethyl acetoacetate and acetylacetone are both tautomeric substances with what is known as a labile hydrogen atom—that is to say, they possess one or other of the two following formulæ respectively :—

Ethyl acetoacetate—

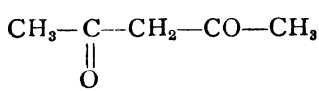


Ketonic.

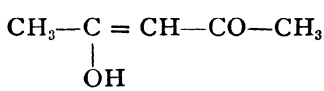


Enolic.

Acetylacetone—

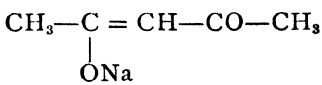


Ketonic.



Enolic.

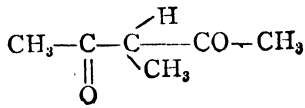
Now, metallic derivatives of both these substances can readily be prepared, in which the labile hydrogen is replaced by an atom of a metal. These substances have generally been considered to be enolic derivatives—that is to say, the sodium compound of acetylacetone has the formula—



The absorption spectra of acetylacetone and its aluminium, beryllium, and thorium derivatives are shown by the curves

[1] Baly and Desch, *loc. cit.*

1, 2, 3, 4, respectively, in Fig. 171, in which the logarithms of the relative thicknesses are plotted; curve No. 5 shows the absorption spectrum of methyl acetylacetone —



On examining the absorption spectra of ethyl acetoacetate and

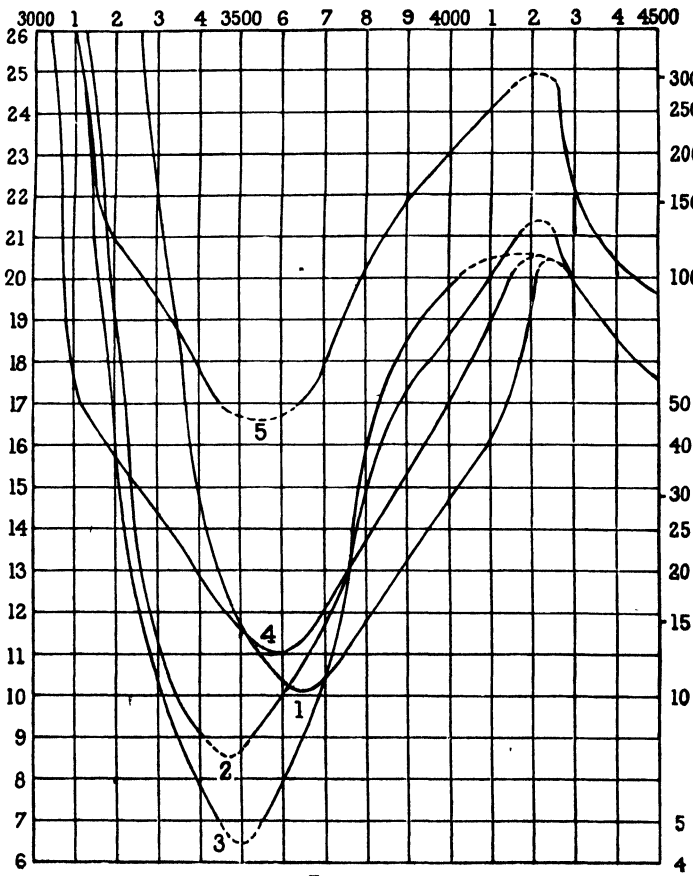
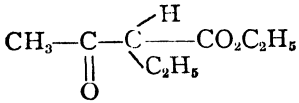


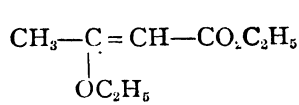
FIG. 171.

of its aluminium derivative, it was found that while the absorption curve of the latter was very similar to those of the acetylacetone compounds, that of the former showed only general absorption without any band at all. These results would seem to point to the fact that ethyl acetoacetate is ketonic, while all the other bodies are enolic. On investigating the spectra of the two ethyl derivatives of ethyl acetoacetate—



Ethyl ethylacetoacetate (ketonic).

and



Ethyl β-ethoxycrotonate (enolic).

it was found that neither of them showed any absorption band at all. It was concluded from this that the absorption band is not due to either of the two possible modifications, but to the oscillation from one form to the other. In order to test this view the action of sodium hydroxide upon ethyl acetoacetate was investigated. It is known that this substance exerts a decided accelerating influence upon the reaction between similar tautomeric substances; it was expected therefore that the addition of sodium hydroxide to ethyl acetoacetate would produce an absorption band. In Fig. 172 curve 1 represents the absorption of the ester in the presence of a small trace of the hydroxide, curve 2 the absorption in the presence of an equivalent quantity of the hydroxide, while curve 4 shows the absorption with an excess of the hydroxide. Curve 3 represents the absorption exerted by the aluminium derivative of the ester. These curves, inasmuch as the absorption band in No. 4 is much more persistent than that in No. 3, very strongly supported the idea. The conclusion was therefore drawn that these tautomeric substances are in a continual state of oscillation between the two forms, and that the persistence of the absorption band is a measure of the relative number of the molecules which are in this oscillating state. This oscillation has been named by Armstrong and Lowry dynamic isomerism, and therefore was it concluded that we have in these absorption bands a means of measuring the dynamic isomerism between two substances in equilibrium with one another.

Before showing how the above conclusion must be slightly modified in view of the later work, mention may be made of some important work carried out by Purvis,[1] who recently has

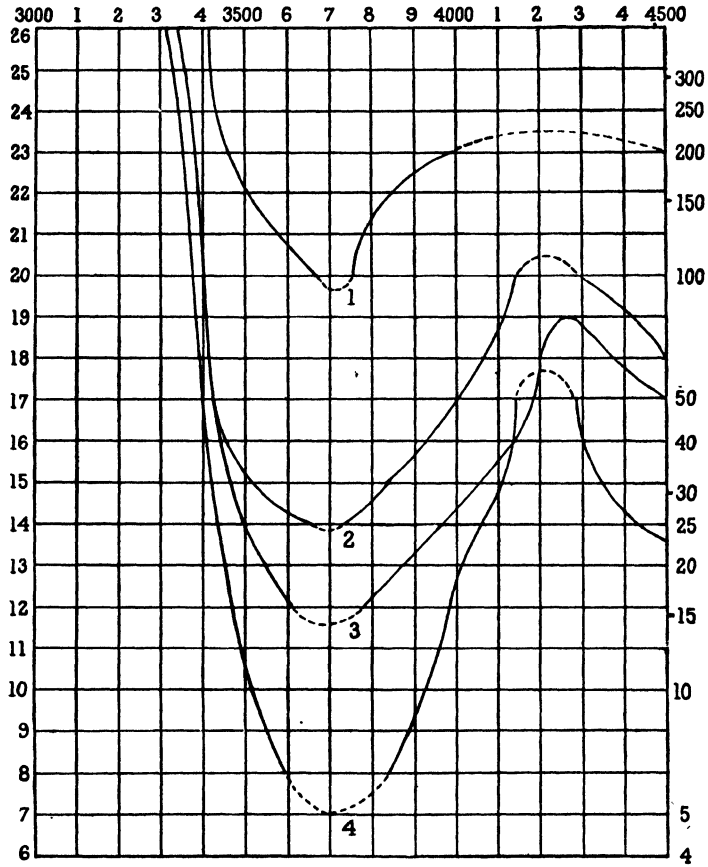


FIG. 172.

devoted himself to a comparative study of the absorption spectra of organic substances in a state of vapour and of

[1] *Chem. Soc. Trans.*, **97**. 692, 1035, 1546, 1648 (1910); **99**. 811, 1699 (1911).

liquid and in solution. A number of papers on this comparison have been published by Purvis, and some important results have been given by him. In the first place, as was shown by Hartley,[1] Friederichs,[2] and Mies,[3] the banded absorption spectra given by benzene and other hydrocarbons in solution are resolved, when the substances are examined in the state of vapour, into groups of lines, and, moreover, that the wave-lengths of these lines can frequently be arranged in series. Purvis has continued this work with pyridine and many other compounds. It is interesting to note, as a result of these experimenters' work, that there is a shift towards the red in

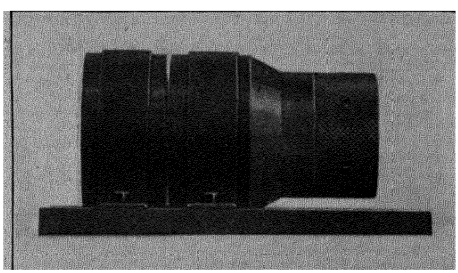


FIG. 173.

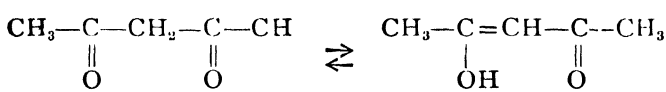
the position of the absorption bands when the substances are examined in solution. In order to deal with the absorption of the substance in the pure form, it is necessary, of course, to use very thin layers, and for this purpose Purvis has devised a special apparatus, by means of which thin films of as small a thickness as 0·001 mm. can be dealt with. The apparatus is shown in Fig. 173, which is a reproduction of a photograph of the instrument kindly sent me by Mr. Purvis. It consists of one fixed quartz plate, and another quartz plate which can be moved by an accurate micrometer screw. Perhaps one of the most interesting results found by Purvis is that, generally

[1] *Phil. Trans.*, **208**. 475 (1908).
[2] *Zeit. wiss. Phot.*, **7**. 357 (1909).
[3] *Zeit. wiss. Phot.*, **3**. 154 (1905).

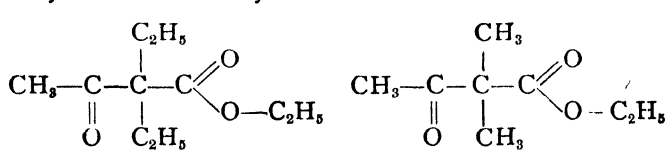
speaking, the thin films do not exhibit selective absorption, whilst their solutions and vapours do.

Some later work upon the relation between the absorption exerted by compounds and their constitution tends rather to modify the conclusions drawn from the earlier work described above. It is not possible to enter here into a detailed account of these more recent observations, but it would seem that very probably the key to the real meaning of chemical action and reactivity is to be found in these relations. Moreover, up to the present no satisfactory theory has been found to explain why a compound should exert its powers of selective absorption, and as the two, reactivity and absorption, seem to be intimately connected, I venture to advance the following theory to explain the observed phenomena of absorption, fluorescence, and phosphorescence.

The main difficulty in connection with the original idea that absorption bands in the ultra-violet exerted by such compounds as acetylacetone are due to such equilibria as are expressed by the reversible equation—



that is to say, that the band is due to the actual oscillation of the hydrogen atom between the carbon and oxygen atoms, is that it has been found by recent physical measurements that such migration of a hydrogen atom is very slow compared with the oscillation-frequency of light. Again, it has been shown by Lowry and Desch[1] that absorption bands are sometimes exhibited by substances in which there is no possibility of a migrating hydrogen atom. Similarly, I have found that the di-ethyl and the di-methyl derivatives of acetoacetic ester



[1] *Chem. Soc., Trans.*, **95**: 807 (1909).

both show absorption bands in the presence of strong sodium ethoxide. It is quite evident in these two cases that the absorption band must be due to some other cause than the migration of a hydrogen atom. Clearly therefore the original idea must be modified.

Perhaps the most important fact that must be taken into consideration is the very profound influence that the solvent has upon the absorption of various substances. A moment's consideration of this influence of the solvent will show that some account must be taken of the residual affinities of the two, solvent and substance dissolved.

Now, if the chemical properties of substances be considered it will be quite evident that every atom or group of atoms in a compound must possess residual affinity to a greater or a less extent, if under residual affinity we include every type of unsaturation whether as regards the primary or the secondary valencies.[1] Generally speaking, in chemistry we say that a compound is unsaturated when one or more of the principal or ordinary valencies is unsatisfied, as, for example, in those cases when we write a double bond. Such compounds as these have the property of forming addition compounds with other substances and so they must possess residual affinity. In addition to this special type of residual affinity we have also the cases of compounds which, though apparently perfectly saturated as regards their principal valencies, yet indeed form double and complex compounds with other substances. It is generally accepted that these properties are due to the so-called contra-valencies. Every atom possesses these contra-valencies developed to a certain extent, and so if under the term residual affinity be grouped every type of unsaturation, it will follow that every atom or group of atoms must possess this residual affinity to a greater or less amount.

Since the possession of residual affinity tends to endow a compound with the power of forming addition compounds with other substances it may be said that the existence of residual affinity is accompanied by the existence of force lines in the surrounding ether. Every atom or group of

[1] Baly, *Zeitschr. Elektrochem.*, **17**. 211 (1911).

atoms must be the centre of a field of force in the ether, the strength of which depends upon the amount of the residual affinity present in each case.

The independent existence of these various fields of force round about one molecule is manifestly impossible, such a condition must be metastable. There must ensue a certain amount of condensing together of the force lines accompanied by the escape of free energy. The resulting condensed system must have a decreased chemical reactivity compared with the original metastable condition. In fact, if the system be entirely closed it will have no chemical reactivity at all, and it is only when the closed system is unlocked that it can show any chemical reactivity. It does not necessarily follow that although the condensing together of the force lines must occur, the resulting system is entirely closed. The system may still possess some small residue of reactivity which, however, in any case will be very much smaller than that of the metastable uncondensed form. Generally speaking, it follows that in order that a compound exert its true reactivity it must be unlocked, so to speak, by some external means.

Now, one way of opening up such a condensed system would be to supply free energy to it. Again, it is a well-known fact that certain reactions are catalysed by the action of light as, for example, the union of hydrogen and chlorine. Before the hydrogen and chlorine molecules can react upon one another it is necessary that their closed systems be opened up, and it would seem that this opening up can be affected by means of the influence of the light rays. The light rays must therefore be doing work against chemical forces.

This at once gives a rational explanation of the absorption of light by substances, namely, that the light is doing work against the chemical forces which tend to produce the closed systems, and that the necessary free energy is supplied in this way.

Now, in some experiments[1] in which the chemical reactivity was measured of substances which exhibit absorption bands it was found that there is an unmistakable relation between the

[1] Stewart and Baly, *Chem. Soc. Trans.*, **89**. 489 (1906).

activity and absorption. The greater the amount of light absorbed the greater is the chemical reactivity. For example, the aliphatic ketones all tend to exert selective absorption of light, and the amount of light absorbed was compared with the velocity with which these substances form oximes. The reaction involved may be exemplified by the case of acetone—

$$CH_3—\underset{\underset{O}{\|}}{C}—CH_3 + NH_2OH = CH_3—\underset{\underset{NOH}{\|}}{C}—CH_3 + H_2O$$

On comparing equal strengths of solutions of some of the homologous ketones and determining the amount of oxine formed in twenty minutes with a fixed concentration of hydroxylamine, the following values were obtained :—

Ketone.	Amount of oxime formed.
Acetone	49·7 per cent.
Methyl ethylketone	39·2 ,,
Methyl propylketone	37·3 ,,
Methyl,isopropylketone	31·5 ,,
Pinacoline	17·0 ,,

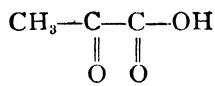
On examining the amount of light absorbed by these compounds it was found that this was very comparable if the amount of absorption is measured by the persistence of the band, *i.e.* the change in concentration over which the band persists (see Figs. 171 and 172). Since the velocity of the chemical reaction involves the reactivity of the CO group in the above compounds, we may speak of this group as forming one centre of activity in the molecule.

It has further been found that if two such centres are present, adjacent to one another in the same molecule, the chemical reactivity is abnormally enhanced, as may be shown by the following comparison between the amounts of the potassium bisulphite compound formed with acetone and ethyl pyruvate respectively, a reaction which is one of simple addition. Just like the oxime reaction quoted above this bisulphite addition gives a measure of the reactivity of the

compound concerned. The following were the amounts of the bisulphite compound obtained in the time given :—

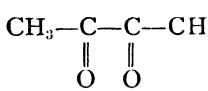
	5 minutes.	10 minutes.	15 minutes.
Acetone	5 per cent.	7 per cent.	9 per cent.
Ethyl pyruvate . .	52 ,,	64 ,,	76 ,,

In ethyl pyruvate there are two CO groups adjacent to one another as shown by its formula—



and the extraordinary enhancement thereby resulting in the chemical reactivity is shown by the above figures.

On examining the absorption exerted by ethyl pyruvate it was found that the maximum of absorption was shifted very considerably towards the longer wave-lengths. This shift is even more pronounced in the case of diacetyl—



so much so that the compound is coloured yellow. It seems, therefore, that the mutual influence of two centres of activity is to shift the wave-lengths of the absorption band towards the longer wave-lengths, and that this is accompanied by an increase in the chemical reactivity of the compound. Now, this mutual influence between two centres of activity is not confined to those cases where both are situated within the same molecule, for it has been found to take place within certain limits when two compounds are intimately mixed, such as occurs when one is dissolved in the other. If one compound which gives an absorption band is dissolved in another, the residual affinity of which differs from that of the first, then the absorption band is shifted towards the longer wave-lengths. At the same time in all those cases in which it is possible to

investigate the matter the chemical reactivity is found to be enhanced. Now, it is evident, on the theory advanced above, the greater the difference be between the residual affinities of the two, the greater will be the mutual influence between the two, and the more will the condensed system of force lines of the solute be opened up, owing to their being penetrated by the force lines of the solvent. This must clearly enhance the chemical reactivity of the solute, and this reactivity will arrive at a maximum when the condensed system is completely opened. It is hardly necessary to insist that the chemical reactivity must be looked upon not as that of the solute alone, but that of the system given by the solvent and the solute together.

It may be pointed here that the whole phenomenon of the reaction between a base and an acid to give a salt has been followed by the spectroscope, and the observations fully support the general theory here advanced. If the case of a weak base dissolved in a solvent such as absolute alcohol or benzene, then, since the difference between the residual affinities of the base and solvent is not sufficient entirely to unlock the condensed force system of the former, it will be necessary that this unlocking of the system be carried further before the base can react with the acid to form the salt. This further unlocking can readily be seen to take place on the addition of a small trace of acid. If, say, $\frac{1}{10}$th to $\frac{1}{5}$th eq. of hydrogen chloride in the same solvent be added to a solution in alcohol of a weak base, such as *p*-aminobenzaldehyde, a red colour is developed.[1] This solution now shows a new absorption band; if the quantity of acid be now increased slowly, and the absorption observed, it will be seen that it steadily changes to that of the true hydrochloride. This has been observed in a number of cases, and proves the existence of the intermediate phase when the base is opened up sufficiently to react with the acid. In extension of this it may be added that this opening up can readily be produced by the action of other solvents than alcohol or benzene containing hydrochloric acid. For example, bases like benzidine and the so-called leuco-bases of the dye-stuffs, such as diamidodiphenylmethane, are opened up by solution

[1] Baly and Miss Marsden, *Chem. Soc. Trans.*, **93**. 2108 (1908).

in solvents like nitrobenzene, and, although themselves colourless, give magnificent red solutions.

It would seem that the well-known catalytic influence of traces of certain acids upon the reactions of bases is to be explained in this way, namely, that the condensed system of the base is opened up by the trace of acid, with the result that the chemical activity is greatly enhanced, and the velocity of reaction increased. In fact, the whole of the phenomena of catalysis is susceptible of explanation on the lines of this theory, since the catalyst would appear to be an agent capable of opening up the condensed system of one or more of the reacting compounds, so that their velocity of reaction is increased.

On these lines the profound influence of the solvent upon the absorption spectra of substances may be explained. It has already been pointed out that the mutual influence of two centres of residual affinity causes a shift of the absorption maximum towards the longer wave-lengths. The amount of the mutual influence which takes place, and the resulting absorption are functions of the new system of solvent and solute which is produced. The failure of Kundt's rule is therefore not surprising, for the shift in the absorption bands is not necessarily a function of the optical properties of the solvent, but is a function of the relation between the residual affinity of the solvent and that of the solute. It also follows that Beer's law must fail to hold in certain cases where there is a marked mutual influence between solvent and solute. If, for example, at a given concentration this influence is not the maximum possible for a pair of substances, then this influence will change when the solution is further diluted. The result will be that the absorption exerted by the two solutions cannot be comparable as required by Beer's law.

As a further extension of the theory it may be pointed out that if the residual affinity of the two, solvent and solute, be continually increased so that they become more and more differentiated, a stage will eventually be arrived at, when definite compounds will be produced. The simple influence of solvent upon solute is therefore a chemical reaction in

embryo, and there seems no reason to postulate anything but a smooth transition from this embryo to true chemical reaction when stable salts are formed. The essential difference between the two extremes is that in the case of true salt formation, one or more electrons would seem to have passed over from one atom to another. When two substances act upon one another, and their two force fields become inter-locked, there must exist a potential gradient between them. It is possible to conceive that when this potential difference reaches a certain limiting value, the electrons then move over along the lines of force with the formation of a true salt. Conversely, the phenomenon of hydrolysis of salts in water may be attributed to the fact that the potential gradient along the force lines formed by the mutual influence of salt and water molecules, is greater than between the various portions of salt molecules. The electrons then redistribute themselves until an equilibrium becomes established, with the result that hydrolysis takes place, the amount of which depends upon the relative mass of the water present.

In considering the effect of the mutual influence of substances upon each other, it is manifest that the greatest effect will take place at those points where the potential gradient within the condensed systems is most marked, and therefore the reactivity of such binary systems will be most evidenced at these points. Chemical reaction, therefore, may be said to result from the opening up of the condensed system of one substance by the influence of the force lines of another substance of different residual affinity, and the maximum activity will evidence itself at that point where the potential gradient of the condensed system is the greatest.

It follows from this that the ionic dissociation phenomena form one special case of chemical reactivity. Reactivity results from the partial or complete unlocking of the condensed systems; these systems become ionised when the effect of the solvent is such that the force lines between any two portions of the molecule become entirely opened up, and the two portions, which have now formed systems with the solvent, act as separate entities.

Although all that has been said above refers to solutions, yet, of course, the same is true of any mixture of substances in which the force fields can mutually interfere. For example, the admixture of a foreign gas with the vapour of an absorbing substance must be expected to alter the position of the absorption bands of the latter. That such is the case seems to have been proved by Wood and Dufour (see page 465).

Again, the extraordinary difference between the absorption exerted by many substances in various states, as discovered by Purvis (see page 485), can be explained on these lines. Substances such as aniline exert no selective absorption when in the liquid condition, but do so in the state of vapour and in solution in alcohol or some other solvent. The differences Hartley and Purvis have noticed between the absorption of compounds in the vapour state and in solution is naturally due to the fact that in the latter case the solvent has partially opened the condensed field of the aniline, and it is this combined system that is exerting the absorption, while in the former case the light is acting on the aniline molecules alone. On the other hand, Purvis' discovery that a very thin film of liquid aniline exerts no selective absorption shows that under these circumstances the force fields are entirely closed, and cannot be opened by the light, which therefore can do no work on the system. This latter and similar observations strongly support the present theory, for it would seem to follow that no work can be done by light on an entirely closed system, and therefore no selective absorption will be exerted.

We may extend this theory to include the phenomenon of fluorescence, and for the moment especially that of organic compounds. It has been already pointed out how the influence of the force field of the solvent must naturally be most evidenced at that portion of the molecule of the solute where the potential gradient of the condensed system of the latter is steepest. In the foregoing it has been assumed that the opening up of the condensed system of every molecule is a single process; but this is not necessarily the case, for where the systems resulting from complex molecules are concerned, it is quite possible for the unlocking to take place in separate

stages. As an example of this, the aminoaldehydes and aminoketones referred to above may again be quoted. When in alcoholic solution these substances are opened up to a certain limited extent by the action of the solvent, and the light is able to act, thereby completing the process begun by the solvent. The addition of a trace of acid to the solution induces a further stage in the opening up, so that a greater wave-length of light is now absorbed, this energy being used to complete this second stage. An inorganic example of a salt which is opened up in two stages is the double cyanide of potassium and silver. This is normally ionised into potassium and silver cyanide ions; but with increasing dilution the second stage becomes evident, namely, the formation of some silver and cyanogen ions.

Now, it is perfectly evident that the various stages in the unlocking process must be closely connected together, and it may at once be assumed, in the event of the unlocking taking place in stages, that the second stage will not take place until the first stage is complete, and that, in general, each successive stage will not begin unless the previous stage is complete. The result of this may perhaps be understood more clearly from the following: let A represent the completely closed system of a complex molecule, and B, C, D, etc., the several stages in the opening up of this system. Further, let A, under the influence of a suitable solvent and of light, be opened up into B, and let the wave-length of the light required be λ_B. Now let A be opened up to C by means of a second solvent, and light of wave-length λ_C. Then, as far as experiment has shown at present, λ_C is greater than λ_B. Since the opening of A into the form C is brought about by the absorption of light of wave-length λ_C, so the converse must be true, namely, that the condensing together of the system C to give the system A must be attended by the evolution of light of wave-length λ_C. Now, if by any means the form A be converted into the form B, which results in the complete opening up of a portion of the system, it would seem naturally to follow, as a result of the fact that B and C are intimately connected, that B cannot return to A without influencing in some way the

force lines of the whole system. It is not possible to conceive of a portion of a closely interwoven locked system being opened without the whole system being affected. The partial opening of the system to give the condition B must affect the whole. The next possible system under the conditions of the experiment is that which we have called C. The restoration of the system, as disturbed by the influence of the light rays, does not seem possible without a disturbance being brought into play which involves the system C. Now, it has already been shown that the process C → A must be accompanied by the evolution of light of wave-length λ_C. It follows, therefore, that the restoration to the form A from the form B must involve the form C, with evolution of light of wave-length λ_C; and as it has been shown that A is converted to B by the influence of light of wave-length λ_B in an appropriate solvent, so this absorption of light λ_B must be accompanied by the evolution of the rays λ_C. In other words, the substance fluoresces. It may be pointed out at once that the form C may not be the only one concerned; it is quite possible that the successive forms D, E, etc., may be brought into play, each giving out light of characteristic wave-length, always provided that the several forms are all intimately connected under the experimental conditions as postulated above.

It is perfectly possible to subject this theory to practical test. It is evident that if the process C → A gives out light of wave-length λ_C, A should, in the presence of a suitable solvent, be converted into C by absorption of this light λ_C. In other words, it should be quite possible, by the use of an appropriate solvent, to influence a substance so that it absorbs light of the same wave-length as the fluorescent light it emits in another solvent. This close relation between fluorescence and absorption has been found in several cases. Dr. Krulla, working in my laboratory, examined, amongst others, the cases of the aminoaldehydes and ketones mentioned above, and finds that these substances in alcoholic solution emit, under the influence of ultra-violet light, fluorescent light of the same wave-length as those rays absorbed by the compounds in presence of small traces of hydrochloric acid. These results afford considerable support to the theory.

In dealing with the processes above, examples were drawn from organic chemistry, because it happens that more is known about the relation between constitution and absorption, and because moreover the majority of fluorescing substances belong to this group of compounds. Exactly the same argument, however, can be applied to inorganic compounds, the only difference being that the necessary conditions are not realised so frequently, the necessary conditions being that there exist a closely connected series of stages in the opening up of the closed systems. In order to obtain the fluorescence, the actual opening of the first stage must be brought about by light, and not by the solvent alone. As ionisation may be considered to be the evidence of a complete opening up, as far as that particular stage is concerned, so it is not surprising that inorganic salts, as a rule, do not absorb light or fluoresce. It is more probable that complex salts with two or more stages could be made to fluoresce in other solvents than water, which do not tend so greatly to ionise them. Judging from the known cases in organic compounds the optimum condition would appear to be that particular concentration in a suitable solvent which opens the force systems of the molecules in such a way that the light rays can do work on them and complete the first stage.

To return to the processes which are involved, it is clear that there are two, which are quite distinct: the opening up of the closed system and the reverse action, namely, the closing up of the system to its original form. Although under all the conditions dealt with above the velocity of the second is probably equal to the first, it is perfectly possible to conceive of conditions under which the second is slower than the first. As was pointed out in Chapter XIII., under "Phosphorescence," this will result (in the case of fluorescent compounds) in the emitted light persisting after the disturbing or exciting influence is cut off. Such conditions may indeed be realised in the case of solid solutions, for here, owing to the restrained molecular and intramolecular motions, and also to the concentrations of the force fields, the velocity of restoration of the opened system to the equilibrium conditions may well be

much retarded, and, indeed, reduced to zero. In the former case we find persistence of the phosphorescence after the exciting influence has been cut off, and in the latter we find no phosphorescence at all, but only thermo-luminescence; that is to say, the disturbed system, being in a metastable condition from its containing an abnormal amount of free energy, only can return to the equilibrium condition when the molecular and intramolecular motions are increased by raising the temperature. This restoration, of course, is accompanied by the evolution of the free energy as light which corresponds to the particular system concerned. The presence of more than one maximum of phosphorescence would seem to indicate that more than one partially opened system is brought into play. It is hardly necessary to point out that the variations in the maxima of phosphorescence of a single substance with the temperature is explicable on these lines.

Again, this theory affords a reason why pure substances will not phosphoresce, for, as a result of the theory, it is necessary that the influence of an external force field be brought to play before a substance can be made susceptible to radiant energy. When so influenced the radiant energy is absorbed, doing work against the chemical forces and opening the closed system. Care must be taken, however, not to dogmatise too strongly on the matter of the inability of light to act upon pure substances. The power of response to the action of light must depend on the property of each substance. It is impossible, from our present knowledge, to lay down as a law that no pure substance can exert selective absorption, and that no pure substance ever can phosphoresce. Since light has the power to open up systems in solution, it is not safe to extrapolate this to the point on the curve where no solution is present. The response to radiant energy must always depend upon the specific property of the substance and the physical state in which it exists.

In conclusion it may be said that there is some temptation to extend these conceptions to the case of ordinary emission spectra and series of lines. If we postulate a series of systems B, C, D, E, etc., which represent successive and closely

connected stages between tne entirely opened up and metastable system and that which is completely closed, we should expect the wave-lengths of the light λ_B, λ_C, λ_D, λ_E, etc., corresponding to these to be connected by a simple formula. In the passage of the free atom to the completely condensed systems of molecules we should expect to find the emission of all the rays λ_B, λ_C, λ_D, etc., which would form a spectral series.

On the other hand, Humphreys in his valuable paper, dealt with on page 639, explains the many phenomena by the existence of atomic magnetic fields. In order to co-ordinate the two theories, it would only be necessary for us to accept the fact that the external evidence, from a chemical point of view, of these magnetic fields is what the chemists call residual affinity, and there seems no valid reason against this being possible.

CHAPTER XV

THE NATURE OF SPECTRA

SPECTRA may be divided into three classes—continuous spectra, banded spectra, and line spectra. Continuous spectra are those which contain the whole scale of wave-lengths, such as are usually given by incandescent solid substances; certain cases of continuous spectra are recorded as having been given by gases, but about these very little is known, and they need not be considered here. Banded spectra, both in emission and absorption spectra (excluding those of certain substances in solution), can always be resolved into groups of very fine lines. Each group of lines has a head; that is to say, the lines in one direction get closer and closer until they run together, forming a sharp edge called the head. This head may either be on the red or blue side of the band, the band being degraded either towards the blue or towards the red. The appearance of these spectra under low dispersion is that of a channelled spectrum. Such spectra are always given by compounds when these are undissociated, and also by certain elementary substances, an example of which is nitrogen in a vacuum tube under the influence of the electric discharge without a Leyden jar. About the spectra of compounds very little is known, on account of the experimental difficulty connected with their observation; they are so readily decomposed under the various exciting influences we apply to them in order to produce luminescence. Amongst those which are known to be spectra of a compound are the so-called carbon oxide spectrum, the cyanogen and the silicon tetrafluoride spectra, the latter presenting a band degraded towards the red. About the spectra of compounds, Kayser very rightly points out how great a field for valuable work lies here, for we

know so little of their nature, their structure, and general character. "Es liegt hier fruchtbares Arbeitsgebiet noch für Jahre und für zahlreiche Beobachter vor."[1]

About line spectra our ignorance is not so great; by line spectra is meant those spectra consisting of more or less sharply defined lines which are generally distributed without any apparent regularity; characteristic groupings are often visible, but never any repeating structure such as stamps the banded spectrum. In certain spectra there have been discovered harmonic series of lines, by means of which considerable similarities are noticed between the spectra of elements of the same chemical family, and then, further, there have been recorded certain observations upon the characteristics of the lines themselves, their structure, *i.e.* the complexity of the radiations forming one "line," their "length" in the spark and arc, and finally their general appearance. The regularities in linear spectra and the work on spectral series will be treated fully in Chapter XVII.; about the nature of the lines themselves a few words may be said here.

When the lines of the arc spectrum of a metal are individually examined, they will be found as a general rule to differ materially in appearance amongst themselves. They are by no means all equally well defined; some of them are sharply defined on both sides, while others are sharply defined on one side, the other side being nebulous and diffused; there are further to be seen frequently lines which are nebulous on both sides. Distinction may therefore be drawn between four types of lines, those which are well defined at both edges, those which are diffused only towards the red, those which are diffused towards the blue, and lastly, those which are diffused on both sides. It is interesting to note that the lines which belong to the same spectral series are always of the same character, and that we have, for example, in this way a sharp series and a diffuse series belonging to each alkali metal. The importance of these characteristic appearances of the lines is thus manifest, and in all spectral work care should be taken to note the character of all the lines measured, because in any

[1] *Handbuch der Spectroscopie*, vol. ii. p. 222.

attempt to arrange the lines in series, such observations will be of the greatest importance.

These differences in character of the lines of the spectrum of a substance are chiefly noticeable in the case of arc and spark spectra. In the spectra of gases in vacuum tubes the lines are almost always very narrow and sharply defined; this is no doubt due to the very low pressure that the gas is exerting. In certain cases, however, it is quite possible to meet with diffused lines in the spectrum of gases at low pressures. An interesting example of this is to be found with krypton and xenon;[1] when the oscillating discharge is passed through these gases, unless the pressure is below a certain small amount, the whole spectrum appears confused, and, indeed, almost continuous. If the pressure is then slowly reduced, the lines begin to appear upon a more or less continuous background, and, gradually increasing in brightness, they finally become quite sharply defined upon a black background. All the lines do not become equally well defined at once, some of the lines remaining more or less hazy until the pressure is reduced to a very low value. These results are very interesting, and not easy of explanation. The effect in certain cases of a small trace of impurity upon the lines of a spectrum is also very curious. It will very often be noticed that the presence of a small quantity of impurity masks the appearance of certain lines of a spectrum; for example, in the case of argon the admixture of a small quantity of impurity frequently masks the green lines given by this gas. This region appears confused, no definite lines being visible, while the red, orange, and blue lines are quite distinct; the removal of the impurity brings out the green lines at once.

The Structure of Spectrum Lines.—The structure of spectrum lines has been several times mentioned on other pages in this book, but more particularly in Chapter IX., on the application of interferential methods to spectroscopy, for it is only by means of these apparatus of great resolving power that investigations have been possible in this direction. Michelson (p. 315) investigated a great number of lines with his

[1] Baly, *Phil. Trans.*, 202. A, 183 (1903).

interference apparatus, and practically found that only one, the red line of cadmium, was a simple line.

The lines given by many metallic vapours at low pressures have been examined by Michelson and by others, and have been found to be complex. Each "line" is composed of a number of radiations differing very slightly in wave-length from one another; generally there have been found a certain number of principal components, and a number of accompanying satellites. The method by means of which Michelson arrived at his results is given fully in Chapter IX., so that these only need be given here.

Hydrogen.—With hydrogen at a pressure of about 1 mm., the red at line $\lambda = 6563$ is a double line the two components of which have a ratio of brightness of 7 : 10; the distance between them is 0·14 A.U., and their half-width is 0·049 A.U. The blue line at $\lambda = 4860$ is again double, with the same ratio of brightness of the two components; the distance between them is 0·08, and their half-width 0·057.

Oxygen under reduced pressure.—The orange red line $\lambda = 6158$ is a triple line; the components have their intensities in the ratio 1 : 1 : $\frac{1}{2}$, and their distances apart are 1·51 and 0·84 respectively, and their half-width is 0·027.

Sodium.—The results obtained from metallic sodium in the vacuum tube were so varied that a complete study was impossible. The following results were obtained under very low pressure and a temperature of 250° C. The D lines are both very close pairs, each pair being separated by about 0·02 A.U.; the intensities in each being about 10 : 8. Each of the components of the double yellow-green line at mean wave-length $\lambda = 5687$ is a single line. The orange-red double at $\lambda = 6156$ seems to have a feeble component, and the doubles at $\lambda = 5150$ and 4982 are very similar.

Zinc.—Some observations were made on zinc vapour in vacuum tubes, but the necessary temperature melted the glass. The red line at about $\lambda = 6360$ is single, and has a half-width of 0·013. The blue line at about $\lambda = 4811$ has a small component nearly 0·2 A.U. distant.

Cadmium in a vacuum tube at a temperature of 280° gives

a red line at $\lambda = 6439$, which is quite simple, with a half-width of 0·0065. The green line $\lambda = 5086$ is a close double whose intensity ratio is 5 : 1; the distance between the components is 0·022, and their half-width 0·0048. The blue line at $\lambda = 4800$ is similar.

Thallium.—Thallium chloride was used in vacuum tubes. The green line gives a visibility curve, which can be explained by the line having two components, each of which is double.

Mercury.—The yellow line at $\lambda = 5790$ possesses a companion of feeble intensity at a distance of about 0·24 A.U.; the line itself consists of a principal component with a faint double near to it. The intensities appear to be about in the ratio 10 : 2 : 1; and the distances 0·12 and 0·012 A.U. respectively. The yellow line at $\lambda = 5770$ appears to be a double the components of which have the ratio of intensities 3 : 1 and are 0·019 A.U. apart. The green mercury line $\lambda = 5461$ is most complex; the constituent lines are so fine that Michelson was able to extend his visibility curve to 400 mm. difference of path. The curve showed that the line is at least quadruple, with one bright component and three weaker ones. The violet line at $\lambda = 4358$ appears to have a faint component at a distance of 0·16 A.U.

It must be remembered that these values of Michelson's were obtained from his visibility curves; when one of these was obtained for a particular source an equation was found which as nearly as possible expressed the results, and from this the distribution of intensity in the source was calculated. Fabry and Perot, with their interferometer, were able actually to see the lines resolved and to measure their distances from one another, but not their breadths. Fabry and Perot's apparatus and method have been described at length in Chapter IX., and the results they obtained were as follows :—

The green line of thallium at $\lambda = 5439$ is triple, having two equally faint components on the red side, their distance being 0·02 and 0·12 A.U. respectively. The green ray of mercury is triple, the distance of the two weaker components being 0·1 and 0·009 A.U. respectively; both these components are on the red side of the principal line.

The yellow ray at $\lambda = 5791$ has a weak component on the blue side at a distance of 0·14 A.U.

The yellow ray at $\lambda = 5770$ has a weaker component on the red side at a distance of 0·05 A.U.

Cadmium. The red ray is perfectly simple, but the green ray is double, having a weak component on the more refrangible side at a distance of 0·03 A.U. The blue ray has two faint components of equal brightness, and both at the same distance, namely, 0·10 A.U.

These values differ to a slight extent from Michelson's results, but Fabry and Perot point out that their results give, on calculation, curves which quite agree with the visibility curves obtained by Michelson.

Recent work, however, shows that the complexity of radiation is even greater than evidenced by these two researches. During the last year or two several papers have been published on this subject, and particular reference may perhaps be made to the following authors, Gehrcke and von Baeyer,[1] Janicki,[2] Nagaoka,[3] and Stansfield.[4] The following table may be given of the results for the principal lines of mercury as obtained by Gehrcke and von Baeyer and by Janicki. The figures given represent the differences in wave-length (expressed in 10^{-2} $\mu\mu$) of the satellites from that of the principal line. The method employed by Gehrcke and von Baeyer was that of crossed interferometer plates (see p. 352), and the values are the means of those obtained by the crossing of three pairs of plates, while Janicki used an echelon grating. In the third and fifth columns are given the intensities of the lines with a maximum intensity = 1.

Nagaoka and Stansfield have found that the green line of mercury is even more complicated than appears from the above table. Stansfield has found 17 components, while Nagaoka, using a 35 plate echelon grating, found as many as 19 components of this line.

[1] *Berlin Ber.*, (1905) 1037, and *Ann. der Phys.*, **20.** 269 (1906).

[2] *Ann. der Phys.*, **19.** 36 (1906).

[3] *Nature*, **77.** 23 (1908), and *Mathematico-Physical Soc., Tokyo, Proc.*, **5.** 2 and 140 (1909); also *Phys. Zeitschr.*, **10.** 609 (1909).

[4] *Nature*, **78.** 8 (1908).

Wave-length of principal line.	Gehrcke and von Baeyer.		Janicki.	
	Satellites.	Intensity.	Satellites.	Intensity.
5790	−2·02	4	−2·51	10
	−1·28	1	−1·87	10
			−1·19	5
			+0·84	9
	+1·43	2	+1·32	7
			+1·68	10
	+2·41	3	+2·30	7
5769			−1·13	8
	−0·56	2	−0·50	4
	+0·47	1	+0·46	3
			+0·87	10
			+1·20	10
5461	−2·41	2	−2·32	5
	−1·11	5	−0·99	10
	−0·66	4	−0·66	7
	+0·90	1	+0·88	3
	+1·34	3	+1·33	8
4359	−1·71	2		
	−1·17	4	−1·12	1·5
	−1·08	4	−0·97	1·5
			−0·52	7
	−0·19	1	−0·23	1
	+0·24	5	+0·20	5
	+0·48	5	+0·43	4
			+1·05	1·5
	+1·15	5	+1·21	1·5
	+2·04	3		
4348	−0·48	1	−0·46	5
	+0·55	3	+0·53	7
	+0·82	2	+0·83	7
4339	none visible		−1·2	10
			+0·6	10
4078	−0·81	2	−0·76	6
	−0·46	2	−0·46	6
			+0·32	10
	+0·50	1	+0·49	4
	+0·80	3	+0·74	9
4047	−1·15	4	−1·11	3
	−0·53	1	−0·51	1·3
	+0·75	3	+0·67	2
	+1·38	2		

In reference to the complex structure of certain spectrum lines, Exner and Haschek [1] have investigated with an echelon grating the structure and distribution of intensity in certain lines in the spectra of a number of elements, and they claim to have found undoubted evidence of the variation both in the number and in the relative intensity of the principal line and the satellites, and also in the relative intensity of the satellites amongst themselves. These variations are produced by slight alterations in the current and the density of the vapour of the element in question. The result of these variations is that with a spectroscope of small revolving power, such as a grating, the position of the whole line appears to shift.

The Breadth of Spectrum Lines.—It has been long known that the width of the spectrum lines of a substance increases when the pressure is increased; this was first noticed by Ångström [2] in 1853 in the case of hydrogen, and further examined by many other observers, among the earliest of whom may be mentioned Wüllner,[3] and Lockyer and Frankland.[4] That the lines do not, however, become infinitely narrow as the pressure falls to zero has been shown by Michelson, who has carried out by means of his interferometer very valuable quantitative work upon this subject. In Chapter IX. will be found an account of Michelson's method of determining the visibility curves of the lines from which he calculates the "half-width." If the intensity distribution of a line of finite width is plotted on a curve of which the abscissæ x are oscillation frequencies and the ordinates some function of x, then Michelson defines the half-width of the line to be the value of x when the function of $x = \frac{1}{2}$. Michelson found that the distribution of intensity cannot be very far different from that required by Maxwell's law, namely, that—

$$\phi(x) = e^{-h\frac{x^2}{a^2}}$$

[1] *Wiener Ber.*, **116**. 2*a*, 323 (1907).

[2] *Pogg. Ann.*, **94**. 141 (1855).

[3] *Ibid.*, **137**. 339 (1869).

[4] *Proc. Roy. Soc.*, **17**. 288 (1869); see Schuster, *Brit. Ass. Report* (1880), 277.

where e is the base of natural logarithms and p and a are constants.

In 1889 Lord Rayleigh[1] showed from the standpoint of the kinetic theory that the motion of the molecule in the line of sight can produce a broadening of the lines of a spectrum. Several other explanations of the finite breadth of a line have been advanced, but Michelson has shown that at all events the Doppler principle[2] is the principal cause at work when the density is low, thereby neglecting the effect of collisions. In a first paper[3] Michelson, starting from Rayleigh's equation, arrives at the expression—

$$\Delta = \frac{1}{\pi}\sqrt{\frac{\log_e 2}{\pi}}\cdot\frac{V}{v},$$

where Δ is the difference in path (between the two interfering light beams in his apparatus) when the visibility has fallen to half the value it had at the centre of the line, V is the velocity of light, v is the velocity of translation of the molecules of the substance, and λ is the wave-length. From this we have, approximately—

$$\frac{\Delta}{\lambda} = 0{\cdot}15\,\frac{V}{v}.$$

If we take for hydrogen $v = 2000$ metres per second, then—

$$\frac{\Delta}{\lambda} = 22500.$$

Again, if we ignore the difference of temperature between the various substances examined, the velocity v will vary inversely as the square root of the atomic weight, and the number of waves $\left(\frac{\Delta}{\lambda}\right)$ in the difference of path at which the visibility is $\frac{1}{2}$ will be $22500\sqrt{m}$, where m is the atomic weight. Michelson tabulates the results he obtained on the structure of the lines giving the values of $\frac{\Delta}{\lambda}$, both found by experiment and calculated from the formula.

[1] *Phil. Mag.*, **27**. 298 (1889).

[2] For an account of the theory of the Doppler principle, see pp. 641, *et seq.*

[3] *Phil. Mag.*, **34**. 280 (1892).

Substance.	A.W.	λ	Δ	$\frac{\Delta}{\lambda}$	$\frac{\Delta}{\lambda}$ calculated.
Hydrogen	1·0	656	19·0	30000	22500
,,	1·0	486	8·5	18000	22500
Oxygen	16·0	616	34·0	55000	80000
Sodium	23·0	616	66·0	107000	108000
,,	23·0	589	80·0	133000	108000
,,	23·0	567	62·0	109000	108000
,,	23·0	515	44·0	85000	108000
,,	23·0	498	55·0	110000	108000
Zinc	65·5	636	66·0	104000	182000
,,	65·5	481	47·0	98000	182000
Cadmium	112·0	644	138·0	215000	238000
,,	112·0	509	120·0	236000	238000
,,	112·0	480	64·0	134000	238000
Mercury	200·0	579	230·0	400000	317000
,,	200·0	577	154·0	270000	317000
,,	200·0	546	230·0	420000	317000
,,	200·0	436	100·0	230000	317000
Thallium	203·6	535	220·0	400000	322000

In a later paper[1] Michelson gives some further results, in which he includes the substances just given, but he expresses the values as molecular velocities; in the table v_1 are those calculated from the square root of the atomic weight, and v_2 those found from the observations $\left(v = \frac{0{\cdot}15V \times \lambda}{\Delta}\right)$.

Substance.	A.W.	v_1	v_2
Hydrogen	1	2000	1500
Lithium	7	800	1200
Oxygen	16	500	800
Sodium	23	400	400
Magnesium	24	400	650
Iron	56	260	500
Cobalt	59	260	560
Nickel	59	260	500
Copper	63	250	450
Zinc	65	250	450
Palladium	106	190	250
Silver	108	190	250
Cadmium	112	190	220
Gold	196	140	225
Mercury	200	140	140
Thallium	204	140	110
Bismuth	210	140	150

[1] *Astrophys. Journ.*, 3. 251 (1896).

It must be remembered that no allowance is made for temperature in these tables, because of the great uncertainty about its magnitude; under these conditions the agreement between theory and fact is very striking.

In order to show conclusively that the effect of density can be neglected in the above results, Michelson determined the amount of broadening of the lines of hydrogen caused by increasing the pressure, thereby increasing the number of molecular collisions. These collisions tend to limit the number of regular vibrations on account of the more or less abrupt changes of phase, amplitude, or plane of vibration produced, thus causing a widening of the line. The "half-breadths" of the hydrogen red line at different pressures were found to be as follows:—

Pressure in mm.	Half-breadth in A.U.
90·0	0·128
71·0	0·116
47·0	0·095
23·0	0·071
13·0	0·056
9·0	0·053
3·0	0·050
0·5	0·048

These results show that below a pressure of 5 mm. the effect of the collisions has almost entirely ceased, so that with decreasing pressure a limiting breadth of the hydrogen red line (and others too) is reached, and this limiting breadth is due to the Doppler effect; that is to say, it depends upon the substance itself and upon the temperature.

Michelson deduces an expression for the breadth of spectrum lines on the assumption that this is the sum of the separate widths due (1) to the motion in the line of sight, (2) to the limitation of the free path of the molecules. We have then $b = \delta_1 + \delta_2$, where δ_1 and δ_2 are the widths due to (1) and (2) respectively.

First the motion in the line of sight. Rayleigh's

formula,[1] as modified by the definition of visibility,[2] becomes—

$$\text{Visibility} = e^{-\pi\left(\frac{\pi X}{\lambda}\cdot\frac{v}{V}\right)^2},$$

where X is the difference of path in the interferometer, *i.e.* the abscissa on the visibility curve, and v and V are the velocities of translation of the molecules and of light respectively. If, again, Δ, as before, is the value of X, for which the visibility becomes half the value it had when $x = 0$,

then
$$\Delta = \frac{1}{\pi}\sqrt{\frac{\log_e 2}{\pi}}\cdot\frac{V}{v}\lambda.$$

Now, as was shown on p. 314, the half-breadth of a line measured in oscillation frequencies was equal to $\frac{\log_e 2}{\pi\Delta}$, or in wave-lengths to $\frac{\log_e 2}{\pi\Delta}\lambda^2$, so that for the practical complete breadth of the line we have—

$$\delta_1 = \frac{2}{\pi}\frac{\log_e 2}{\Delta}\lambda^2.$$

On substituting the above value of Δ,

then
$$\delta_1 = 2\sqrt{\pi\log_e 2}\cdot\frac{V}{v}\lambda$$
$$= 3\frac{v}{V}\lambda \text{ very nearly.}$$

For the second source of width of the lines Michelson deduces the expression—

$$\delta_2 = \frac{\lambda^2}{\rho}\cdot\frac{v}{V},$$

where ρ is the free path of the molecule.

From these two values for δ_1 and δ_2 we have—

$$b = \frac{v}{V}\lambda\left(3 + \frac{\lambda}{\rho}\right).$$

[1] See p. 508. [2] See p. 308.

To find the effect of temperature and pressure changes according to this formula, we may put v = the molecular velocity at absolute temperature θ, and v_0 = the corresponding velocity at θ_0 (0° C.), m = the molecular weight, d = the actual density, and d_0 the standard density at θ_0, and ρ the length of free path at d_0; we then have—

$$b = \frac{v_0}{V} \cdot \frac{\lambda}{\sqrt{m}} \cdot \frac{\sqrt{\theta}}{\sqrt{\theta_0}} \left(3 + \frac{\lambda}{\rho} \cdot \frac{d}{d_0}\right).$$

In view of the imperfect assumptions made it will be better not to attach too much weight to the value of the constants, but we may examine the general formula—

$$b = \sqrt{\frac{\theta}{m}} \cdot \lambda(a + b\lambda d).$$

Michelson experimentally verified this formula to a certain extent, and found that it may be considered as a very good first approximation to the truth. The following points seemed to be well established:—

1. When the pressure is below one-thousandth of an atmosphere, the second term, $b\lambda d$, may be neglected.

2. Under this condition the width of the line is roughly proportional to the square root of the molecular weight.

3. The width increases as the temperature rises, the rate being not very different from that of the square root.

4. When the pressure is increased, the width increases in a nearly linear proportion.

5. The rate of this increase varies considerably with different substances, but in general it is more rapid the smaller the molecular weight, and while the general results can scarcely be said to prove that the rate is inversely as the square root of the molecular weight, they do not differ much from this proportionality.

6. At low pressures the proportionality with λ is not proved, there being about as much evidence for an increase of δ with λ as for a decrease.

7. At high pressures the width increases with wave-length, but the exact law was not determined.

8. The nature of the surrounding gas or vapour is of secondary importance.

Michelson deals further with the possible broadening due to the direct modification of the period of the vibrating atoms in consequence of the presence of neighbouring molecules. He points out that at pressures below one atmosphere the length of the free path is of the order of one hundred times the radius of the sphere of action of the molecules. It therefore appears that the number of free vibrations is also at least one hundred times as many as those whose period is modified by collision, and the effect of these modified vibrations would be correspondingly small in broadening the spectral lines except at great densities; at these greater densities it seems not unlikely that the mutual influence of the molecules may be of great importance.

Again, where the broadening of the line is unsymmetrical, Michelson shows that such broadening can be explained by certain assumptions concerning the law of action of the molecules on their rates and intensities of vibration. All such lines should, starting from zero pressure, broaden symmetrically at first, and the asymmetrical broadening should not appear until the pressure is very considerable.

Michelson, lastly, makes a very ingenious application of his equation for the breadth of lines to determine the temperature of the ordinary discharge through hydrogen in a vacuum tube. He examined the light from this tube with the interferometer, and plotted the visibility curve; he then heated the tube through 250°, and again plotted the curve. In the latter case the distance at which interference was still visible was about three-quarters the distance at the lower temperature. Assuming the lower temperature to be 50° C. = 323° abs., then the second temperature was about 573° abs. The corresponding ratio of molecular velocities is about $\sqrt{\frac{323}{573}} = \frac{3}{4}$, which agrees with the result of the experiment. If the first temperature had been 7000°, the second would have been 7300° at most, and the molecular velocity ratio $\sqrt{\frac{7000}{7300}} = 0{\cdot}98$, which is so near unity that it would not have been possibe to detect the change in the two visibility curves.

The Length of Lines.—The relative intensity of certain lines in a metallic spectrum is often seen to change when the pressure of the air or the nature of the discharge is altered.[1] The length of the lines will give us considerable information as to how these will behave under different circumstances. If an image of the electric spark between metal poles be focussed by means of a lens on the slit of a spectroscope, so that the direction of the spark is parallel to the slit, it will be seen at once that all the lines do not stretch right along the spark from one electrode to the other. Lockyer and Frankland[2] concluded that the distance each metallic line reached out from the electrode would give some idea as to how the line would behave in the sun. Lockyer followed this up with a series of investigations on the length of lines in spark and arc spectra, and has obtained some extremely important results, both as regards solar spectroscopy and also in connection with the behaviour of the lines of different lengths. In a first paper[3] he observed the spectra of many metals, amongst which were lithium and sodium; magnesium, zinc, and cadmium; strontium and barium; lead, antimony, etc. It must be remembered that the length of the lines does not necessarily depend upon their strength or brightness, for many faint lines are very long, and many strong lines very short. By a long line, therefore, is only meant a line which reaches across the whole spark, quite independently of its intensity; similarly in the case of a short line. One example of this may be given from the spectrum of tin, in which the line at $\lambda = 5630$ is the longest line of all; this line, however, is a faint one, and the lines near it, at $\lambda = 5588{\cdot}5$ and $\lambda = 5562{\cdot}5$, are much brighter, but are quite short. If we consider for a moment the possible conditions prevailing within the electric spark in air between metal poles, it is clear that close up to the poles we shall expect to find an increased density of metallic vapour, and an increased temperature; we are justified, therefore, in assuming that the short lines of the spark spectrum are due to these conditions.

[1] *Cf.* Schuster, *Brit. Ass. Report* (1880), 288.
[2] *Proc. Roy. Soc.*, **18**. 79 (1869).
[3] *Phil. Trans.*, **163**. 253 (1873).

As we shall certainly find these conditions more developed in the centre rather than at the edges of the electric arc, so we can investigate the different lengths of lines in the arc spectra of substances by using a horizontal arc, and focussing an image of it upon the vertical slit of an ordinary spectroscope. This, however, is not suited for the examination of a spark, because the work on the structure of the spark by Schuster and Hemsalech, and by Schenk,[1] has shown us that there are present alternate impulses from each electrode which only reach a short way across the spark gap; it is to these that the short spark lines are due, and therefore in order to differentiate between these and the other lines, the spark must be observed along its length. For this purpose an image of the spark must be focussed upon the slit, and parallel to it.

In Fig. 174 is reproduced a portion of the arc spectrum of iron which shows the different lengths of the lines.

Amongst the conclusions drawn by Lockyer in his papers upon this subject,[2] the following may be mentioned :—

On a reduction of pressure some of the shorter lines rapidly decreased in length and disappeared, while the longer lines remained visible, and were sometimes hardly affected. It was found, for example, that in the case of zinc the lines at $\lambda = 4924$, $\lambda = 4911$, and $\lambda = 4679$ always disappeared when the pressure was reduced to 30 mm., while the long lines at $\lambda = 4810$ and $\lambda = 4721$ were almost unaffected; a rise of pressure to 34 mm. was sufficient to restore the lines.

In the case of the spark spectra of chemical compounds under the same conditions, only the longest lines are to be seen, the short lines being obliterated, while the air lines remain the same. The case of zinc may again be given; in the spark spectrum of zinc chloride the bright but short zinc lines at $\lambda = 4920$ and $\lambda = 4911$ are wanting, while the equally bright long lines at $\lambda = 4809$, $\lambda = 4721$, and $\lambda = 4769$ are present. The longest aluminium lines are also to be seen in

[1] See Chapter XII. p. 406.

[2] *Phil. Trans.*, **163**. 253 (1873); **163**. 639 (1873); **164**. II, 479 (1874); and **164**. II, 805 (1874).

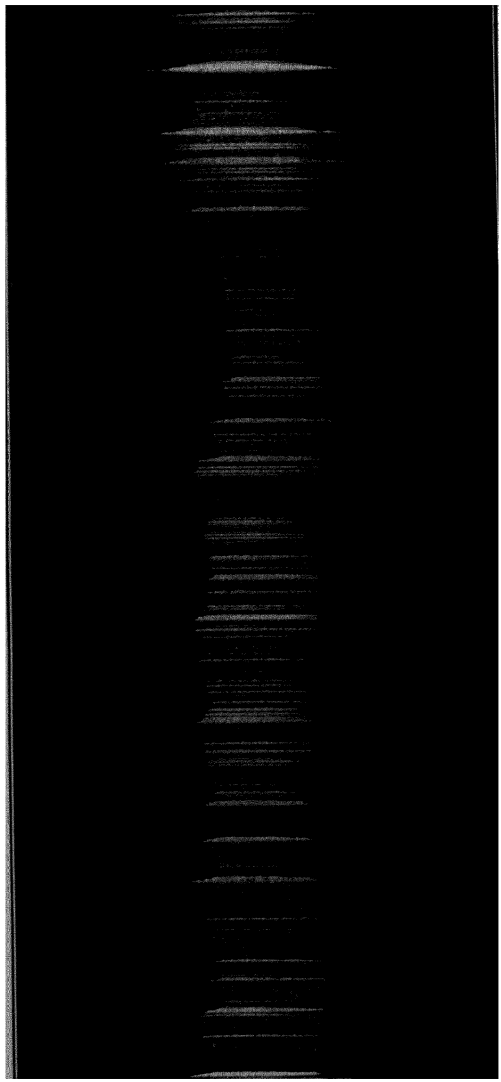


FIG. 174.

the spark spectrum of the chloride, namely, the lines between Fraunhofer's H and K, while the brightest lines in the green and blue are wanting. Many other cases were observed.

In the halides of lead, strontium, barium, magnesium, and sodium, the same facts were observed, and, further, Lockyer proved that the more easily is a compound dissociated, so do more shorter lines of the metal appear; so that if we spark the salts of a metal under exactly the same conditions, the number of the lines of the metal which appear in the spectrum of each salt, or the length of the shortest lines which appear, can be used as a scale of instability of the salt. To take the case of the lead halides—the fluoride shows eleven, the chloride nine, the bromide six, and the iodide four of the lines of metallic lead. The temperature and the strength of the spark, of course, determine the number of the lines visible, and at the lowest temperatures only the longest lines make their appearance, and as it is increased more lines appear, but always in order of their lengths.

The same is true of alloys, which behave in exactly the same way as chemical compounds; in an alloy which contains a very small proportion of one constituent, only the longest lines of that constituent are to be seen. It is possible to prepare an alloy of magnesium which only shows one magnesium line, namely, the longest of all the lines of this element. Lockyer and Roberts-Austen[1] based upon these experiments a method of quantitative analyses of alloys by spectrum observations. Lockyer then considers these results in connection with the solar spectrum, and points out that if an element were present in the solar atmosphere in small quantities, we should only expect to see the longest lines in its spectrum. We have an example to hand of this in the case of aluminium; in the spark spectrum of aluminium chloride, as was stated above, only two lines of this metal are to be seen, namely, the two longest lines at $\lambda = 3962$ and $\lambda = 3944$; these are the only two lines of aluminium visible in the solar spectrum.[2]

[1] *Phil. Trans.*, **164**. 495 (1874).

[2] See also the work of De Gramont and Pollok, p. 405.

Lockyer has further shown that on reducing the temperature it is the longest lines which remain visible; the arc spectrum of zinc, for example, does not contain the two short spark lines at $\lambda = 4924$ and $\lambda = 4911$ referred to above; again, the short spark lines of cadmium at $\lambda = 5377$ and $\lambda = 5336$, and the short magnesium line at $\lambda = 4481$, do not appear in the arc spectra of these metals. A further point is that it is the longest lines in the arc which first show self-reversal;[1] this is only what we should expect from the origin of self-reversal, namely, the absorption by the outer sheath of metallic vapour round the arc of certain rays which are emitted by the central core. The reversal of the lines of various spectra has been the subject of lengthy and important investigations by Liveing and Dewar, whose results in the main confirm the facts discovered by Lockyer.

Plurality of Spectra.—That the same substance can present two entirely different spectra has already been referred to in the section dealing with the filling of vacuum tubes with gases, where it was pointed out how certain gases give one spectrum when illuminated by the ordinary discharge from an induction coil, and a second when a Leyden jar is placed in parallel with the vacuum tube. The first research of importance on the question of the plurality of spectra was by Plücker and Hittorf,[2] who showed that the same substance can give two different spectra. They proved this especially in the case of nitrogen, which they found to give a bright line spectrum when a jar is used, and a banded spectrum when the ordinary discharge passes through a vacuum tube containing the gas. There is also to be observed a second banded spectrum, which is visible only in the negative glow in the vacuum tube; further, Plücker and Hittorf considered that the positive band spectrum of nitrogen consists of two superimposed band spectra. Since the appearance of this paper a great deal of work has been done by various people upon this subject, and many cases of this plurality of spectra have been discovered, but the real meaning of these is not known.

The most important cases of this phenomenon known at

[1] See p. 526.

[2] *Phil. Trans.*, 155. 1 (1865).

the present time are that of nitrogen, already mentioned, also oxygen, chlorine, bromine, and iodine.

As regards nitrogen, the banded spectra can be obtained quite readily by passing the ordinary discharge from an induction coil through a vacuum tube containing air or nitrogen. The capillary portion of the vacuum tube glows with a fine rose light, which gives in a spectroscope the positive band spectrum of nitrogen. This consists in its entirety of a series of bands of fine lines in the red and orange, which show a very characteristic break in their regularity at one point in the deep orange; in the blue and violet occurs a series of bands of fine lines, each band being degraded on the more refrangible side. The bands in the orange have not exactly the same appearance as those in the blue, and it was for this reason that Plücker and Hittorf considered that the two sets of bands belonged to two different spectra. Moreover, they succeeded in obtaining a vacuum tube of nitrogen which, when the ordinary spark was passed, showed the series of bands in the red extending with increasing intensity into the blue, and when the jar discharge was passed showed a series of bands in the blue extending with increasing intensity towards the red. The spectrum seen in the blue glow round the negative pole is quite different from the positive spectrum; the bands are degraded towards the blue, but are in quite different positions from the positive bands, and have quite a different structure.

In reference to Plücker and Hittorf's contention that the positive spectrum really consists of two superimposed spectra, I have several times observed a curious point in the preparation of argon. When argon is separated first from the atmosphere it always contains a small quantity of nitrogen, which is removed by mixing the gas with oxygen and passing sparks through the mixture over potash solution, when the nitrogen combines with the oxygen to form oxides, which dissolve in the potash; the excess of oxygen is then removed by phosphorus. Sometimes the sparking process has not been carried on for quite long enough, so that a trace of nitrogen is still left, and then on filling a tube with the gas the nitrogen glows brilliantly. The negative band spectrum, however, is then not to be seen, but

only the positive band spectrum, which now is separated into two portions, the red set of bands in the capillary portion which glows with pure brick-red colour, and the blue bands in the negative glow; no argon lines are seen.

A somewhat similar observation has been made by Goldstein,[1] who filled a cylindrical vacuum tube about 3 cms. in diameter with nitrogen at a pressure of a few centimetres. The discharge through the gas is then very narrow, and shows the well-known banded spectra in the positive column. If the whole is now immersed in liquid air the positive column gradually increases in diameter, and begins to change colour through golden yellow to a greenish yellow. The spectrum finally only shows the red and yellow bands extending to the green, the blue bands being entirely absent. The apparent reduction of the pressure of the gas on immersion in liquid air is too great to be accounted for by the fall of temperature alone. Goldstein is inclined to believe that the spectrum obtained at the lower temperature is the true spectrum of nitrogen, the ordinary spectrum being due to the admixture of some impurity.

Oxygen is a second instance of an element which presents a great number of spectra. These spectra were examined by Schuster,[2] who describes four different emission spectra as follows: The elementary line spectrum (first mapped by Plücker[3]), which is obtained when the jar discharge is sent through oxygen; the name of "elementary line spectrum" has its origin in the fact that this spectrum is given by oxygen with the spark of highest temperature, and therefore it might be considered as due to a more dissociated oxygen molecule; it is a complex line spectrum. The compound line spectrum is given by oxygen when the ordinary discharge is passed through it in vacuum tubes; this spectrum, which was discovered by Schuster, has been the subject of a complete investigation by Runge and Paschen,[4] who have been able to detect harmonic series in it,

[1] *Verh. d. Deutsch. Phys. Ges.*, **21**. 315 (1904); and *Phys. Zeitschr.*, **6**. 14 (1905).

[2] *Phil. Trans.*, **107**. 37 (1879).

[3] *Pogg. Ann.*, **107**. 518 (1859).

[4] *Ann. der Phys.*, **61**. 641 (1897); and *Astrophys. Journ.*, **8**. 70 (1898).

and hence have given it the name of "series spectrum." The third spectrum of Schuster's is the continuous spectrum, which is to be seen in the phosphorescent glow which appears in the wide portions of the vacuum tube when a very weak discharge is used. To my mind, however, it is doubtful whether this, the phosphorescent glow, is really due to the element oxygen, because it does not make its appearence if great care is taken against the presence of nitrogen. If the oxygen is quite pure there is no glow to be seen, but the presence of a very small amount of nitrogen is sufficient to produce it. The fourth oxygen spectrum is that of the negative glow, first accurately described by Wullner.[1] This is a banded spectrum, with three bands in the red and two in the green; these bands can be resolved into lines.

In addition to these we have two absorption spectra, of which one gives the A, B, and *a* bands in the sun's spectrum, and the second was discovered by Jansen.[2] Then, further, we may include the absorption spectrum of ozone,[3] so that there are six or seven spectra due to oxygen.

Of the halogens iodine is the one which has been most studied, having been made the subject of a complete investigation by Konen.[4]

Amongst the substances which should be mentioned in this section are the new monatomic gases—argon, krypton, and xenon, which give two completely different line spectra, one with the ordinary discharge, and the other with the jar discharge; then, again, there are the much-discussed spectra of carbon and of hydrogen. There has been considerable controversy about the former case, which cannot be entered into here fully for want of space, but an excellent *résumé* of the work up to date is contained in Schuster's report on the Spectra of the Metalloids in 1880.[5] There are known the following spectra: A line spectrum, a band spectrum, known as the candle or

[1] *Pogg. Ann.*, **144**. 481 (1872).
[2] *Brit. Ass. Report* (1888), 547.
[3] Hartley, *Chem. Soc. Trans.*, **39**. 57 (1881).
[4] *Ann. der Phys.*, **65**. 257 (1898).
[5] *Brit. Ass. Report* (1880), 258.

Swan spectrum (after the discoverer), a second band spectrum, usually called the carbonic oxide spectrum, and a third band spectrum, usually called the carbon nitride or the cyanogen spectrum. The battle has really been fought over the second on the list, the Swan spectrum; there is no room for any doubt that the first or line spectrum is due to carbon itself, nor that the last is due to cyanogen. These spectra may readily enough be seen—the line spectrum when the jar spark is sent through carbon monoxide or dioxide, the Swan spectrum at the base of every candle or gas flame, or best in the inner cone of a "roaring" Bunsen burner; the third may be seen by passing the ordinary electric discharge through carbon dioxide in a vacuum tube, and the fourth in the flame of cyanogen in the air, or better in the spectrum of the electric arc between carbon electrodes in air, when it is seen along with the Swan spectrum.

The trouble about the Swan spectrum till recently lay in the question as to whether it was due to carbon itself or to a hydrocarbon. A great number of experiments were made, but the question never was finally decided. The second band spectrum was assigned to carbon monoxide, because both this gas and carbon dioxide were found to give it in vacuum tubes, and the latter is known to be much the more unstable of the two. I found, however, in 1892 that if a vacuum tube is filled with absolutely pure carbon monoxide it gives the Swan spectrum and not the second band spectrum, the admixture of the slightest trace of oxygen being sufficient to destroy the spectrum and substitute the second band spectrum. It seemed at once that the explanation of the spectra was simple on these grounds; the line spectrum being that of the element carbon, the Swan spectrum that of carbon monoxide, and the second band spectrum that of carbon dioxide, since it was given by carbon monoxide and oxygen mixed, and by carbon dioxide itself. For these reasons the second band spectrum was spoken of as the carbon dioxide spectrum in a note about the spectra of mixed gases.[1] Smithells,[2] approaching the question from another side, that of combustion, has made experiments

[1] Baly, *Phil. Mag.*, **35**. 200 (1893).

[2] *Phil. Mag.*, **1**. 476 (1901).

on the spectra of the two gases in vacuum tubes, and shows that the Swan spectrum is given by carbon monoxide when it is absolutely pure. It may be stated at once that the experiment is very troublesome to carry out properly on account of the difficulty in the preparation of absolutely pure carbon monoxide. The best way to prepare it is by the action of strong sulphuric acid on strong formic acid. Both of the acids should be freed from dissolved air by keeping them in vacuo for a time; a strong test-tube thoroughly cleaned with hot chromic acid and water and thoroughly dried is filled with filtered mercury and inverted over a dish containing the same metal. These precautions are necessary to ensure there being no air in the tube between the mercury and the glass. Some of the sulphuric acid is then passed up the tube by means of a bent pipette, and then a few drops of the formic acid. A quantity of the gas is then evolved, which can be introduced into the tube in the manner described on pp. 426 *et seq.* If these precautions are taken, one always obtains the Swan spectrum, the discharge glowing with a brilliant green colour. It seems, therefore, that Smithells is quite justified in his conclusions that the Swan spectrum and so-called carbonic oxide spectrum are due to the monoxide and dioxide of carbon respectively. It has been further shown that when a vacuum tube is filled with pure cyanogen only the cyanogen banded spectrum is obtained, with no trace of the Swan spectrum, and that the presence of oxygen is necessary for the appearance of the banded spectra.[1] Further, Konen[2] (see p. 413) has endeavoured to prove the same point by examining the spectrum of the electric arc between carbon poles under the surface of oxygen free liquids. He did not succeed, however, but admits that his experiments were not conclusive.

Against the above conclusions that the Swan spectrum is due to carbon monoxide, the following results may also be quoted. Watts and Wilkinson[3] observed the spectrum of the spark at atmospheric pressure in certain liquid compounds of

[1] Baly and Syers, *Phil. Mag.*, **2**. 386 (1901).
[2] *Ann. der Phys.*, **4**. 742 (1902).
[3] *Phil. Mag.*, **12**. 581 (1906).

carbon containing no oxygen. The Swan spectrum was noted in each case. Also La Rosa[1] has investigated the spectrum of a carbon rod electrically heated to incandescence. Owing to the fact that the Swan spectrum is obtained when the rod is heated in an oxygen-free space, it would seem that the Swan spectrum must be due to carbon vapour. On the other hand, von Wesendonk[2] describes some experiments in which chlorine is fed into a coal-gas flame burning in air, when a very marked intensification of the Swan bands is obtained. The conclusion is drawn that the Swan spectrum is due to a hydrocarbon.

In spite of the apparently contradictory evidence contained in these later papers, I still feel convinced that the Swan spectrum is to be attributed to carbon monoxide. The extraordinary difficulty of removal of every trace of oxygen from liquids such as those used by Watts and Wilkinson, and above all from a carbon rod, such as was used by Konen and by La Rosa, tends to make the evidence given by these experimenters somewhat inconclusive.

In the experiments described above, when vacuum tubes are filled with pure carbon monoxide, unless special precautions are taken, enough oxygen is dissolved in the sulphuric and formic acids entirely to destroy the Swan bands in the spectrum which is obtained. This being so, it seems somewhat probable that the last-mentioned contradictory results are really due to dissolved or occluded oxygen.[3]

Hydrogen is a gas which presents two spectra, one a simple line spectrum, which is familiar to every one who works with vacuum tubes, containing four lines in the visible region, and a second compound line, or, rather, secondary line spectrum. This is also seen in vacuum tubes filled with hydrogen, and there has been considerable doubt as to whether it is due to hydrogen, and some work by Schuster seems to point to its being due to water vapour.

[1] *Ann. der Phys.*, **34**. 222 (1911).

[2] *Phys. Zeitsch.*, **9**. 151 (1908).

[3] Photographs of the Swan spectrum and carbonic oxide spectrum as given by vacuum tubes containing carbon monoxide and carbon dioxide respectively are reproduced on Plate III. p. 649.

On the other hand, Dufour[1] made a lengthy study of the secondary spectrum, and points out that he could obtain no difference in the relative intensity of the two spectra, primary and secondary, although he used the most elaborate and rigid precautions against the introduction of an impurity. He showed, moreover, that the discharge passed through pure water vapour exhibits no trace of the secondary spectrum. When the condensed spark is used the secondary spectrum disappears, while the spectrum of the brush discharge through hydrogen shows only the secondary spectrum. He also examines the influence of a magnetic field upon the secondary spectrum, and finds that by far the greater number of the lines are uninfluenced. He concludes that the bright line or primary spectrum is due to atomic or dissociated hydrogen, while the secondary is due to molecular hydrogen.

One other case of this plurality of spectra merits mention, and that is the existence of the beautiful banded flame spectra of certain metals, as described by Hartley and Ramage,[2] which have also been measured more accurately by Basquin[3] in the electric arc between metal poles in an atmosphere of hydrogen. That they are due to the metals themselves there seems no doubt (Basquin suggests a hydrogen metallic compound), but very little appears to be known about them. This conclusion that the band spectra are due to the elements and not to any compounds has been fully dealt with by Hartley[4] in a later paper.

These cases of plurality of spectra serve to show what an interesting field of work lies here; no explanation has yet been found of the curious facts described, and there is room for a great development of our knowledge in this direction.

Reversal of Spectrum Lines.—By the reversal of a spectrum line is meant the process by means of which the line appears black on a bright background. This reversing process may be obtained in two ways: 1st, by causing a beam of

[1] *Ann. Chim. et Phys.*, **9**. 361 (1906).
[2] *Trans. Roy. Soc.* Dublin **7**. 339 (1901).
[3] *Proc. Amer. Acad.*, **37**. 161 (1901).
[4] *Proc. Roy. Soc.* **79**. 242 (1907).

light from an incandescent body to pass through the vapour of the substance, when the absorption or reversed lines are seen upon a continuous spectrum as background; 2nd, when the centre of a glowing mass of vapour is at a greater density than the outer layers, as, for example, in the arc. In this case the central portions emit a broadened line owing to the increased density, while the outer layers absorb some of these rays, and as they are much less dense than the central portions, they form only a very fine absorption line, so that an effect is produced of a fine black line in the centre of a broader bright line. This reversal is due to the difference of density of the two layers; if the emission and absorption were the same no lines would be seen. This phenomenon is known as self-reversal, and is especially visible in the spectra of the arc, where the necessary conditions most frequently occur. The ultra-violet lines are generally most easily reversed, and in photographs of the arc spectrum of iron it will generally be found that the principal ultra-violet lines are self-reversed.

A great deal of work upon the reversal of lines has been done by Liveing and Dewar, and by Lockyer. Into this there is no need to enter, but certain points in connection with self-reversal may be considered. It will nearly always be found that self-reversal begins with the lines in the ultra-violet, and extends further into the visible spectrum as the conditions therefor are improved. Liveing and Dewar,[1] however, point out that this is not the case with lithium, whose lines reverse in the order—red, orange, blue, green, violet.

In connection with this the discovery of the stars which have both bright and dark lines is of great interest. A considerable number of these stars have been discovered since Wolf and Rayet first noticed the existence of three in 1867. These stars show the hydrogen spectrum, and Campbell[2] at the Lick Observatory found that the hydrogen lines are in part dark and in part bright; that is to say, the hydrogen lines α and β are bright, while all the others are reversed.[3]

[1] *Proc. Roy. Soc.* **35.** 76 (1883).

[2] *Astrophys. Journ.*, **2.** 177 (1895), and, also, Scheiner's *Astronomical Spectroscopy*, Frost's Translation, pp. 268 *et seq.*

[3] See also Kayser, *Astrophys. Journ.*, **14.** 313 (1901).

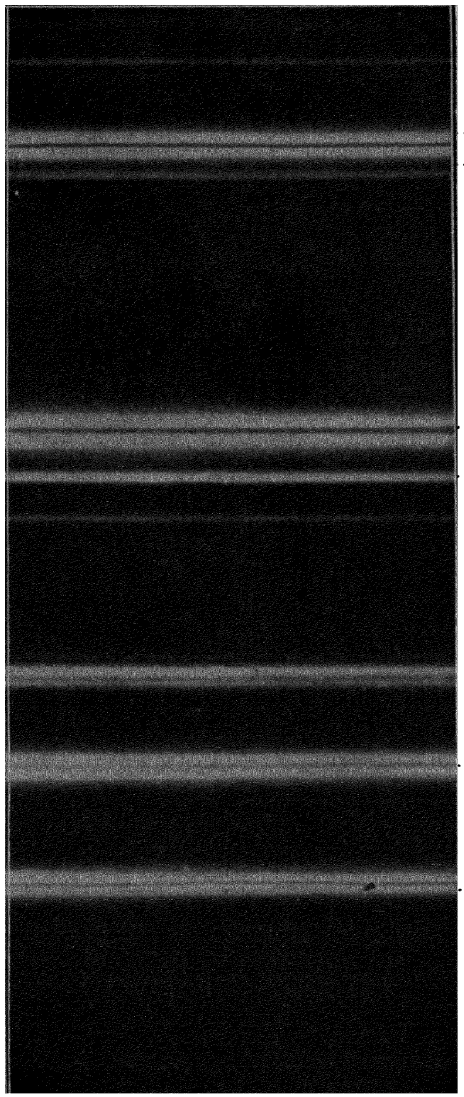


FIG. 175.

When the arc spectrum of the iron is photographed, particularly in the higher orders of a grating, very many lines will be found to be self-reversed; on the negative they appear as black lines with a very fine transparent centre. When the line is symmetrically reversed, the measurement of their centre is readily enough made by fixing the cross-wire in the eyepiece upon the centre of the reversed portion. In certain cases unsymmetrical lines are reversed, and then unsymmetrical reversal is obtained, and considerable errors in determination of the position of the line will ensue unless care be taken in the setting of the cross-wires. 'When the vapour of the substance is very dense in the arc, *i.e.* when a great deal of the substance is used, at times a multiple reversal shows itself; Jewell[1] explains this by the presence of a series of concentric layers of vapour of maximum and minimum density round the arc. One photograph of Jewell's showed four reversals in the magnesium line at $\lambda = 2852$; Kayser is inclined to view this effect on the plate as being due to a succession of changes of position of the reversal. Liveing and Dewar say, however, that they have seen the effect with the eye. In Fig. 175 is reproduced a portion of the arc spectrum of iron. This is enlarged from a photograph taken of the second order spectrum given by the Rowland grating at University College, London; an idea of the scale is shown by the wave-lengths of the lines; it is very nearly 1 cm. for 1 A.U., which would make the whole spectrum from $\lambda = 7600$ to $\lambda = 2000$, 560 metres long. The self-reversal is clearly shown in the four principal lines.

The self-reversal may also be seen in spark spectra, as, for example, in the case of cadmium when one or two of the lines in the ultra-violet are frequently found to be self-reversed. Similarly also it is easy to obtain the green line of mercury self-reversed when a discharge is passed through mercury vapour under low pressure. Wood[2] has also obtained self-reversal of the red hydrogen line when the condensed spark discharge is passed through rarefied hydrogen in a vacuum tube with a long capillary portion which is viewed end on.

[1] *Astrophys. Journ.*, **3**. 96 (1896).
[2] *Phys. Zeitsch.*, **7**. 926 (1906).

CHAPTER XVI

THE ZEEMAN EFFECT

In 1896 Zeeman discovered that if a Bunsen flame fed with small quantities of sodium chloride was placed between the poles of a powerful electro-magnet, and its spectrum examined, then, when the exciting current was turned on, the D lines were seen to be broadened, regaining their original appearance when the current ceased. This was also found to be the case with the reversed D lines obtained in the usual way by absorption. This phenomenon, as Zeeman pointed out, is a natural result of H. A. Lorentz's theory of electro-magnetic radiation. In this theory it is assumed that the chemical atom consists of a number of small electrically charged particles with a definite mass, called electrons, which are vibrating about a common centre, and that light consists of transverse vibrations in the ether set up by the vibrations of these electrons. When a substance is placed in a magnetic field, the motions of the electrons are influenced so that changes are made in their vibration periods. Zeeman pointed out that, as a simple result of this theory, the motions of the electrons may be resolved into three components, one in straight lines parallel to the magnetic lines of force, and the other two at right angles to them; the two last may be resolved into two circular motions (right- and left-handed) around an axis parallel to the lines of force. Evidently the first rectilinear motion will not be influenced by the magnetic field, while on the other hand the two circular motions will be altered, the period of one being shortened and that of the other lengthened. If the lines of magnetic force run towards the observer, and the electrons be

negatively charged, then the right-handed motion will be retarded and the left-handed motion accelerated. On these grounds it is easy to predict the effect on the lines of a spectrum.

Let us consider, in the first place, the effect if we examine the light evolved from some source placed in a powerful magnetic field, looking along the lines of force. Under these circumstances the first component of the motion of the electrons, that is to say, those electrons moving parallel to the lines of force, cannot emit any light in our direction, since they are not moving transversely to the line of vision; these particles are simply moving backwards and forwards in the sight line, and therefore they will give rise to light waves at right angles to the sight line, but not in directions parallel to it. The two circular components, on the other hand, will give rise to two circularly polarised rays, and as the one circular component is accelerated, and the other retarded by the magnetic field, the two resulting circularly polarised rays will have different oscillation frequencies; with a sufficiently powerful spectroscope these two rays will be seen separated. Since the action of the magnetic field restrains one of the circular motions just as much as it accelerates the other, it follows that we should see in the spectroscope, instead of a single line, a doublet, whose components are situated at an equal distance on either side of the position of the original line, and are circularly polarised, one in the right-handed and the other in the left-handed sense.

If now, in the second place, the light be viewed across the lines of force, then effects will be produced by all three components. The first component, that is the electrons vibrating parallel to the magnetic lines of force, will give rise to waves which are plane polarised, the vibrations being parallel to the lines of force. Since these motions are not influenced by the magnetic field, the oscillation frequency of the resulting waves will be the same as that of the undisturbed light. The two circular components will now be seen sideways, and the electrons will act as if they were simply vibrating in straight lines up and down, or perpendicular to the lines of force.

They will thus give rise to plane polarised light waves, the vibrations being perpendicular to the lines of force. As in the previous case, since the two circular motions have not the same period, therefore two of these plane polarised rays will be emitted, one having an oscillation frequency greater and the other less than that of the original light. When, therefore, the light is viewed across the lines of force, each spectrum line should be seen to be split symmetrically into three lines, and each line should be plane polarised, the two outside components having their plane of polarisation parallel to the lines of force, and the middle component with its plane of polarisation perpendicular to the lines of force.

With the apparatus at his disposal, Zeeman[1] was not at first able to split the spectrum lines into doublets or triplets, but he found that the lines were widened, and that the edges were polarised exactly in the way he expected from the theory. In order to view the light along the lines of force, he took an electro-magnet with holes bored through the poles, and so placed it that the axes of the holes and the centre of the diffraction grating were on the same straight line. Between the grating and the eyepiece were placed a quarter-wave plate, to convert the circular polarised light into plane polarised, and a Nicol prism. The plate and the Nicol were relatively placed in such a way as to extinguish right-handed circularly polarised light, and the cross-wires of the eyepiece were set upon the bright line as seen. When the current through the magnet was reversed, the spectrum liné was seen to move. Without the use of the quarter-wave plate and the Nicol a widened line was seen. The quarter-wave plate and the Nicol extinguished the one edge which was circularly polarised in the right-handed direction; on reversing the current the other edge now became circularly polarised in the right-handed sense, and was extinguished, so that the line appeared to move its position. Similarly Zeeman was able to prove that when the light was examined across the lines of force, the widened line then seen had its edges plane polarised, the plane of polarisation being perpendicular to the length of the line. Michelson[2] was able

[1] *Phil. Mag.* (5), **43**. 226 (1897). [2] *Ibid.* (5), **44**. 109 (1897).

by means of his interferometer to show that the components of a line could be separated, and afterwards Zeeman[1] succeeded in seeing with a grating spectroscope both the magnetic doublet and triplet with the cadmium line $\lambda = 4800$.

In a later paper, Zeeman[2] published some results of measurements between the two outer components of some triplets obtained by viewing the light across the lines of force. The sharp spectra of zinc, cadmium, copper, and tin were used, condensed sparks from an induction coil being made to pass between electrodes of the particular metal, and the poles of the magnet were brought up as close to the spark as possible without disturbing it. The resulting triplets were photographed, the middle component being extinguished by means of a Nicol prism, so as to leave the two outer components free from any contamination, and thus more readily measurable. Zeeman found that the separation of the two outer components varied considerably from line to line even in the same spectrum; for example, in the case of the three zinc lines $\lambda = 4811$, $\lambda = 4722$, and $\lambda = 4680$, the separation was equal to 0·8, 0·9, and 1·1 A.U. respectively, while with the three lines $\lambda = 3345$, $\lambda = 3303$, and $\lambda = 3282$ the separation was too small to be measured. It is important to notice, as Zeeman pointed out, that the first-mentioned lines belong to the second subordinate series, while the last three belong to the first subordinate series (see p. 590). Exactly similar results were obtained with the other metals named.

Preston,[3] who worked with a full-size Rowland grating, found that the "normal triplet" is by no means always obtained when a line is examined across the lines of force, but that doublets, quartets, and sextets are often obtained. Analysis of these groups by a Nicol prism showed, however, that they can all be considered as derived from the normal triplet, the doublet by the absorption of the middle line, the quartets either by the doubling of the middle line or the absorption of the middle line and doubling of the two outer components, and the sextet by the doubling of all three lines of the triplet.

[1] *Phil. Mag.* (5), **44**. 55 and 255 (1897).
[2] *Ibid.* (5), **45**. 197 (1898). [3] *Ibid.* (5), **45**. 325 (1898).

Preston pointed out that if λ be the wave-length of any line, and if $d\lambda$ be the difference in wave-length between the two outer components of a triplet produced in a magnetic field of strength H, then in electro-magnetic units—

$$\frac{d\lambda}{\lambda^2} = \frac{e}{m} \cdot \frac{H}{2\pi v},$$

where e is the charge on an electron, m its inertia, and v the velocity of light. That is to say, the distance expressed in oscillation frequencies between the two outer components of a triplet is proportional to the magnetic force, and further, in a constant field this distance must be equal for all lines for which $\frac{e}{m}$ is the same. Preston, as the result of his observations of the spectra of magnesium, zinc, and cadmium, was able to prove this to be true, inasmuch as he found that $\frac{d\lambda}{\lambda^2}$ is the same for all the lines of the natural harmonic series as found by Kayser and Runge, and by Rydberg, and, further, that it is the same for the corresponding lines in the homologous spectra of different substances. He also noticed that the magnetic effect differed in character on the lines of the different series; thus in the case of the natural triplet series of magnesium, zinc, and cadmium, the first line became a diffuse and probably complex triplet in the magnetic field, the second line became a quartet, and the third line a pure triplet.

Before entering into a description of the results that have been more recently obtained in the investigation of this phenomenon, we may here with advantage deal with the experimental methods employed in the work. It is first of all, of course, necessary that the magnet employed be powerful, and also that the poles be brought very close together in order to obtain as strong a field as possible, for, as shown above, the separation of the components of a line depends directly upon the strength of the magnetic field. The general theory of the half-ringed magnet and the best conditions for construction have been given by du Bois,[1] but these cannot

[1] *Ann. der Phys.*, 1. 199 (1900).

be entered into here. Amongst the most powerful magnets which have been used for this work is one used by Stewart and Gray.[1] This instrument was made of cast-steel, whose magnetic permeability coincided very nearly with that of wrought iron. It is rectangular in shape, and is about 3 feet long by about $1\frac{1}{4}$ foot deep. A large magnetising coil surrounds the yoke, and extends over its whole length. The poles are provided with smaller coils, about 1 foot in length, having, respectively, 1140 and 1170 turns of copper wire of No. 9 standard wire gauge. The coils can stand easily a current of 16 amperes, and for short periods 50 or 60 amperes. The field intensity between the poles is exceedingly great, probably not far short of 50,000 C.G.S. units.[2]

Runge and Paschen[3] have used an instrument which gave fields up to 30,000 C.G.S. units.

The second and a most important consideration is that the intensity of the magnetic field be equal; that is to say, it is very necessary that the light rays which are focussed to form a point on the slit should only come from parts of the light source which are under equal magnetic stress. Unless care is taken that this is the case, it is evident that good definition of the resolved spectrum line is quite impossible. Except in the case of a concave grating this condition is readily enough obtained by focussing an image of the light source upon the slit by means of a convex lens, for clearly in this case all the light falling upon the centre of the slit comes from those portions of the light source lying in a horizontal plane passing through the centre of the magnetic field. For this purpose Runge and Paschen make use of wedge-shaped pole pieces to their magnet, which are set with their acute edges facing one another in a horizontal plane. In this way the magnetic lines of force are very concentrated in a horizontal plane; in this plane also lie the source of light, the axis of the focussing lens, and the centre of the slit. Under these circumstances alone can the best definition of the magnetic components be seen.

[1] *Proc. Roy. Soc.*, **72**. 16 (1903). [2] *Nature*, **65**. 54 (1901).
[3] *Abhan. d. Berl. Akad.*, 1902.

When as the analysing spectroscopic instrument a concave grating is used, the astigmatism alters the conditions very considerably; a single point on the slit is not focussed as a point in the spectrum line, but is drawn out to a line (see p. 188), the length of which depends upon the angle of incidence at which the light falls on the grating.

Each point of a spectrum line is formed by the unison of the rays from several points on the slit, and therefore cannot under ordinary circumstances receive rays from points in the light source, which are all under the same magnetic stress. To obtain anything like good definition special precautions must be taken to surmount this difficulty. It was shown before (Chapter VI., p. 189) that in the case of a concave grating the slit forms one, a vertical, focus of a spectrum line, and that there is another, a horizontal, focus lying a certain distance outside the slit. This is represented in Fig. 68 (p. 189) by the line EF, and it was pointed out that a wire stretched across the incident beam at EF is focussed as a horizontal line along the spectrum. The distance of the centre of this line from the slit depends upon the angle of incidence of the light on the grating, and is equal to $\rho(\sin i \tan i)$, where ρ is equal to the radius of curvature of the grating and i the angle of incidence. If now this horizontal focus lies inside the light source, then there will be a point in the spectrum which receives light waves from points in the light source which lie in a horizontal plane of equal magnetic force. If, however, the horizontal focus does not lie in the light source it is possible to make it do so by means of cylindrical lenses placed in front of the slit.[1]

It has been proved by Preston, by Runge and Paschen, and by Stewart, Gray, Houstoun, and McQuistan that the separation of the components of a line is proportional to the magnetic field, and that the separation of the components of all corresponding lines in spectra is proportional to their oscillation frequency; it is therefore a simple matter, from measurements made on lines with one strength of field, to calculate the separations corresponding to another field strength

[1] See Runge in Kayser's *Handbuch der Spectroscopie*, vol. ii. chapter ix.

if the separations occurring with one line in the two field strengths be known. In other words, one can express the strength of the field in terms of the separation occurring with one line taken as a standard, and in the examination of the complete spectrum all the measurements can be referred to this standard line; finally, the strength of field producing definite separation of the standard line is determined by some external means, and from this the whole of the measurements of the lines are calculated for the same field strength.

Attention may now be drawn to the best methods of production of the illumination. As will readily be seen, the exciting of the substance to be examined must be made in as small a space as possible, owing to the necessity for having the poles of the magnet very close together. For this reason the ordinary flame spectrum, as obtained with a Bunsen burner, cannot be used, as the flame is far too clumsy; then, again, the lines are not sufficiently fine to permit of accurate work. The fine flame produced by an oxyhydrogen blast may be used, but none of these methods are so satisfactory as the electric spark from an induction coil, which is made to pass between electrodes of the metal dealt with. The best way is to cause the sparks to pass in the direction of the magnetic lines of force, as otherwise they will be dragged out of the most intense part of the field by the action of the field itself. It is necessary in this case to bore small holes in the poles of the magnet to admit the electrodes, care being taken to insulate them from the iron of the magnet. Runge and Paschen place one electrode on the acute edge of one of the pole-pieces as a thin strip of foil. In the secondary circuit of the induction coil self-induction coils are introduced, as well as Leyden jars, to make the lines as fine as possible;[1] without this it is often impossible to resolve some of the lines. If the spectra are required of salts in solution, the solutions may be dropped on to the electrodes. In the case of gases these are enclosed, of course, in vacuum tubes with capillary portions. These are best used in a horizontal position, the discharge being viewed end-on through a quartz or fluorite window. Care must be

[1] Hemsalech, *Comptes Rendus*, **129**. 285 (1899). See p. 407.

taken that no portion of the capillary reaches out beyond the ends of the pole-pieces.

For examination of the spectra, instruments of high resolving power must, of course, be used, such as a large grating apparatus or an echelon spectroscope; an interference apparatus may also be employed, such as Fabry and Perot's interferometer, or the instrument devised by Lummer.[1]

For examination of the direction of polarisation, one may employ, as Preston[2] showed, a double image prism or rhomb of calc-spar placed between the light source and the first lens; this will separate the light into two beams, and two images will be formed upon the slit one above the other, and two spectra will be seen one above the other, one containing the components polarised in one sense, and the other those polarised in the other sense.

When the ultra-violet region is being worked with, and quartz lenses are used, it is necessary, owing to the rotation of the plane of polarisation by the quartz, that the calcite rhomb be put between the light and the first lens.

When viewing along the lines of force, the pole of the magnet should be bored to allow the passage of the light to the slit. This may be avoided[3] by the use of a small totally reflecting prism fastened to the front of one of the poles. This has the advantage of not disturbing the regular distribution of the lines of force as does the bored hole, but, on the other hand, it prevents the poles being brought so close together.

The circularly polarised rays are examined in exactly the same way, but with the addition of a quarter-wave plate.

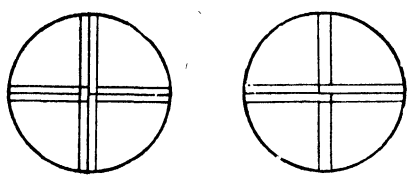
Cornu[4] made use of the following arrangement for visual observation: A thin metal strip perpendicular to the spectrum lines is fixed behind the eyepiece, and by use of a Wollaston prism two images of the strip are seen, one corresponding to the horizontally polarised rays, and the other to those polarised perpendicularly; the width of the strip is so adjusted that the two images of the strip are seen against one another. The

[1] Chapter IX. [2] *Loc. cit.*
[3] Kent, *Astrophys. Journ.* **13**. 288 (1901).
[4] *Comptes Rendus*, **125**. 555 (1897).

perpendicularly polarised rays of the spectrum are hidden by the perpendicularly polarised image of the strip, and therefore at this place one sees only the horizontally polarised rays, and *vice versa*. When the magnet is not excited, a spectrum line will be seen through both pictures of the strip; but when the current is turned on, a normal triplet will be seen, as shown in Fig. 176 at *a*.

Along the lines of force the same separation of the components is to be seen when a quarter-wave plate is used in addition, as shown in Fig. 176 at *b*.

Experimental Results.—Although many lines in the magnetic field are seen across the lines of force to split into



a *b*

FIG. 176.

three components—the normal triplet—yet this is by no means the rule, and nearly every line belonging to Kayser and Runge's and Rydberg's séries deviates from this, giving as a rule more than three components. Several types of decomposed lines have been observed which, as has been above pointed out, repeat themselves for the lines of the same series of one element, and further also for the corresponding lines of homologous elements. Amongst the investigations in the direction of measurement and observation of the various types, that carried out by Runge and Paschen may be briefly described as follows:[1]—

The most complete investigation of the resolution of lines has been carried out by these observers on the spectrum of mercury. This element, according to Kayser and Runge, gives a spectrum which amongst its lines possesses a first and second

[1] *Astrophys. Journ.*, **15**. 157 and 333 (1902); *Phys. Zeitschr.*, **3**. 441 (1902); *Berl. Ber.*, (1902) 380 and 720.

subordinate group,[1] each of which, however, consists of three series, the formulæ for which differ only by a constant. The intensities of the lines fall very rapidly as the oscillation frequencies increase, and Kayser and Runge were able to trace the series by reason of the fact that they examined the spectrum of the mercury arc. For the observation of the Zeeman effect it is impossible to do this, on account of the enforced distance between the poles of the magnet, and therefore Runge and Paschen were obliged to use the vacuum tube filled with mercury vapour; and thus, on account of the weakness of the light, they were only able to observe the first two or three members of each group. While each line of the second subordinate group is simple, the lines of the first subordinate group, on the other hand, are accompanied by satellites of smaller oscillation frequency; thus the lines of the first series have three, the lines of the second have two, and the lines of the third one satellite. All the lines of the six series, with their satellites, are decomposed in the magnetic field.

In the case of the second subordinate group the lines of the three series give three different types, one for each series, and the distances between the components in all members of the same type, when measured in oscillation frequencies, are the same according to Preston's law. Runge and Paschen's measurements in a field of about 24,600 C.G.S. units are as follows, the letters *p* and *r* meaning that the members are polarised parallel or at right angles to the lines of force:—

	r	*r*	*r*	*p*	*p*	*p*	*r*	*r*	*r*
a_2	−2·13	−1·62	−1·07	−0·53	0	+0·55	+1·06	+1·63	+2·17
b_2	−2·15	−1·62		−0·57		+0·54		+1·64	+2·16
c_2	−2·17				0				+2·18

The appearance of the lines is shown in Fig. 177.

[1] A series of lines is a number of lines in a spectrum whose oscillation frequencies can be expressed by a general formula; in mercury and certain other metals there occur triplet series, *i.e.* three series which obey very closely allied formulæ. Such a complex series is here called a group, leaving the word "series" to represent the set of lines which obey one single definite formula. See next chapter.

The type c_2, or that of the lines of the third series of the second subordinate group, does not correspond with the normal triplets, as in the latter case the separation in the same field is equal to 2·14, while in the type c_2 it is equal to 4·35.

The type b_2 may be considered as derived from c_2 by the splitting of each member. The intensity of the two middle components is greater than that of the two outside ones, and of the outside components the inner one is always the stronger. The electronic oscillations giving rise to the two middle components are parallel to the lines of magnetic force, and therefore when the line is seen along the lines of force they vanish. This proves that in this case a free motion of the electrons parallel to the lines of force cannot be taking place,

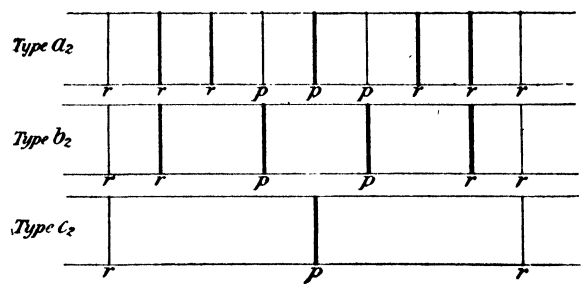


FIG. 177.

because such a vibration would not be disturbed by the field; the motion parallel to the force lines must therefore be combined with a motion which is not parallel.

The type a_2 can be considered as derived from c_2 by the tripling of each member. The three middle components in this case are not brighter than the outside ones, and the centre of the three is the brightest. Of the side components perpendicular to the force lines the innermost two are the brightest. Sometimes in the case of the green mercury line $\lambda = 5461$ it was found that of the three outside components on each side of the middle one was the brightest. Runge and Paschen attribute this to the fact that probably this line is accompanied by satellites which are themselves split by the magnetic force,

and that sometimes the components of the satellite fall in the same place as those of the chief line, and sometimes they do not, according to the strength of the field. That this is the case has been shown by Lummer and Gehrcke,[1] for they find the line to be composed of a (probably triple) principal line, five bright, and two faint satellites, one of which is probably double—altogether eleven lines. Runge and Paschen, as a result of their measurements, consider that the distance between the various components with an increase in the strength of the field increases in equal proportion throughout; that is to say, with a given increase of the magnetic field the distance between the components of all the types increases by the same ratio. Reese[2] and Kent[2] both think that in the case of a type a_2 the

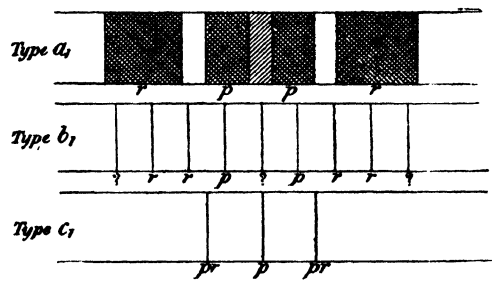


FIG. 178.

relative increase is rather greater than in the other types, and they also consider that the increase is not proportional to the increase in field strength, being a little too small with large field strengths. Runge and Paschen consider that as these observers did not succeed in separating all the components of the type a_2, it is probable that the light source was not entirely within the strongest part of the field, so that they attributed their measured separations to too strong a field.

The first subordinate group of triplets, all the members of which are accompanied by satellites, give again different types, three for the three members of each triplet, three for the three

[1] See p. 505. [2] *Astrophys. Journ.*, **12**. 127 (1900); **13**. 294 (1901).

satellities of the first member of the triplet, two for the two satellites of the second member, and, lastly, the type of the single satellite of the third member of the triplets.

The three principal types corresponding to the three members of the triplets are shown at a_1, b_1, and c_1 in Fig. 178.

The components of the type a_1 are broad, and the two

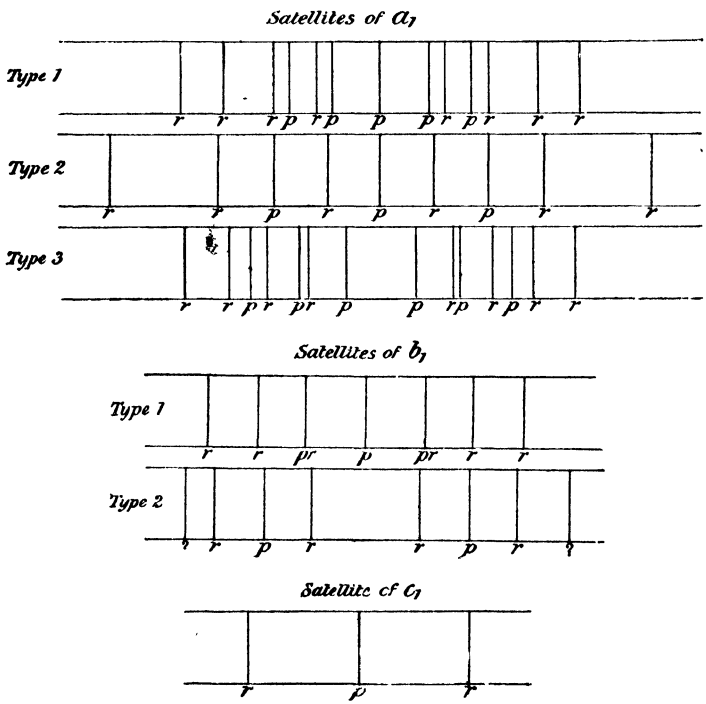


FIG. 179.

middle ones run into one another; in type c_1 *pr* means that two lines fall together, a parallel and perpendicular component respectively. The satellites give the types as shown in Fig. 179.

The following measurements were obtained by Runge and Paschen in a field of 24,600 C.G.S. units:—

PRINCIPAL LINES.

a_1		−1·28		−0·32p		+0·36p		+1·27
b_1	−1·60(?)	−1·20	−0·80	−0·40p	o(?)	+0·37p	+0·77	+1·19 +1·57(?)
c_1			−0·60pr	op		+0·60pr		

SATELLITES OF a_1.

	−2·06	−1·61		−1·14	−0·92p	−0·62	0·51p	op
−2·81		−1·67		−1·10p		−0·58		op
	−1·98	−1·56	−1·35p	−1·19	−0·81p	−0·76		−0·37p
+0·47p	+0·68	+0·97p	+1·08		+1·60	+2·07		
+0·54			+1·09p		+1·65		+2·76	
+0·38p	+0·77	+0·82p	+1·15	+1·33p	+1·58	+1·99		

SATELLITES OF b_1.

	−1·55	−1·10	−0·58pr	op	+0·67pr	+1·09	+1·69
−1·85(?)	−1·58	−1·06p	−0·57		+0·57	+1·07p	+1·59 +2·12(?)

SATELLITES OF c_1.

−1·14	op	+1·12

Runge and Paschen point out that distances of about ±1·10 occur very often in this table of measurements; this distance is about the same as that in the case of the normal triplets, which is ±1·07. It is also interesting to note how in the types a_2, b_2, c_2 the distances are all multiples of ±0·54, and further that this distance is half that which occurs with the normal triplets.

Normal triplets were observed in the cases of the lines at λ = 5790, 4916, 4348, 4108, 3907, 3902, and 2848, the mean distances of the components being—

−1·06	o	+1·08

There are also three more triplets, with distances—

−1·24	o	+1·25
−1·31	o	+1·34
−1·61	o	+1·65

The strong line at λ = 2537 was split into two components, each of which consists of a parallel and perpendicularly

polarised line lying together, the distance between the two components being $\pm 1{\cdot}79$.

The above types repeat themselves in the spectra of those elements whose spectral series are analogous to that of mercury, namely, magnesium, calcium, strontium, zinc, and cadmium. The most accurate observations have been made upon the lines giving the types a_2, b_2, c_2, *i.e.* the second subordinate group. These elements, however, differ from mercury in that they have not so many satellites accompanying the lines of the first subordinate group, and, further, the satellites lie so near the principal lines that their observation is very difficult, especially in the magnetic field. As far as Runge and Paschen's measurements go, they seem to prove that in equal magnetic fields the same separation of the components of the lines occurs with these elements as already given for the mercury lines. This confirms Preston's original observations.

It is perfectly evident from these and other observations that the motions of the electrons are not so simple as might have at first been supposed. The normal triplet resulting from the simple theory does not by any means occur very frequently, and the structure of the resolved lines shows that the conditions are very complex. It has been suggested that each atom of a chemical element consists of a central positively charged mass with the system of negatively charged electrons in motion round about it, very similar to the ring system of the planet Saturn with electrical substituted for gravitational attraction. Nagaoka has shown that it is possible to account for both band and line spectra by vibrational disturbances occurring in such a system. It is generally accepted that the negative charge residing on each electron and its mass are always the same, and that the various chemical atoms differ amongst themselves in the number of electrons present, and also possibly in the mass of the central positive nucleus.

Runge and Paschen calculate the ratio of the charge e to the mass m from their measurements of the normal triplets in the mercury spectrum. The difference of oscillation frequency between the two outer components is $2{\cdot}14$ in a field of 24,600 C.G.S. units, if by oscillation frequency we define the number

of waves in 1 centimetre. From Preston's equation, given before (p. 533), we have—

$$2{\cdot}14 = \frac{e}{m} \cdot \frac{H}{2\pi v}.$$

Hence, putting H = 24600—

$$\frac{e}{m} = 1{\cdot}6 \times 10^7.$$

In electrolysis $\frac{e}{m} = \frac{N}{A} \times 10^4$, where N and A stand for valency and atomic weight respectively; hence for hydrogen $\frac{e}{m} = 10^4$. Then, assuming that the charge on the negative particle is equal to the unit charge in electrolysis, it follows that the mass of the electron is about one-sixteen-hundredth of the mass of a hydrogen atom. This agrees with the conception given above that the mass of the positively charged particle is so large compared with the negatively charged particle that it takes no part in the vibrations giving rise to the line. The forces which set the negative particles in motion will, indeed, also move the positive nuclei, but on account of their inertia being more than a thousand times greater, the motions produced, and hence the disturbances in the magnetic field, will be correspondingly smaller.

Turning our attention to the spectra of the alkali metals, we have, as described in Chapter XVII., three series of pairs, or six series altogether; that is to say, one principal group and a first and second subordinate group, each group being a series of pairs. Similar groups exist in the spectra of copper and silver, and in those of aluminium, indium, and thallium, only in the last three the principal series have not yet been discovered.

In sodium as yet only the two D lines have been observed in the magnetic field, and as these two form the first member of the principal series, we are thus able to determine the type of the principal series. D_1 gives in the magnetic field four components, and D_2 six components, and in each case the two innermost components are polarised in the plane parallel to

the lines of force. The measurements of the distances between the components as given by Runge and Paschen are as follows, the numbers being in the scale of oscillation frequencies and referring to a field of about 32,000 C.G.S. units:—

D_1	− 1·88	− 0·90p		+ 0·93p	+ 1·85	
D_2	− 2·28	− 1·43	− 0·47p	+ 0·46p	+ 1·35	+ 2·36

It will be seen how the numbers are very closely, in the case of D_1, even, and in the case of D_2, odd multiples of 0·46. These may, therefore, be represented by the accompanying diagram (Fig. 180).

The principal series in copper and silver, of which only the first terms are known, show exactly the same types with equal separation in the same field. The second subordinate group

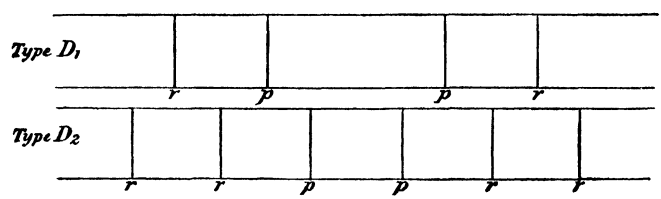


FIG. 180.

shows, as far as observed, the same types as the first group, but in a reversed sense; that is to say, in each pair of the second subordinate group the line with the smaller value of oscillation frequency shows the type of D_2, while the type of D_1 is given by the line with the greater oscillation frequency. This inversion agrees with the general connection Rydberg discovered between the principal and the second subordinate series (*vide* p. 581).

The first subordinate series gives other types in the magnetic field. In the case of copper, silver, aluminium, and thallium, in every pair the line of smaller frequency is accompanied on the side nearer the red by a satellite. Both of the lines of each pair are split into three, like the normal triplets, and the components of the line of smaller frequency are

abnormally thick, and the components of the other lie very close together. The satellite gives eight components, six at right angles to the lines of force and the two innermost parallel; of all these lines no accurate measurements have as yet been made. It is interesting to note how the same types are to be found in elements so far removed from one another in a chemical sense as aluminium and thallium on the one hand and copper and silver on the other.

The same types are also to be found in the case of certain lines in magnesium, calcium, strontium, and barium, and probably also zinc and cadmium, namely, those lines which Rydberg showed to be pairs with equal difference of frequency. By observation in the magnetic field Runge and Paschen have shown that these lines entirely correspond to the pairs observed in the case of sodium, copper, silver, aluminium, and thallium. The H and K lines of calcium, $\lambda = 3969$ and 3934, give the types of D_1 and D_2 respectively, and therefore must form the first member of the principal series of calcium, corresponding to the D lines themselves, the silver lines at $\lambda = 3383$ and 3281, and the copper lines at $\lambda = 3274$ and 3248. The two calcium lines at $\lambda = 3737$ and 3706, which have the same frequency difference as the H and K lines, show the D_1 and D_2 types in reversed order, and therefore these lines form a pair in the second subordinate series. The first subordinate series is represented by the lines $\lambda = 3179{\cdot}45$ and $\lambda = 3158{\cdot}98$, of which the first named is accompanied by a satellite. The type agrees entirely with that of the first subordinate series in copper, silver, aluminium, and thallium. This agrees with Rydberg's apportioning of the lines, which is thus entirely confirmed.

The following table includes the lines in the spectra of magnesium, calcium, strontium, and barium, which give the same types as occur in the cases of sodium, copper, silver, aluminium, and thallium :—

	Principal series.		First subordinate series.			Second subordinate series.	
	D_1 type.	D_2 type.	Type of satellite, *i.e.* eight components.	Triplet.	Triplet.	D_2 type.	D_1 type
Magnesium .	2802·80	2795·63		2798·07	2790 88	2936·61	2928·74
Calcium . .	3968 63	3933·83	3181·40	3179·45	3158·98	3737·08	3706·18
Strontium. .	4215·66	4077·88	3475·01	3464·58	3380·89	4305·60	4161·95
Barium . .	4934·24	4554·21	4166·24	4130·88	3891·97	4000·13	4525·19

Some observations have also been carried out upon the resolution of the lines of helium and the green line of mercury ($\lambda = 5461$) by Gray, Stewart, Houstoun, and McQuistan,[1] who used an echelon grating as the spectroscopic apparatus. They only carried their observations up to a field strength of about 10,000 G.C.S. units, owing to the fact that with higher field strengths the light became too feeble. The results obtained across the lines of force show quite clearly that the separation of the components is proportional to the field strength. All the lines resolved themselves into normal triplets, and from the measured separations the following values were obtained:—

	Wave-length.	$\frac{\delta\lambda}{H}$	$\frac{\delta\lambda}{H\lambda^2}$	$\frac{e}{m}$
Helium	5016	$1{\cdot}61 \times 10^{-5}$	$6{\cdot}41 \times 10^{-5}$	$1{\cdot}21 \times 10^{7}$
,,	5876	$2{\cdot}07 \times 10^{-5}$	$6{\cdot}00 \times 10^{-5}$	$1{\cdot}13 \times 10^{7}$
,,	6678	$2{\cdot}90 \times 10^{-5}$	$6{\cdot}49 \times 10^{-5}$	$1{\cdot}22 \times 10^{7}$
Mercury	5461	$2{\cdot}12 \times 10^{-5}$	$7{\cdot}12 \times 10^{-5}$	$1{\cdot}34 \times 10^{7}$

When with the given line of mercury under observation the field strength was increased to 13,000 G.C.S. units, the centre component of the normal triplet was doubled, while each of the outer components was tripled. The polarisation of the two triplets and of the central doublet was the same as that of the lines from which they originated. In all fields up to

[1] *Proc. Roy. Soc.*, **72**. 16 (1903).

13,000 C.G.S. units, the faint companion to the helium D_3 line was not tripled, but only doubled.

Along the lines of force the following results were obtained :—

	Wave-length.	$\frac{\delta\lambda}{H}$	$\frac{\delta\lambda}{H\lambda^2}$	$\frac{e}{m}$
Helium	5016	$1{\cdot}75 \times 10^{-5}$	$6{\cdot}95 \times 10^{-5}$	$1{\cdot}31 \times 10$
,,	5876	$2{\cdot}25 \times 10^{-5}$	$6{\cdot}50 \times 10^{-5}$	$1{\cdot}23 \times 10$
,,	6678	$3{\cdot}13 \times 10^{-5}$	$7{\cdot}01 \times 10^{-5}$	$1{\cdot}32 \times 10$
Mercury	5461	$1{\cdot}88 \times 10^{-5}$	$6{\cdot}31 \times 10^{-5}$	$1{\cdot}20 \times 10$

Some very important and valuable work has been carried out by Purvis[1] on the magnetic resolution of the lines in the spectra of metals for which no series relations yet are known. The metals especially studied by Purvis were the following: Vanadium, platinum, iridium, palladium, rhodium, ruthenium, titanium, chromium, manganese, lead, tin, antimony, bismuth, and gold. In this work a large concave grating of 21 feet radius was used and the measurements were all made upon photographs. In the case of these metals it was found that most of the lines gave triplets, but that these triplets differed as regards the sharpness and separation of their components. Again, the components of the strongest lines are found not in all cases to be the most widely separated. The weaker lines gave much larger values of $d\lambda$ than the stronger lines, and further, the value of $\frac{d\lambda}{\lambda}$ for the components of some of the triplets formed simple multiples of the values for the other components. It was found also that the same types were repeated in each spectrum and also close analogies were found to exist between the types given by analogous metals such as rhodium and palladium. Perhaps the most interesting part of Purvis' work deals with the occurrence in the spectra of gold, lead, antimony, bismuth, and tin of types analogous

[1] *Trans. Phil. Soc. Cambridge*, **20**. 193 (1906); *Proc. Phil. Soc. Cambridge*, **13**. 82 (1905); **13**. 325 and 354 (1906); **14**. 41 and 217 (1907); **15**. 45 (1909); *Phys. Zeitschr.* **8**. 594 (1907).

to those found by Runge and Paschen for the principal and subordinate series of sodium, copper, silver, aluminium, magnesium, thallium, calcium, strontium, and barium. For example, it was shown above that the silver line $\lambda = 3383$ and the copper line $\lambda = 3274$ gave resolutions similar to that of the D line. This close similarity is shown in the following table:—

Cu	Ag	Au	Pb	Pb	Sb	Sb	Mean.
3274	3383	3029·3	3740·1	2873·4	3722·9	3638	
+2·03	+2·05	+2·15	+2·00	+2·05	+2·21	+2·11	+2·08
+0·97	+0·96	+0·99	+0·95	+0·97	+1·01	+0·99	+0·98
0	0	0	0	0	0	0	0
−0·97	−0·96	−0·99	−0·95	−0·97	−1·01	−0·99	−0·98
−2·03	−2·05	−2·15	−2·00	−2·05	−2·21	−2·11	−2·08

It will be noticed that the distances are multiples of about 0·98. The tendency of these metals to show reversals and to give ill-defined components in the case of the lines of high refrangibility prevent very accurate measurements, so that although the lines gold $\lambda = 2676$, antimony $\lambda = 2668$, and bismuth $\lambda = 2989$, give quadruplets analogous to the above, yet the values of $\frac{d\lambda}{\lambda^2}$ are not so accurately comparable, as may be seen from the following table:—

Gold	Antimony.	Bismuth.	Mean.
2676·1	2668·9	2989·1	
+1·95	+2·26	+1·99	+2·07
+1·06	+1·00	+0·82	+0·96
0	0	0	0
−1·06	−1·00	−0·82	−0·96
−1·95	−2·26	−1·99	−2·07

In the third table below are given certain lines, the

resolutions of which are very comparable, and it is interesting to notice that the mean value of $\frac{d\lambda}{\lambda^2}$ is the same as that of the outer component given above.

Lead	Lead.	Tin.	Tin.	Tin.	Tin.
4062·3	3639·7	3175·1	3009·2	3033	2840
+2·12 0 −2·13	+2·07 0 −2·04	+2·12 0 −2·12	+2·00 0 −2·02	+2·12 0 −2·16	+2·00 0 −2·02
Tin.	Antimony.	Bismuth.	Gold.	Gold.	Mean.
2706·6	3029·9	4121·7	3898	2913·6	
+2·19 0 −2·22	+1·95 0 −2·00	+2·22 0 −2·22	+2·17 0 −2·12	+2·01 0 −1·98	+2·08 0 −2·08

Perhaps one of the most important extensions of the Zeeman effect is that which has been carried out in recent years in its application to absorption bands. Reference may first be made to a paper by Zeeman,[1] in which he deals with the magnetic rotation of the plane of polarisation in the neighbourhood of an absorption band. In a later paper, Zeeman and Geest[2] show that if light is passed through sodium vapour under very reduced pressure parallel to the magnetic lines of force, the plane of polarisation is rotated positively for all periods lying outside the components of a doublet, but in a negative direction between those of the two components. On the other hand, if the light traverses the sodium vapour normally to the magnetic field double refraction is observed. These results follow naturally from Voigt's magneto-optic theory. Then the resolution of the

[1] *Koninh. Akad. Wetensch. Amsterdam, Versl.*, **11.** 6 (1902).
[2] *Ibid.*, **13.** 516 (1905).

absorption bands given by various crystals in the magnetic field has been studied by J. Becquerel, who finds that in the case of xenotime examined by means of light transmitted normally to the magnetic field, the displacement of the bands is much greater than would be expected from a knowledge of the Zeeman effect, and furthermore the band at $\lambda = 5221{\cdot}4$ is circularly polarised in an opposite sense to that previously observed. Becquerel afterwards points out that his experiments on xenotime show that both positive and negative electrons are similarly present, for which $\frac{e}{m}$ can reach a value of $1{\cdot}1 \times 10^8$, which is 6 to 10 times greater than that of the cathode corpuscles. In a further paper, Becquerel publishes some more results on xenotime and tysonite, some of the experiments described having been carried out at the temperature of liquid air.[2] These results of Becquerel have been confirmed by Dufour,[3] who found that the flame spectra of the fluorides and chlorides of calcium, barium, and strontium gave bands which, when viewed in a magnetic field parallel to the lines of force, showed circular polarisation in a direction indicating the presence of positive electrons. Similar results were also obtained with the secondary spectrum of hydrogen, the lines of which were grouped in three classes—those which do not show the Zeeman effect, those which show it normally, and those which show it abnormally. This latter effect Dufour attributes to the presence of positive electrons. Becquerel's observations at the temperature of liquid air were afterwards extended by him and Kamerlingh Onnes,[4] for they examined the banded absorption spectra of a number of minerals down to as low as $-259°$ C. in the magnetic field. The advantage of this method is that the bands become very narrow and frequently resolve themselves into lines, and the

[1] *Comptes Rendus*, **142.** 775 and 872 (1906); **143.** 890 (1906); **144.** 132 (1907).

[2] *Ibid.*, **144.** 682 (1907).

[3] *Ibid.*, **146.** 118, 229 and 634 (1908); *Phys. Zeitschr.*, **10.** 124 (1909).

[4] *Konink. Akad. Wetensch. Amsterdam, Proc.*, **10.** 592 (1908).

observations afford strong support to the argument in favour of the existence of positive electrons.

In a later paper, Dufour[1] showed that the magnetic resolution of certain emission lines of chromium is not symmetrical with regard to the undisturbed line, but to a line shifted towards the blue. This has been confirmed by Becquerel[2] for the doublet of the absorption band of xenotime.

Similar asymmetric resolutions were observed by Dufour[3] in the case of the halogen salts of calcium and strontium. This asymmetry is found to be proportional to the square of the magnetic field strength. Although Dufour, as stated above, finds evidences of asymmetry in certain cases of the Zeeman effect, yet he was not the first to discover this phenomenon, for Zeeman[4] himself found it in the case of the yellow line of mercury $\lambda = 5791$. He found also that the mercury line $\lambda = 5770$ gives a perfectly symmetrical triplet. In the case of the asymmetric triplet given by $\lambda = 5791$, the distance between the middle line and the component on the blue side is greater than the distance between the central line and the component on the red side, and the difference between these two distances is defined as the asymmetry. In magnetic fields of 15,000–30,000 gauss, the asymmetry amounts to from 0·025 to 0·048 A.U. Gmelin[5] criticised these observations of Zeeman, saying that the outer components of the triplets are perfectly symmetrically placed as regards the original position of the undisturbed line, but that the central line of the triplet does not occupy the same position as the original line.

Again, von Baeyer and Gehrcke[6] also investigated the magnetic resolution of the above two lines, and in neither case did they detect any asymmetry of the outer components.

[1] *Comptes Rendus*, **148**. 1594 (1909).
[2] *Ibid.*, **149**. 200 (1909).
[3] *Ibid.*, **150**. 614 (1910).
[4] *Koninк. Akad. Wetensch. Amsterdam, Proc.*, **10**. 551 (1907).
[5] *Phys. Zeitschr.*, **9**. 212 (1908).
[6] *Vehr. d. Deutsch. Phys. Ges.*, **10**. 357 and 423 (1908).

They concluded that Zeeman's observations of asymmetry were due to the fact that the middle component is broad and ill-defined.

Zeeman[1] showed how the Fabry and Perot étalon can be used for the examination of the magnetic resolution, and by the use of this apparatus he succeeded in proving conclusively that the mercury line $\lambda = 5791$[2] is asymmetrically resolved, and that the asymmetry is not to be explained by a difference in the position of the middle line of the triplet from that of the original line. He also noticed similar cases of asymmetry among the tungsten and molybdenum lines. By the use of an echelon grating, Zeeman[3] has finally confirmed his observations.

The investigation of the asymmetric resolution first observed by Zeeman for the bands of tungsten and molybdenum was continued by Jack.[4]

A considerable amount of work has been done during the past six years on the types given by emission lines in the magnetic field; for example, Lohmann examined a few lines of mercury, helium, and neon, and found that the mercury line $\lambda = 5770$ gives in weak fields a normal triplet which is resolved into a nonet in stronger fields. This nonet possesses an abnormal distribution of intensity, because the strongest of its components vibrating perpendicularly to the lines of force appears at the outside of the system. This also appears in the neon spectrum. Generally speaking, the types of resolution in neon are very numerous, with but little regularity amongst them. Only two pairs occur with equal frequency difference, and there is no fundamental difference interval, as appears in the mercury spectrum. The observed types are derived from the normal triplet by its resolution into 2, 3, 4, or 5 components. Three of the nonets show normal intensity distribution, and four of them the abnormal as specified above for the mercury line $\lambda = 5770$.

[1] *Koninkl. Akad. Wetensch. Amsterdam, Proc.*, **10**. 440 (1908).

[2] *Archives Néerlandaises*, **13**. 260 (1908).

[3] *Ibid.*, **14**. 267 (1909).

[4] *Proc. Roy. Soc. Edinburgh*, **29**. 75 (1908-1909); *Ann. der Phys.*, **28**. 1032 (1909).

Runge[1] deals with a number of lines showing complex types of resolution, and finds that there is always some simple relation between the distance of the various components from the centre of the undisturbed line. These distances he finds to be multiples of the normal interval a. He finds the actual aliquot parts to be $\frac{a}{2}, \frac{a}{3}, \frac{a}{4}, \frac{a}{5}, \frac{a}{6}, \frac{a}{7}, \frac{a}{11}$ and $\frac{a}{13}$. This is known as Runge's Law.

Lohmann[2] shows that each of the helium lines is resolved into a normal triplet the separation of which is the same for all, and is directly proportional to the strength of the field. The two satellites of the line $\lambda = 5876$ are each resolved into two triplets, which have the same separation as the normal triplets, so that it would seem that the helium atom must be the simplest of all the known elements.

Nagaoka[3] describes the resolution of the mercury line $\lambda = 5770$ which gives a nonet, and he also finds that Runge's Law is obeyed. The difference in the vibration of the lines can be expressed by—

$$0, \quad \pm\frac{a}{8}, \quad \pm\frac{8}{8}a, \quad \pm\frac{9}{8}a, \quad \pm\frac{10}{8}a,$$

where $a = \frac{e}{m} \times \frac{H}{4\pi}$. He points out that three different classes of nonets may be derived from the normal triplet, namely, (1) as above.

$$(2)\ 0, \quad \pm\frac{a}{4}, \quad \pm\frac{4}{4}a, \quad \pm\frac{5}{4}a, \quad \pm\frac{6}{4}a.$$

$$(3)\ 0, \quad \pm\frac{a}{2}, \quad \pm\frac{2}{2}a, \quad \pm\frac{3}{2}a, \quad \pm\frac{4}{2}a.$$

Of these (1) is represented by the mercury line $\lambda = 5770$, (2) by the neon lines $\lambda = 6678$ and $\lambda = 6005$, and (3) by the mercury line $\lambda = 5461$. Possibly there is a fourth type :—

[1] *Phys. Zeitschr.*, **8**. 232 (1907).
[2] *Ibid.*, **9**. 145 (1908).
[3] *Nature*, **83**. 276 (1910).

$$0, \quad \pm\frac{a}{16}, \quad \pm\frac{16}{16}a, \quad \pm\frac{17}{16}a, \quad \pm\frac{18}{16}a,$$

and the copper line $\lambda = 5105$ seems to belong to this type.

Nagaoka further points out that triplets which show broadening of the line and no asymmetry in strong fields and give values of $\frac{e}{m}$ greater than $1{\cdot}87 \times 10^7$ belong to some of the intermediary types.

It appears from later researches that the statement that the magnetic resolution is proportional to the field strength is not strictly true. Voigt has pointed out that the displacement of the outer components of the Zeeman triplets plotted against the strength of the magnetic field is represented by an hyperbola approximating asymptotically to a straight line in strong fields where most of the previous observations have been made. Nagaoka and Amano[1] have shown that the Voigt effect can be observed on the gold line $\lambda = 6276$ in a field of 240 gauss, and on following the curve to strong fields it is represented approximately by an hyperbola with very short axis. Similar effects were also observed with the gold line $\lambda = 5835$ and the copper line $\lambda = 5105$. In a later paper Nagaoka has shown that the linear relation holds good in the case of observations parallel to the lines of force, and that $\frac{d\lambda}{H}$ is constant between 180 and 14000 gauss for the three helium lines $\lambda\lambda = 6678$, 5879, and 5016. Across the lines of force $\frac{d\lambda}{H}$ is not constant in weak fields. In the case of the helium line $\lambda = 5876$, the curve representing the relation between H and $d\lambda$ is such that it increases very slowly up to when $H = 800$, and then rapidly up to when $H = 1700$. It then bends, and between $H = 2000$ and $H = 14000$ it follows an accurately straight course. The constant value of $\frac{d\lambda}{H}$ in the strong fields is smaller than the constant value obtained along the lines of force. Nagaoka

[1] *Nature*, **79**. 221 (1908), and *Mathematico-Physical Soc., Tokyo, Proc.*, **4**. 421 (1908) and **5**. 278 (1910).

points out that there is a striking similarity between the curve for the transversal effect and that of the magnetisation of ferromagnetic substances and also that his results explained the discrepancy in the values of $\frac{e}{m}$ determined from longitudinal and transverse measurements.

Perhaps one of the most brilliant applications of the Zeeman effect is that by Hale[1] to the investigation of sunspots. It had been previously shown by him that sunspots consist of vortices. He succeeded in doing this by photographing the solar surface by means of the Hα hydrogen rays with the large spectro-heliograph at Mount Wilson observatory. Since the solar prominences are known to consist of glowing hydrogen it is evident that such photographs will show clearly the distribution of hydrogen upon the surface of the sun. These photographs showed clear evidences of powerful cyclonic movement and also the absorption of a dark hydrogen flocculus into the disturbed area of a spot on July 3rd, 1908. The mean of six observations gave the velocity of the flocculus as 106 kilometres per second. Discussing the magnetic field associated with large sunspots, Hale suggests that there should exist magnetic lines of force perpendicular to the plane of the vortex. If this were true, the light from the spot radiated along these lines, should, of course, produce a doubling of the spectrum lines, with the two components circularly and oppositely polarised. Hale found the iron line $\lambda = 6302{\cdot}71$ to be doubled, thus clearly proving the existence of the magnetic field within the spot.

In a second paper Hale[2] gives more exhaustive evidence in support of the conclusions of his first paper. It is evident that if the magnetic field does exist, as the spot reaches the edge of the sun, the doublet should appear as a triplet since the observation will then be made across the magnetic lines of force. The difficulty of such observations will be apparent when it is considered that the image of the spot becomes reduced to a narrow line difficult to keep on the slit of the

[1] *Astrophys. Journ.*, **28**. 100 (1908).
[2] *Ibid.*, **28**. 315 (1908).

spectroscope, but sufficient evidence was obtained to indicate that the components are plane polarised, as would follow from the simple theory. There is no reason to doubt, therefore, that sufficient evidence has been gained to justify the statement that sunspots are in reality vortices with high velocity, and that the rotating particles give rise to a magnetic field of force.

Although, perhaps, strictly speaking, it should not be dealt with in this chapter, yet it is difficult to pass by without mention the work of Wood[1] upon the magneto-optics of sodium vapour. When plane polarised white light is passed through sodium vapour in a magnetic field along the lines of force, a Nicol prism set to extinction will now transmit a brilliant orange light. When this light is analysed in the spectroscope it is seen to consist of a large number of bright lines in the greenish blue and in the red. These lines form the magnetic rotation spectrum, and Wood has shown that they are narrow regions, possibly less than a tenth of an Ångström wide, in which the light has been rotated through various degrees, enabling it to pass through the analysing Nicol. A full description of Wood's work would take far too much space, but reference may be made to his many papers on the subject.

Reference may also be made to the important work upon the Zeeman effect by Moore,[2] King,[3] Stock,[4] and Babcock.[5]

[1] *Phil. Mag.*, **10.** 408 (1905); **12.** 499 (1906); **14.** 145 (1907); **15.** 274 (1908); **18.** 530 (1909). *Astrophys Journ.*, **18.** 94 (1903); **30.** 339 (1909), **33.** 72 (1911). *Phys. Rev.*, **21.** 41 (1905). *Phys. Zeitsch.*, **11.** 1195 (1910).

[2] *Astrophys Journ.*, **28.** 1 (1908); **30,** 144 and 178 (1909); **33.** 385 (1911). *Phys. Zeitschr.*, **10.** 297 (1909).

[3] *Astrophys. Journ.*, **30.** 1 (1909).

[4] *Phys. Zeitschr.*, **10.** 694 (1909).

[5] *Astrophys. Journ.*, **33.** 207 (1911).

CHAPTER XVII

SERIES OF LINES IN SPECTRA

OF the older work on this subject there is no need to make mention, because, although certain regularities had been noticed, the first important work to come under our consideration is that by Balmer, who was the first to show that the lines of a spectrum could be expressed by a formula. This important discovery was made with the hydrogen elementary spectrum. Balmer[1] showed that the wave-lengths of the first nine lines of the hydrogen spectrum can be expressed by the equation—

$$\lambda = h\frac{m^2}{m^2 - 4} \times 10^{-8} \text{ cm.},$$

where h is a constant and m is given the values 3, 4, 5, 6, etc., up to 11. The value of h was found to be 3645, and the calculated values of the wave-lengths of the lines agreed with the values actually measured within the limits of experimental error. As the number of hydrogen lines was extended into the ultra-violet from their discovery in the stars, and in the solar prominences and "flash" spectrum, and as their wave-lengths were better determined, it was found that Balmer's formula gave results which agreed in a most surprising way with those actually measured; proof was thus afforded that the wave-lengths are functions of successive whole numbers, that is to say, the lines of the hydrogen spectrum form a series, and the wave-lengths of any line can be expressed as a simple function of its number in the series. In order to show how accurately this formula expresses the measured wave-lengths, the following measurements obtained by Evershed[2] from photographs of the

[1] *Ann. der Phys.*, **25**. 80 (1885).

[2] *Phil. Trans.*, **197**. A, 381 (1901), and **201**. A, 457 (1903).

solar eclipse of January 22, 1898, may be given. The column headed "calculated" contains the values obtained from the formula of Balmer, in which h is put equal to 3646·13. The wave-lengths have been reduced to vacuum; the last column gives the differences between the observed and calculated values.

HYDROGEN SPECTRUM.

Designation.	Observed.	Calculated.	Difference.
α	6563·07	6563·03	+0·04
β	4861·57	4861·52	+0·05
γ	4340·53	4340·63	−0·10
δ	4102·00	4101·90	+0·16
ϵ	3970·33	3970·22	+0·11
ζ	3889·15	3889·20	−0·05·
η	3835·51	3835·53	+0·02
θ	3798·00	3798·04	−0·04
ι	3770·73	3770·77	−0·04
κ	3750 27	3750·30	−0·03
λ	3734·53	3734·51	+0·02
μ	3721·98	3722·08	−0·10
ν	3712·13	3712·11	+0·02
ξ	3704·01	3704·00	+0·01
o	3697·28	3697·29	−0·01
π	3691·70	3691·70	±0·00
ρ	3686·96	3686·97	−0·01
σ	3682·94	3682·95	−0·01
τ	3679·52	3679·49	+0·03
υ	3676·51	3676·50	+0·01
ϕ	3673·87	3673·90	−0·03
χ	3671·53	3671·48	+0·05
ψ	3669·55	3669·60	−0·05
ω	3667·83	3667·82	+0·01
Series No. 27	3666·25	3666·24	+0·01
,, ,, 28	3664·74	3664·82	−0·08
,, ,, 29	3663·55	3663·54	+0·01
,, ,, 30	3662·36	3662·40	−0·04
,, ,, 31	3661·31	3661·35	−0·04
,, ,, ∞	Theoretical limit	3646·13	—

It can be seen at once from Balmer's formula that if m be put less than 3, indeterminate and negative values are obtained; and further, as m becomes larger the value of the coefficient $\frac{m^2}{m^2 - 4}$ becomes nearer to unity, and therefore we may say that the end of the series ($m = \infty$) lies at $\lambda = h =$

3646·13. It will be seen that as we advance in the series towards the ultra-violet the lines are nearer and nearer together, until the theoretical limit is reached. The agreement between the calculated and found values, as will be seen, is extraordinarily close.

At the present time we know of the existence of similar series in the line spectra of certain elements, and for this knowledge we are indebted to Rydberg, and to Kayser and Runge, who have found formulæ which express with a considerable degree of accuracy the lines which belong to these series. Rydberg published a full description of how he obtained his formula, and the results of its application to known results in the *Transactions of the Royal Swedish Academy* in 1890.[1] Runge,[2] in 1888, stated that he had discovered a number of harmonic series in the spectra of certain elements, and that these can be expressed by a formula of the type—

$$\frac{1}{\lambda} = a + \frac{b}{n} + \frac{c}{n^2} \text{ or } \frac{1}{\lambda} = a + \frac{b}{n^2} + \frac{c}{n^4}.$$

Balmer's formula may be looked upon as a specially simple case of the above; for, instead of

$$\lambda = h\frac{m^2}{m^2 - 4}$$

we may put $$\frac{1}{\lambda} = A\frac{m^2 - 4}{m^2}, \text{ where } A = \frac{1}{h},$$

and $$\frac{1}{\lambda} = A + \frac{B}{m^2}, \text{ where } B = -4A.$$

Rydberg, however, claims to have been using his formula before 1885, when Balmer's was first published.

Rydberg has given a very complete description of how he arrived at his formula in the paper above referred to, and it is necessary to discuss this work very fully in order to understand the extremely interesting results he has obtained in the connection between the various series of lines belonging to the

[1] *K. Svenska Vetensk. Akad. Hand.*, vol. xxiii., No. 11 (1890)

[2] *Brit. Ass. Report* (1888), 576.

same element as well as the actual expression of the lines in series.

Two very important observations, one by Hartley and the other by Liveing and Dewar, must first be mentioned. In the first place, Hartley[1] found that if the lines in a spectrum are expressed in oscillation frequencies and not in wave-lengths, then the differences between the components of the doublet or triplet are the same for all the doublets or triplets in the same spectrum. Hartley only examined the triplets in the spectra of magnesium, zinc, and cadmium, and as an example three triplets of the zinc spectrum may be given—the oscillation frequencies are only given to four figures—

		Diff.		Diff.	
1	2079	910	2989	582	3571
Diff.	39		39		38
2	2118	910	3028	581	3609
Diff.	18		18		20
3	2136	910	3046	583	3629

The numbers 1, 2, and 3 refer to the first, second, and third members of the triplets; it will be seen that the difference between the first and second member is about 39, and between the second and third it is about 18.

The second discovery, by Liveing and Dewar,[2] was that of the existence of homologous series of lines, although they did not find the law of the series. They established also the existence of a series of lines which are sharp, and a similar series of diffuse lines.

Rydberg calculated the oscillation frequency of the observed lines in a great number of elementary spectra, and selected the doublets and triplets of constant frequency difference. It should be pointed out that by the oscillation frequency Rydberg means the number of waves contained in 1 centimetre, and as the accuracy of the measurements he deals with are great compared with the accuracy of the determination of the index of refraction of air as known at that time, they are not reduced to vacuum. As regards the doublets and triplets, these may often

[1] *Chem. Soc. Trans.*, **43**. 390 (1883).
[2] *Phil. Trans.*, **174**. 187 (1883).

be recognised by the eye, as, for example, in the case of sodium, but often the components are very far removed from one another, there being a considerable number of rays in between them. The names of doublet and triplet might be thus considered as rather misnomers, were they not defined in the first place as merely pairs or trios of lines with a constant frequency difference. In speaking of these differences in frequency, for simplicity's sake we will use Rydberg's notation throughout, and speak of the frequency difference of a doublet as ν, and that between the first two and second two members of a triplet as ν_1 and ν_2. Further, the component of a doublet or triplet with the smallest frequency is called n_1, and the next in order of magnitude n_2, and the third member (of a triplet) n_3; we therefore have—

$$\nu = n_2 - n_1 \text{ with a doublet,}$$

and $\nu_1 = n_2 - n_1$

and $\nu_2 = n_3 - n_2$ } with a triplet.

As was said before, Rydberg calculated the frequencies of the known lines of a number of elements, and selected the doublets and triplets of constant frequency difference therefrom. Then, assuming that analogous rays of a spectrum are functions of a series of consecutive whole numbers, or, in other words, that the analogous rays form a simple series, he attempted to find the graphical relation between the rays. He placed the wave-length upon the ordinates and the number of the ray in the series on the abscissæ, calling the least refrangible of the analogous rays number 1. In this way he obtained for the double and triple series two or three curves, which became parallel to one another when oscillation frequencies were used instead of wave-lengths.

If now we consider the case of sodium and take the least refrangible rays of the doublets, we then have, on Ångström's scale—

m	λ	m	λ	m	λ
1	8199	5	5155·0	9	4543·6
2	6160	6	4983·0	10	4496·4
3	5895	7	4751·4	11	4423·0
4	5687	8	4667·2	12	4393·0

where m is the order or number of the rays. On plotting these numbers Rydberg found that they did not form a regular curve, but that the points lay first on the one side and then on the other side of a mean curve; this anomaly disappeared entirely when the ray at $\lambda = 5895$ was suppressed, and the remaining rays were taken alternately to form two series, thus—

m	1	2	3	4	5	6
λ_1	8199	5687	4983·0	4667·2	4496·4	4393
λ_2	6160	5155	4751·4	4543·6	4423·0	

Now, as each of these rays is the component of a doublet, we have evidently two series of pairs, or four series of lines. It is most important to remember that Liveing and Dewar observed all these rays, and found that those in the upper line are all diffuse, and that those in the lower line are sharp, so that one could distinguish between the two series independently of the curves just described.

It was found on comparing the curves together that they all had the same general shape, and therefore Rydberg concluded that they could all be expressed by a common formula. As the curves appeared to approximate to rectangular hyperbolas, Rydberg first took the formula—

$$(\lambda - \lambda_0)(m + \mu) = \text{constant, in wave-lengths,}$$

or $$(n - n_0)(m + \mu_1) = C_1, \text{ in oscillation frequencies,}$$

where λ_0, μ and n_0, μ_1 are constants.

Rydberg then calculated the wave-lengths from this formula—

$$\lambda = \lambda_0 + \frac{C}{m + \mu},$$

and found that very fair approximations to the measured values were obtained. Rydberg satisfied himself in this way that the wave-lengths and oscillation frequencies of a series of analogous lines in the spectrum of an element are functions of a series of consecutive whole numbers.

Rydberg next considered the differences between the oscillation frequencies of the successive numbers of the series, and he found that these differences (Δn) become smaller as one goes higher into the series; this, of course, naturally follows

from the fact that the lines of a series get closer together as one advances in the series. The values of Δn were calculated for all the series which could be recognised, and Rydberg obtained in this way series of decreasing values of Δn, one series for each naturally occurring series of spectral lines. Each of these series of values of Δn seemed to be perfectly comparable, so that when these values were arranged according to the magnitude of any term, all the other terms followed one another in the same order of magnitude. This can be best explained by means of the table given by Rydberg of the values of Δn which he obtained.

VALUES OF Δn.

Name of series.	Between $m = 1$ and $m = 2$.	Between $m = 2$ and $m = 3$.	Between $m = 3$ and $m = 4$.	Between $m = 4$ and $m = 5$.	Between $m = 5$ and $m = 6$.	Between $m = 6$ and $m = 7$.	Between $m = 7$ and $m = 8$.	Between $m = 8$ and $m = 9$.
Li (P_{12})	16026·8	5542·4	2556·6	1364·4	824·6	533·8	369·5	258·9
Na (D_1)	—	5386·7	2484·9	1357·9	813·9	523·5	—	—
Ca (D_1)	—	4996·7	2323·9	1246·3	723·4	—	—	—
Na (P_1)	13314·9	4751·4	2280·2	1233·5	—	—	—	—
Tl (S_2)	12278·3	4395·1	2089·6	1213·0	732·4	465·6	350·1	250·2
K (P_1)	11685·9	4303·8	2050·3	1158·0	723·0	451·8	322·5	245·5
Mg (S_1)	10679·5	4017·2	1957·5	1116·5	685·6	—	—	—
Ca (S_1)	8943·7	3507·8	1759·3	1015·0	620·6	—	—	—
Na (S_1)	7484·8	3165·6	1647·0	962·6	600·1	407·6	—	—
K (D_1)	—	2842·7	1507·5	881·2	550·5	385·8	256·9	—
Mg (D_1)	6241·8	2775·3	1476·7	868·4	561·4	—	—	—
Zn (D_1)	5812·3	2636·4	1416·8	862·7	—	—	—	—

In the first column are given the symbols of the elements and the designation of the series, which will be fully explained later. The second column contains the differences between the frequencies of the first and second terms of the series given, the third column contains the frequency differences between the second and third members, and so on. In the table the series are so arranged that the frequency differences in the second column form a descending scale in order of magnitude;

this was done because all the terms of the second column were not known. It will be seen that with very few exceptions all the terms in the other columns are arranged in descending order of magnitude, and further, that the first term of each column is smaller than the last term of the preceding column. Rydberg also expresses these results as follows. The differences between the corresponding terms of any two series of values of Δn have the same sign.

The next step taken by Rydberg was to plot the values of Δn as given in the above table against the series of whole numbers (m) 1, 2, 3, etc.; the curves obtained in this way all had the same shape, so that it seemed probable that they could be made to coincide with one another throughout their length by simply shifting them parallel to the axis of m. This we can express by saying that if Δn is a function of m for one curve, then the general equation to all the curves is—

$$\Delta n = F(m + \mu),$$

where μ is a constant. From this Rydberg derives the equation for a spectral series—

$$n = n_0 - f(m + \mu),$$

where n is the frequency, n_0 is a constant, and $f(m + \mu)$ some function of $(m + \mu)$, which has the same form and the same constants for every member in every series.[1]

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[1] PROOF—

$$\begin{aligned} n_m &= n_{m+1} - \Delta n \\ n_m &= n_{m+1} - F(m + \mu) \\ n_{m+1} &= n_{m+2} - F(m + 1 + \mu) \\ n_{m+2} &= n_{m+3} - F(m + 2 + \mu) \end{aligned}$$

Now, we know that n approaches a limit n_0 when $m = \infty$, and the form of the series of Δn and the shape of the corresponding curves leads us to suppose that the limit of Δn or $F(m + \mu) = 0$ when $m = \infty$; we have, therefore—

$$n_m = n_0 - \sum_m^{\infty} F(m + \mu).$$

For another series we have—

$$n'_m = n'_0 - \sum_m^{\infty} F(m + \mu').$$

Now, the two sums which enter into these equations have the

If we put $f(m+\mu)=\frac{C}{m+\mu}$ we have the equation—

$$n = n_0 - \frac{C}{m+\mu}.$$

We have already seen that a very similar equation—

$$\lambda = \lambda_0 + \frac{C}{m+\mu}$$

expresses a series with a very rough approximation. Considering the shape of the curves already described, obtained by plotting λ against m, the next simplest equation is—

$$n = n_0 - \frac{N_0}{(m+\mu)^2},$$

where N_0 is another constant.

This equation Rydberg finds to answer extraordinarily well, and is the equation he finally adopts; in it N_0 is a constant for all series and all substances, n_0 is the value of n when $m = \infty$; that is to say, it is the theoretical limit of the series, and is generally known as the convergence frequency, and μ is a characteristic constant of the substance or series.

Now, Balmer's hydrogen equation may be considered as a special case of this formula, for if instead of his equation for the wave-length—

$$\lambda = h\frac{m^2}{m^2-4}$$

we put $$n = n_0\frac{m^2-4}{m^2},$$

when $$n = \frac{10^8}{\lambda} \text{ and } n_0 = \frac{10^8}{h}$$

---

same number of terms, and we know that any term in one of the sums only differs from the corresponding term in the other by the value of the constant μ; then one of the sums is changed into the other if μ is changed to μ', whence it follows that there are only two different values of the same function of μ.

Next, putting $$\sum_m^{\infty} F(m+\mu) = f(m+\mu),$$

we have the general equation—

$$n = n_0 - f(m+\mu).$$

then we have $$n = n_0 - \frac{4n_0}{m^2}$$

which equation is evidently the same as Rydberg's general equation, if N_0 in the latter $= 4n_0$ and $\mu = 0$.

In making use of the formula—

$$n = n_0 - \frac{N_0}{(m + \mu)^2},$$

it must be remembered that Rydberg does not claim that it reproduces the measurements of the frequencies of lines with absolute accuracy—he recognises that it is only a very near approximation to the true relations. In comparing the calculated and observed values of frequencies by means of this formula, and by means of the formula of Kayser and Runge, no one will deny that the agreement is often better in the second case. Kayser and Runge's formula expresses a series of lines sometimes with extraordinary accuracy, but there its use ceases, while by Rydberg's formula we are able to trace the connection between the different series, and even to calculate the wave-lengths of the lines of one series from the equation to another series.

The methods of calculating the constants may now be described.

First, to calculate the constant N_0. This has been done once and for all from the Balmer formula for hydrogen. From this formula we have—

$$h = \lambda \frac{m^2 - 4}{m^2}.$$

In calculating the value of h, Rydberg used the old values of the wave-lengths of the hydrogen lines as follows:—

$$h = \lambda \frac{m^2 - 4}{m^2}.$$

Therefore—

$$\begin{aligned} h &= 6562{\cdot}10 \times \tfrac{5}{9} (\text{for } m = 3) = 3645{\cdot}611 \\ &= 4860{\cdot}74 \times \tfrac{3}{4} (\text{for } m = 4) = 3645{\cdot}555 \\ &= 4340{\cdot}10 \times \tfrac{21}{25} (\text{for } m = 5) = 3645{\cdot}684 \\ &= 4101{\cdot}20 \times \tfrac{5}{9} (\text{for } m = 6) = 3645{\cdot}510 \\ &\qquad\qquad\qquad\qquad \text{Mean} = 3645{\cdot}590 \end{aligned}$$

From this $$N_0 = \frac{4 \times 10^8}{3645{\cdot}590} = 109721{\cdot}6.$$

From later measurements of the wave-lengths of hydrogen reduced to vacuum, Rydberg finds the value of this constant to be 109675·00,[1] which he uses in all his more recent work. The other constants n_0 and μ are characteristic of each series or substance, and therefore must be found for each series; before one can calculate them, it is necessary to know all the wave-lengths, or rather oscillation frequencies of the members of the series in question. In order to obtain the very best approximations to the true frequency of the lines Rydberg proceeds as follows. It will be remembered that a complete series consists of a number of terms, each of which is double or triple, and that there is always a constant frequency difference between the first and second and the second and third members respectively along the whole series. In the case of a triplet series, for example, as many triplets as possible are picked out, and the values of the frequency differences ν_1 and ν_2 are found; the mean values of ν_1, ν_2, and $\nu_1 + \nu_2$ are obtained from these, and with the help of these mean values the frequencies of all the second and third members of the triplets are reduced to the scale of the first members; that is to say, from all the second members ν_1 is subtracted, and $\nu_1+\nu_2$ from all the third members. In this way three values for the first member of each term is found, and the mean of these three in each case gives probably a far closer approximation to the true frequency of the first member of each term than the measured value. Perhaps an example will make this clear.

SHARP SERIES OF MAGNESIUM.

m	2	3	4	5	6	7
S_1	19293·8	29973·3	33990·5	35948·0	37064·5	37750·1
ν_1	41·1	40·5	40·5	40·0	42·3	42 8
S_2	19334·9	30013·8	34031·0	35988·0	37105·8	37792·9
ν_2	19·8	24·4	11·6	23·4	20·6	
S_3	19354·7	30038·2	34042·6	36011·4	37126·4	—

[1] *Paris International Reports.* From Evershed's values or hydrogen, given on p. 472, N_0 is 109705·33.

From these the mean values of ν_1, ν_2, and $\nu_1 + \nu_2$ are found to be 41·4, 20·6, and 62·0 respectively, and thus we may reduce all observations to the scale of S_1 as follows :—

S_1 obs.	19293·8	29973·3	33990·5	35948·0	37064·5	37750·1
S_2 red.	19293·5	29972·4	33989·6	35946·6	37064·4	37751·5
S_3 red.	19292·7	29976·2	(33980·6)	35949·4	37064·4	—
Means	19293·3	29974·0	33990·1	35948·0	37064·4	37750·8

This last row of means is adopted as the best value of the frequencies of the first members of the triplets. Attention may be called to the fact here that since ν_1, ν_2 are the differences between the first and second and the second and third members of the triplets, the equations for the three members are the same, except that the value of n_0 differs in each case by the amounts ν_1 and ν_2.

The method of calculation of the constant μ may now be considered.

If n_m and n_{m+1} are the frequencies of two consecutive terms of a series, we have—

$$n_m = n_0 - \frac{N_0}{(m+\mu)^2} \text{ and } n_{m+1} = n_0 - \frac{N_0}{(m+1+\mu)^2},$$

whence $\Delta n = n_{m+1} - n_m = \frac{N_0}{(m+\mu)^2} - \frac{N_0}{(m+1+\mu)^2}$;

it is evident, therefore, that Δn is independent of the constant of the series N_0.

Now, clearly μ lies between 0 and 1, or may be considered as the fractional portion of the quantity $m + \mu$, for if μ were greater than 1, then we could consider m as being increased by 1, and μ again as only the fractional part of the quantity. The finding of μ is rendered much more simple by this arrangement, which in reality makes no difference to the meaning of the equation. The simplest way to find μ is by means of an interpolation table, and Rydberg gives such a table in his paper; this table contains all the values of the term $\frac{N_0}{(m+\mu)^2}$ for all the values of m from 1 to 9, and all the values of μ from 0·00 to 1·00 differing by 0·01. There are also given

the values of Δn, or differences between every two successive values of $\frac{N_0}{(m+\mu)^2}$ formed by increasing m to $m+1$. This table is, unfortunately, calculated out with $N_0 = 109721{\cdot}6$, but with a little trouble any one can calculate such a table with the new constant $N_0 = 109675{\cdot}00$.

In using this table for the finding of μ, first of all the values of Δn for the series are found, and as an example the series of thallium may be quoted as given by Rydberg, for which the values are as follows:—

λ	n	Δn	m
3517·8	28426·9		2
		5845·5	
2917·8	34272·4		3
		2644·3	
2708·8	36916·7		4
		1418·0	
2608·6	38334·7		5
		850·3	
2552·0	39185·0		6
		544·8	
2517·0	39729·8		7

From the table we find that the difference in the value of $\frac{N_0}{(m+\mu)^2}$,

1. When $m = 2$ and $m = 3$ is 5886·2 for $\mu = 0{\cdot}89$ and 5832·8 for $\mu = 0{\cdot}90$
2. When $m = 3$,, $m = 4$,, 2662·3 ,, $\mu = 0{\cdot}89$,, 2644·0 ,, $\mu = 0{\cdot}90$
3. When $m = 4$,, $m = 5$,, 1425·9 ,, $\mu = 0{\cdot}89$,, 1417·8 ,, $\mu = 0{\cdot}90$
4. When $m = 5$,, $m = 6$,, 851·4 ,, $\mu = 0{\cdot}89$,, 847·4 ,, $\mu = 0{\cdot}90$
5. When $m = 6$,, $m = 7$,, 548·8 ,, $\mu = 0{\cdot}89$,, 544·3 ,, $\mu = 0{\cdot}91$

Evidently the value of μ is given by 1. as $0{\cdot}89 + \frac{40{\cdot}7}{53{\cdot}4} \times {\cdot}01$, by 2. as $0{\cdot}89 + \frac{18}{18{\cdot}3} \times 0{\cdot}011$, by 3. as $0{\cdot}89 + \frac{7{\cdot}9}{8{\cdot}1} \times 0{\cdot}01$, by 4 as $0{\cdot}89 \times \frac{1{\cdot}1}{4{\cdot}0} \times 0{\cdot}01$, and by 5. as $0{\cdot}89 + \frac{4}{4{\cdot}5} \times 0{\cdot}02$.

Now, in finding the mean of all the fractions thus given Rydberg weights the values according to the square of the wave-length of the lines; these fractions are, respectively, multiplied by 100, 73, 68, 65, 63, which are the relative weights to be given, then all the numerators are added together and divided by the sum of all the denominators. In this way the

mean comes out to 0·0082, and thus the value of μ is found to be 0·8982.

We have, finally, to find the constant n_0, which may be done as follows:—

Writing the equation—

$$n_0 = n + \frac{N_0}{(m + \mu)^2},$$

the value of n_0 can at once be found for all the analogous lines of the series, and their mean is adopted as n_0. To take an example, the above given values may be used of thallium, for which we have found that—

$$n_0 = n + \frac{109721{\cdot}6}{(m + 0{\cdot}8982)^2}.$$

The values of the last term are calculated for $m = 2, 3, 4$, etc., since these are the numbers of the lines in the series as given above; to the values thus obtained the corresponding frequency n is added, and thus as many determinations of n_0 are obtained as there are lines in the series. These values are weighed as before described according to λ^2, and the mean is then adopted as the constant; in this case its value was found to be 41490·2.

The complete equation is, therefore—

$$n = 41490{\cdot}2 - \frac{109721{\cdot}6}{(m + 0{\cdot}8982)^2}.$$

Relation between the Series belonging to One Element.—There are existent in the spectra of all the alkali metals three different series, namely, the sharp, diffuse, and principal series; the last series Rydberg called the principal series, as it contains the most important lines of the spectrum. It has already been stated that the sharp and nebulous series consist of either doublets or triplets, and the statement may be made that each element possesses two or three sharp series parallel to one another, and the same number of nebulous series also parallel to one another, and the frequency differences of corresponding rays are constant for each element. If, then, n_1, n_2, and n_3

represent the values of the constant n_0 for each of the sharp or nebulous series, we have—

$$n = n_1 - \frac{N_0}{(m+\mu)^2}$$
$$n = n_2 - \frac{N_0}{(m+\mu)^2}$$
$$n = n_3 - \frac{N_0}{(m+\mu)^2}$$

and $n_2 - n_1 = \nu$ in the doublet series, and in the triplet series $n_2 - n_1 = \nu_1$ and $n_3 - n_2 = \nu_2$. There are thus four or six series with each element, and Rydberg calls them the first, second, or third sharp or nebulous series as the case may be. The three sharp series form the sharp group, and similarly we have the nebulous group.

Now Rydberg has found that the value of the constant n_0 is the same for the corresponding sharp and nebulous series. In other words, the convergence frequencies of the corresponding series are the same in the sharp and nebulous groups. If, therefore, we write δ for μ in the equation for the diffuse series, and σ for μ in the sharp series, we have the equations—

Sharp Group.	Nebulous Group.	
$n = n_1 - \frac{N_0}{(m+\sigma)^2}$	$n = n_1 - \frac{N_0}{(m+\delta)^2}$	First series.
$n = n_2 - \frac{N_0}{(m+\sigma)^2}$	$n = n_2 - \frac{N_0}{(m+\delta)^2}$	Second series.
$n = n_3 - \frac{N_0}{(m+\sigma)^2}$	$n = n_3 - \frac{N_0}{(m+\delta)^2}$	Third series.

These equations show fully the connection between the six series. The principal series is a pair series, and had only been properly investigated in the alkali metals, though later Rydberg found them in other substances, as we shall see later on. The pairs in this series have not a constant frequency difference, for the components of each pair get closer together as the order number rises. Evidently, therefore, the two series should have the same convergence frequency, for, since as m gets larger the pairs become closer together, therefore at the limit

when $m = \infty$ they should be an infinitely small distance apart. This is experimentally borne out by the values of n_0 actually obtained. The more refrangible line of the pairs is always the stronger line, so that Rydberg calls the series of less refrangible lines the weak, and the other the strong principal series. The equations are as follows :—

$$n = n_0 - \frac{N_0}{(m + \mu_1)^2},$$

$$n = n_0 - \frac{N_0}{(m + \mu_2)^2}.$$

The connection between the principal series and the sharp series is exceedingly interesting and important. Rydberg found that in the case of sodium, potassium, and rubidium the frequency difference between the members of the first pair of the principal series was almost exactly equal to the constant frequency difference of the pairs of the sharp and nebulous series. We may, therefore, put—

$$\nu = n_0 - \frac{N_0}{(m + \mu_1)^2} - \left\{ n_0 - \frac{N_0}{(m + \mu_2)^2} \right\},$$

whence $$\nu = \frac{N_0}{(m + \mu_2)^2} - \frac{N_0}{(m + \mu_1)^2}.$$

Rydberg has, however, found a very close relation between the sharp and principal series, namely, that they are both parts of the same series with two variables. He arrived at it in this way : In the case of lithium the pairs which undoubtedly exist in the spectrum have not been resolved, so that we have only three series—the principal, sharp, and nebulous series—each term of which is in reality a close pair. Now, Rydberg found for the sharp series of lithium—

$$n = 28601 - \frac{109721{\cdot}6}{(m + 0{\cdot}5951)^2},$$

and for the principal series—

$$n = 43487{\cdot}7 - \frac{109721{\cdot}6}{(m + 0{\cdot}9596)_2},$$

where $m = 2, 3, 4$, etc., for the sharp series, and 1, 2, 3, etc.,

for the principal series. The value $m = 1$ in the first equation gives a negative value of n because the expression $\frac{109721{\cdot}6}{(m + 0{\cdot}5951)^2}$ then equals 43123·7. Now this number is not far from the constant 43487·7 of the principal series equation; again, putting $m = 1$ in the second equation, then—

$$\frac{109721{\cdot}6}{(m + 0{\cdot}9596)^2} = 28573{\cdot}1,$$

a number very close to the constant 28601 of the sharp series equation. Within a close approximation, then, we may write for the principal series—

$$\frac{n}{N_0} = \frac{1}{(1 + 0{\cdot}5951)^2} - \frac{1}{(m + 0{\cdot}9596)^2},$$

and for the sharp series—

$$\frac{n}{N_0} = \frac{1}{(1 + 0{\cdot}9596)^2} - \frac{1}{(m + 0{\cdot}5951)^2}.$$

Or, more generally—

$$\frac{n}{N_0} = \frac{1}{(1 + \mu)^2} - \frac{1}{(m + \sigma)^2} \text{ for the sharp series,}$$

and $$\frac{n}{N_0} = \frac{1}{(1 + \sigma)^2} - \frac{1}{(m + \mu)^2} \text{ for the principal series.}$$

Putting $m = 1$ in both equations, we obtain the same numerical values of n, but the value obtained from the sharp series equation is negative. The first term of the sharp series is the same as the first term of the principal series; in this case the red ray of lithium $\lambda = 6708$. Referring again to the equation for the principal series of lithium given above, and putting $m = 1$—

$$n = 43487{\cdot}7 - \frac{109721{\cdot}6}{(1 + 0{\cdot}9596)^2},$$

but $\frac{109721{\cdot}6}{(1 + 0{\cdot}9596)^2}$ has already been shown to be equal to 28573·1, which is the constant n_0 of the sharp series. In other words, the difference between the convergence frequencies of the principal and sharp series is equal to the frequency of the first

line of the principal series. This relation was later discovered independently by Schuster, and is generally known as the Rydberg-Schuster law.

These relations are very important for several reasons. In the first place, it is possible to calculate the whole of the principal series from the sharp series as follows :—

The sharp series equation is—

$$n = n_0 - \frac{N_0}{(m+\sigma)^2},$$

Putting $m = 1$ we get the negative value of n, which is the first line of the principal series; further, the value of $\frac{N_0}{(1+\sigma)^2}$ is the convergence frequency of the principal series. From these two terms the rest of the calculation is easy. Rydberg applied this in a brilliant manner to the lines of hydrogen; this will be again referred to.

One point more about this connection between the two series; in the alkali metal series each of the terms is a pair, so we therefore have two equations for the principal, and two for the sharp series—

$$\left.\begin{array}{ll} (1) & \frac{n}{N_0} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_1)^2} \\ (2) & \frac{n}{N_0} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_2)^2} \end{array}\right\} \text{Principal series.}$$

$$\left.\begin{array}{ll} (1) & \frac{n}{N_0} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\sigma)^2} \\ (2) & \frac{n}{N_0} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\sigma)^2} \end{array}\right\} \text{Sharp series.}$$

It is a natural consequence of what has gone before that the two series correspond in such a way that the more refrangible ray in the case of the first is analogous to the less refrangible ray of the second, and *vice versâ*. This can readily be seen from the equations; let us put $\mu_1 > \mu_2$, then evidently equation (1) of the sharp series refers to the component rays of the pairs which have the smaller frequency, *i.e.* the less refrangible ray of the pairs, while equation (2) refers to the

more refrangible ray. Putting $m = 1$, then clearly equation (1) of the principal series (which is analogous to equation (1) of sharp series) will refer to the rays with larger frequency, and equation (2) of the principal series refers to the less refrangible rays. The conditions in the principal series are reversed, so to speak, from what they were in the sharp series. This is shown very clearly by the relative brightness of the component lines in the pairs of the two series; for example, in the principal series of the alkali metals the more refrangible component of the pairs is the brighter in each case; in the sharp series it is the less refrangible ray which is the brighter. It is more strikingly, perhaps, shown by means of the Zeeman effect. In Chapter XVI., p. 545, it was shown how the principal series showed two types of resolution, one for the more refrangible ray of each pair, and one for the less refrangible ray; the same types exactly are shown by the sharp series, but in the reverse order, that is to say, the type of D_1, as it is called, is shown by the more refrangible ray of the pair, and the type of D_2 by the less refrangible ray.

Rydberg also deals with another series, one which is attendant on the nebulous series. He was only able to recognise it in the case of thallium, but quite rightly presumed its existence with other elements; it occurs as a series of satellites accompanying the nebulous series. In this series the frequency difference between these rays and the corresponding ray of the nebulous series itself decreases with increase of m. The secondary series have, therefore, the same convergence frequencies as the nebulous series proper.

We may now give the complete scheme for the whole spectrum of an element showing triplets. In this table $\mu_1 > \mu_2 > \mu_3$.

NEBULOUS GROUP.

1st nebulous series	$\frac{n}{N_0} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\delta')^2}$	D'_1
2nd ,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\delta')^2}$	D'_2
3rd ,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\mu_3)^2} - \frac{1}{(m+\delta')^2}$	D'_3

SECONDARY GROUP (NEBULOUS).

1st	secondary series	$\frac{n}{N_0} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\delta'')^2}$	D''_1
2nd	,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\delta'')^2}$	D''_2
3rd	,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\mu_3)^2} - \frac{1}{(m+\delta'')^2}$	D''_3

SHARP GROUP.

1st	sharp series	$\frac{n}{N_0} = \frac{1}{(1+\mu_1)^2} - \frac{1}{(m+\sigma)^2}$	S_1
2nd	,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\mu_2)^2} - \frac{1}{(m+\sigma)^2}$	S_2
3rd	,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\mu_3)^2} - \frac{1}{(m+\sigma)^2}$	S_3

PRINCIPAL GROUP.

1st	principal series	$\frac{n}{N_0} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_1)^2}$	P_1
2nd	,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_2)^2}$	P_2
3rd	,, ,,	$\frac{n}{N_0} = \frac{1}{(1+\sigma)^2} - \frac{1}{(m+\mu_3)^2}$	P_3

There are thus twelve equations, which contain only six constants, if we do not include N_0, which is the same for every series and substance.

In speaking of any line Rydberg uses the symbols given above for the series, and puts the number of the line in its series. Thus Cd [D] means all the rays of the nebulous group of cadmium, including the primary Cd [D'] and the secondary Cd [D'']. Again, Na [P_1. 1] means the first line of the first principal series of sodium, which is the D_2 line, because the first principal series contains the lines of the pairs which have the greater frequency; this is due to the fact that Rydberg views the principal series as really part of the sharp series. Similarly, Rb [S_2 2] is the second line of the second sharp series of

rubidium; it will be remembered that the first line is the first line of the second principal series.

Rydberg gives in the latter portion of his paper the results of the application of his formulæ to the spectra of many metals, and though they need not be reproduced here in any way, on account of the fact that they refer to Ångström's scale, and, further, because the wave-lengths he had to hand were not as accurate as they are at the present time. However, some very interesting conclusions are drawn by him in certain cases, which may be mentioned here.

In the case of the alkali metals the three groups of series have been recognised, though in the case of rubidium and cæsium very few terms indeed were found, only one each, for example, in the sharp and principal series of cæsium. In lithium the series were only found to be single, probably, as Rydberg said, because the pairs were too close to be separated. He pointed out that the frequency difference of the pairs increased with the atomic weight of the elements, and that therefore it would be very small with lithium.

In the spectra of the metals copper, silver, gold, mag nesium, and calcium, Rydberg found certain pairs of constant frequency difference, which he assigned to the principal and the sharp series, an arrangement which has been entirely confirmed by the Zeeman effect.

Before leaving Rydberg's work to treat of Kayser and Runge's in the same domain, attention may be drawn to a brilliant confirmation he made of his theory in connection with the hydrogen spectrum. I have already pointed out how Balmer's formula expressed the whole of the lines of the so-called elementary line spectrum of hydrogen. We may write this formula in the same form as Rydberg's, thus—

$$n = 27418{\cdot}75 - \frac{109675{\cdot}00}{(m+1)^2},$$

where $m = 2, 3, 4$, etc.

Now, in 1896 Pickering[1] discovered in the spectrum of the

[1] *Astrophys. Journ.*, 4. 369 (1896).

star ζ Puppis, which shows the hydrogen spectrum strongly, a new series of lines which is clearly related to the known hydrogen spectrum. Pickering showed that their wave-lengths could be expressed by the modified Balmer's formula—

$$\lambda = 4650\frac{m^2}{m^2 - 4} - 1032.$$

In a further publication Pickering[1] united both the series of hydrogen to one formula as follows: he put $m = \frac{n}{2}$ in the usual Balmer formula, and thus obtained—

$$\lambda = 3646{\cdot}1\frac{n^2}{n^2 - 16}$$

where $n = 6, 8, 10, 12$, etc. He then found that the new series was obtained by putting $n = 11, 13, 15, 17$, etc.

Now, Kayser[2] at once pointed out that there are serious reasons against uniting these two series into one; among these may be asked—If they all belong to one series, why do we always in terrestrial spectra see only the half of the series?

Rydberg[3] brings more conclusive evidence forward in favour of Kayser's views. He first of all shows that the two series have the same convergence frequency, and then finds that the equation for the second series is as follows:—

$$n = 27418{\cdot}79 - \frac{109765{\cdot}00}{(m + 0{\cdot}500737)^2},$$

whence he obtained the following values at 16° and 760 mm. in air:—

m	5	6	7	8	9	10
λ obs.	4201·6	4026·5	3924·9	3858·6	3817·2	3783·4
λ calc.	4201·54	4027·31	3925·18	3859·76	3815·17	3783·35
Diff.	+0·06	−0·81	−0·28	−1·16	+2·03	0·05

The two series thus behave like the nebulous and sharp series

[1] *Astrophys. Journ.*, **5**. 92 (1897).
[2] *Ibid.*, **5**. 243 (1897). [3] *Ibid.*, **6**. 233 (1897).

of hydrogen, and therefore the same deductions may be drawn from them as from the same series with other elements.

Rydberg gives in this paper a most interesting list of the various values of the constant μ he obtained at a later date, which may be given in the following table; according to our notation these are values of δ and σ:—

Element.	Nebulous series.	Sharp series.
Hydrogen	1·000000	0·500737
Helium	0·997273 0·996084	0·858110 0·701464
Lithium.	0·998063	0·597337
Sodium	0·988436	0·649840
Zinc	0·905336	0·269148
Cadmium	0·906478	0·327899
Silver	0·982165	0·447358
Copper	0·975792	0·399765

Now, as was shown above, it is possible to calculate the principal series from a knowledge of the sharp series, and Rydberg does this for hydrogen from the values found for this series. We have the combined formula for the two series in—

$$\frac{n}{109675{\cdot}00} = \frac{1}{(m_1 + 1)^2} - \frac{1}{(m_2 + 0{\cdot}5)^2},$$

using 0·5 instead of 0·50073. For the sharp series $m_1 = 1$ and $m_2 = 1, 2, 3, 4$, etc., and for the principal series $m_2 = 1$, while m_1 varies. From this equation the following values for then principal series were obtained:—

m_1	1	2	3	4	5
n	21325·69	36558·33	41889·75	44357·44	45697·91
λ	4687·88	2734·55	2386·50	2253·74	2187·60

The values of n are for vacuum, but those of λ are reduced to air at 16° and 760 mm. in order to agree with the observations. Now, only the first of this series would appear in the spectra of stars on account of the absorption by the atmosphere. This line, if seen, ought to be extraordinarily brilliant,

like the red line of lithium and the D lines of sodium. As a matter of fact, there are in several stars of the fifth type a strong line at $\lambda = 4688$, which is clearly the same line; further, also, Hale and Keeler point out in a footnote to Rydberg's paper that there is a line at 4687 in the spectra of several nebulæ. It is clear, therefrom, that we have here the beginning of the principal series. Finally, the following table of the new lines was published by Pickering:[1]—

HYDROGEN SHARP OR SECOND SUBORDINATE SERIES.

Designation.	Observed.	Calculated.			
		Pickering.		Rydberg.	
		m		*m*	
α'	—	5	10128·1	2	10117·3
β'	5413·6	7	5413·9	3	5412·8
γ'	4542·4	9	4543·6	4	4543·3
δ'	4200·7	11	4201·7	5	4201·5
ϵ'	4026·0	13	4027·4	6	4027·3
ζ'	3924·0	15	3925·2	7	3925·2
η'	3860·8	17	3859·8	8	3859·8
θ'	3815·7	19	3815·2	9	3815·2
ι'	3783·4	21	3783·4	10	3783·4

We may now turn to Kayser and Runge's work on spectral series, and here we shall see that most excellent results are obtained by their formula, but that no relations are given between the various series. Rydberg says that the formula is only an interpolation formula which aims at expressing the observed results with the greatest possible accuracy; Kayser,[2] however, strenuously maintains that the formula is not an interpolation formula in the true sense of the word, as ordinary interpolation formulæ do not express the results so well. Schuster[3] says that the simplicity of the calculation is in favour of Kayser and Runge, but that Rydberg's formula brings out better the regularity and irregularity in the distribution of the lines.

[1] *Astrophys. Journ.*, **6**. 230 (1897).
[2] *Handbuch der Spectroscopie*, II, 526.
[3] *Nature*, **57**. 320 (1898).

Kayser and Runge's formula is in the nature of a converging series, and usually the following gives the best results:—

$$\frac{1}{\lambda} = A + Bm^{-2} + Cm^{-4},$$

but in certain cases, as we shall see, better agreement between observed and calculated numbers is obtained by the use of the formula—

$$\frac{1}{\lambda} = A + Bm^{-2} + Cm^{-3}$$

It must be remembered that both these formulæ are only the first terms of a converging series, and that the terms containing higher powers of m are omitted; this is of no importance when m is large, that is to say, for the smaller wave-lengths, but in the earlier numbers of the series, when m is small, the results obtained by the formula do not agree well with those observed, and this Kayser and Runge say is due to the want of terms of higher powers of m, *e.g.* Dm^{-6}, etc., in the first formula.

After Runge published his preliminary notice,[1] Kayser and Runge set to work to apply the formula to as many elements as possible; in order to ensure as great an accuracy as possible, they determined the indices of refraction of air for different values of pressure, temperature, and wave-length, and their results were as follows:[2]—

$$10^7(\mu_0 - 1) = 2878{\cdot}7 + 13{\cdot}16\lambda^{-2} + 0{\cdot}316\lambda^{-4},$$

where λ is expressed in $\mu\mu$ and the results refer to air at 0° C. and 760 mm. pressure. The value at other temperatures ($t°$) can be obtained from the equation—

$$\mu_t - 1 = \frac{\mu_0 - 1}{1 + \alpha t},$$

where α is the coefficient of expansion of air 0·00367.

To reduce the wave-length of any line to vacuum it is only necessary to divide it by the index of refraction of air for

[1] *Loc. cit.* [2] *Abh. d. Berl. Akad.* (1893).

that wave-length under the given conditions of temperature and pressure. A simpler method is to construct a table of corrections to be applied in reduction of wave-lengths to vacuo, from which the amount to be subtracted from the wave-length or added to the oscillation frequency is found by inspection.[1]

Kayser and Runge's investigations of the spectral series appeared during 1890–93, and I give here some of the numerical results obtained by them for certain metallic spectra, which show the agreement usually obtained between the observed and calculated values.[2] I also give the values for the same lines, which I have calculated from Rydberg's formula, using the values of the constants μ he gave in 1897 [3] and 1900,[4] which are calculated upon Kayser and Runge's measurements. It is necessary to point out that Kayser and Runge give different names to the series which Rydberg calls the nebulous and sharp series. The names adopted by these authors are the first and second subordinate series respectively. Kayser and Runge adopt these names in place of those of Rydberg, because the series concerned are not always sharp or diffused as the case may be. Schuster has proposed the name of associated series.

In the following table are given the wave-lengths of the lines of the lithium arc spectrum as determined by Kayser and Runge, together with the values obtained by calculation with their formulæ; in the last columns are given the values as calculated from Rydberg's equations. In connection with these last it must be pointed out that Rydberg only gives the value of P_∞, S_∞, and σ and δ in his tables; μ was found for the principal series from the equation—

$$\frac{N_0}{(1+\mu)^2} = S_\infty,$$

as was described above. It will be seen that the agreement is extraordinarily good, considering that this method of finding μ is

[1] For a full table of the corrections, see Watts's *Index of Spectra*, Appendix E, p. 52.

[2] *Abh. d. Berl. Akad.*

[3] *Loc. cit.*

[4] *International Reports*, vol. ii. p. 200 (Paris, 1900).

only supposed to be approximate. The stars against the figures of Kayser and Runge's calculations mean that these were the numbers actually used in determining the constants of their equation. As was pointed out before, when the more refrangible lines are used for determining the constant, the calculated values of the less refrangible lines are considerably wrong, owing to the want of a term containing n^{-6}.

LITHIUM SPECTRA.

λ	Intensity.	Principal series.		First subordinate series.		Second subordinate series.	
		Kayser and Runge.	Rydberg.	Kayser and Runge.	Rydberg.	Kayser and Runge.	Rydberg.
		m	*m*	*m*	*m*	*m*	*m*
8127·3	(?)	—	—	—	—	3 8192·0	2 8113·52
6708·2	10*r*	3 6600·08	1 6710·04	—	—	—	—
6103·77	10*r*	—	—	3 6103·77*	2 6104·74	—	—
4972·11	7*d*R	—	—	—	—	4 4972·11*	3 4973·29
4602·37	9*r*	—	—	4 4602·37*	3 4603·82	—	—
4273·44	5*d*R	—	—	—	—	5 4273·44*	4 4274·73
4132·44	8*d*	—	—	5 4132·44*	4 4133·57	—	—
3985·94	3*d*R	—	—	—	—	6 3985·94*	5 3988·52
3915·2	6*d*	—	—	6 3915·40	5 3916·34	—	—
3838·3	1*d*R	—	—	—	—	7 3835·47	6 3835·83
3794·9	5*d*	—	—	7 3795·25	6 3796·08	—	—
3718·9	3*d*	—	—	8 3721·15	7 3721·90	—	—
3670·6	1*d*	—	—	9 3672·01	8 3672·69	—	—
3232·77	8*r*	4 3232·77*	2 3230·48	—	—	—	—
2741·39	6*r*	5 2741·39*	3 2740·88	—	—	—	—
2562·60	5*r*	6 2562·60*	4 2562·63	—	—	—	—
2475·13	4*r*	7 2475·33	5 2475·63	—	—	—	—
2425·55	3*r*	8 2425·56	6 2426·14	—	—	—	—
2394·54	1*r*	9 2394·25	7 2395·15	—	—	—	—
2373·9	(?)	10 2373·15	8 2374·39	—	—	—	—
2359·4	(?)	11 2364·22	9 2359·79	—	—	—	—

* The lines thus marked were used in the calculation of the constants of the formula.

The equations Kayser and Runge used were as follows:—

Principal series . . $\frac{10^8}{\lambda} = 43584{\cdot}73 - 133669n^{-2} - 1100084n^{-4}$

1st subordinate series $\frac{10^8}{\lambda} = 28586{\cdot}74 - 109825{\cdot}5n^{-2} - 1847n^{-4}$

2nd „ „ $\frac{10^8}{\lambda} = 28666{\cdot}69 - 122391n^{-2} - 231700n^{-4}$

Arc Spectrum of Sodium.

λ	$\frac{1}{\lambda}$	Intensity.	Kayser and Runge.			Rydberg.		
			Principal series.	First subordinate series.	Second subordinate series.	Principal series.	First subordinate series.	Second subordinate series.
			m	*m*	*m*	*m*	*m*	*m*
8194·76[1]	12202·92	—	—	3 8194·76*	—	—	2 8203·10	—
8184·33[1]	12218·47	—	—	3 8184·33*	—	—	2 8191·51	—
6161·15	16230·74	8*d*R	—	—	4 6161·15*	—	—	3 6158·66
6154·62	16247·96	8*d*R	—	—	4 6154·62*	—	—	3 6152·15
5896·16	16960·19	9*r*	3 5818·7	—	—	1 5894·39	—	—
5890·19	16977·38	10*r*	3 5804·6	—	—	1 5888·42	—	—
5688·26	17580·07	8*d*R	—	4 5688·26*	—	—	3 5689·70	—
5682·90	17596·65	7*d*R	—	4 5682·90*	—	—	3 5684·14	—
5675·92	17618·29	3*d*V	—	—	—	—	—	—
5670·40	17635·44	3*d*V	—	—	—	—	—	—
5153·72	19403·46	6*d*	—	—	5 5153·72*	—	—	4 5155·30
5149·19	19420·53	5*d*	—	—	5 5149·19*	—	—	4 5150·73
4983·53	20066·10	6*d*R	—	5 4983·53*	—	—	4 4984·36	—
4979·30	20083·14	5*d*R	—	5 4979·30*	—	—	4 4980·09	—
4752·19	21042·93	4*d*	—	—	6 4752·19*	—	—	5 4754·15
4748·36	21059·90	3*d*	—	—	6 4748·36*	—	—	5 4750·26
4669·4	21416·03	4*d*R	—	6 4668·45	—	—	5 4670·31	—
4665·2	21435·31	3*d*R	—	6 4664·68	—	—	5 4666·56	—
4546·03	21997·21	3*d*	—	—	7 4544·86	—	—	6 4547·54
4542·75	22013·10	2*d*	—	—	7 4541·36	—	—	6 4543·88
4500·0	22222·22	2*d*	—	7 4497·32	—	—	6 4499·55	—
4494·3	22250·41	2*d*	—	7 4493·80	—	—	6 4496·07	—
4423·7[2]	22605·51	—	—	—	8 4421·95	—	—	7 4425·56
4420·2[2]	22623·41	—	—	—	8 4418·65	—	—	7 4422·20
4393·7[2]	22759·86	—	—	8 4392·83	—	—	7 4395·31	—
4390·7[2]	22775·41	—	—	8 4389·40	—	—	7 4391·99	—
4343·7[2]	23021·85	—	—	—	9 4342·44	—	—	9 4347·02 9 4343·77
4325·7[2]	23117·65	—	—	9 4323·94	—	—	7 4326·64 7 4323·42	—
3303·07	30274·87	8*r*	4 3303·07*	—	—	2 3315·73	—	—
3302·47	30280·37	8*r*	4 3302·47*	—	—	2 3315·15	—	—
2852·91	35051·93	6*r*	5 2852·91*	—	—	3 2858·79 3 2858·60	—	—
2680·46	37307·03	4*r*	6 2680·46*	—	—	4 2683·64 4 2683·55	—	—
2593·98	38550·80	2*r*	7 {2593·95 2593·89	—	—	5 2596·00 5 2595·95	—	—
2543·85	39310·49	1*r*	8 {2543·75 2543·61	—	—	6 2545·38 6 2545·35	—	—
2512·23	39805·27	1*r*	9 {2511·77 2511·58	—	—	7 2513·34 7 2513·33	—	—

The lines thus marked were used in the calculation of the constants of the formula.

[1] These lines were measured by Lehmann.

[2] Liveing and Dewar.

The constants in Rydberg's equations were—

Principal series . . .	$P_\infty = n_0 = 43482{\cdot}53$	$\mu = 0{\cdot}958841$
1st subordinate series	$D_\infty = 28582{\cdot}54$	$\delta = 0{\cdot}998063$
2nd „ „	$S_\infty = 28582{\cdot}54$	$\sigma = 0{\cdot}597337$

In the preceding table the same is given for sodium, where the pairs are calculated; it will be seen that in certain cases of the most refrangible lines the components of the pairs have not been separated. It will again be observed that the agreements are extremely good except in the case of the first member of the principal series from Kayser and Runge's formula, which is explained by them as being due to the want of a term containing m^{-6}.

Kayser and Runge's equations are—

Principal series, (1) $\frac{10^8}{\lambda} = 41542{\cdot}51 - 130233m^{-2} - 800791m^{-4}$

(2) $\frac{10^8}{\lambda} = 41550{\cdot}33 - 130710m^{-2} - 793751m^{-4}$

1st subord. „ (1) $\frac{10^8}{\lambda} = 24492{\cdot}32 - 110585m^{-2} - 176{\cdot}6m^{-4}$

(2) $\frac{10^8}{\lambda} = 24510{\cdot}21 - 110606m^{-2} - 177{\cdot}6m^{-4}$

2nd „ „ (1) $\frac{10^8}{\lambda} = 24549{\cdot}12 - 120726m^{-2} - 197891m^{-4}$

(2) $\frac{10^8}{\lambda} = 24565{\cdot}83 - 120715m^{-2} - 197935m^{-4}$

In Rydberg's equations we have the following constants—

$$N_0 = 109675{\cdot}00.$$

Principal series, P_∞, or convergence frequency 41452·61—

(2) Line of less frequency $\mu = 1{\cdot}116329$
(1) Line of greater frequency $\mu = 1{\cdot}117072$

First subordinate or nebulous series, $d = 0{\cdot}649840$—

(1) $D_{1\infty}$, or convergence frequency 24470·13
(2) $D_{2\infty}$, „ „ „ 24487·32

Second subordinate or sharp series, $\sigma = 0{\cdot}988436$—

$$(1)\ S_{1_\infty} = 24470{\cdot}13$$
$$(2)\ S_{2_\infty} = 24487{\cdot}32$$

The table and constants give a very clear picture of the series lines in the sodium spectrum. In brief, these are three series of pairs, two series in which the pairs have a constant frequency difference of 17·19 and the same convergence frequencies, and a third series of pairs which have the same convergence frequency, and therefore consists of pairs which get closer and closer as the order number rises; the first member of this series has the same frequency difference as that of the two other series, 17·19.

This is Rydberg's scheme, and one which is borne out by the actual values. It is common to all the alkali metals, but in lithium the pairs have not yet been definitely separated. It must be understood that the lists do not necessarily include all the lines measured in the spectra of the elements.

For potassium and rubidium, Rydberg[1] gives the following values of the convergence frequencies :—

	Principal series.	Mean of sharp and nebulous series.
K_1	35008·92	13053·46
K_2	35008·92	12995·61
Rb_1	33706·66	12837·51
Rb_2	33705·59	12606·76

Kayser and Runge point out that the frequency difference between the pairs of the principal series is not far removed from being inversely proportional to the fourth power of the number of the line in the series; by the number of the line is meant the numbering in their own equation, when $n = 3$ for the first line. If n be made less than this, negative values will be obtained as a rule; these negative values may, perhaps, have a real meaning, but reference can here only be made to Kayser's *Spectroscopie*, vol. ii. chap. viii., where a complete account of all his joint work with Runge is given, and to which I am indebted for their values and measurements given in this chapter.

[1] *International Reports*, vol. ii. p. 212 (Paris, 1900).

When we come to the divalent metals, then, the series become more complicated. In magnesium, calcium, strontium, zinc, cadmium, and mercury, Kayser and Runge have measured two complete series of triplets, or first and second subordinate groups of three series. The corresponding series in the two groups have the same convergence frequency, and each group has triplets of constant frequency difference. Now it has been found that the first subordinate series of triplets has accompanying satellite series, but the second subordinate series has no satellites.[1] As far as is known at the present time the first member of the triplet has three satellites, the second member two satellites, and third member one satellite. This structure of the triplets has been most completely observed in the case of mercury. In the case of calcium the first triplet of the first subordinate series is the following :—

4456·81 4456·08 4454·97	First line with two satellites.
4435·86 4435·13	Second line with one satellite.
4425·61	Third line.

It is better shown in oscillation frequencies—

	First line.	ν_1	Second line.	ν_2	Third line.
	22437·57	105·97	22543·54	52·21	22595·75
	3·68		3·71		
First satellite	22441·25		22547·25		
	5·59				
Second satellite	22446·84				

A complete triplet in the spectrum of mercury is the following : [2]—

3663·46 3663·05	1	3131·95 3131·66	2	2967·64	3
3655·00 3650·31		3125·78		2967·37	

[1] This satellite series was first noticed by Rydberg in the case of thallium ; the satellite series have the same convergence frequency as the corresponding series in the first subordinate group (see above, p. 489).

[2] Runge and Paschen, *Astrophys. Journ.*, **14**. 49 (1901).

or in oscillation frequencies—

	ν_1		ν_2	
27296·60	4632·39	31928·99	1767·82	33696·81
3·05		2·96		3·06
27299·65	4632·30	21931·95	1767·92	33699·87
60·13		60·06		
27359·78	4632·23	31992·01		
35·15				
27394·93				

The triplet principal series in these elements has not been discovered.

Now there exist in these spectra certain pairs of constant frequency difference which Rydberg attributed to the principal and two subordinate series of doublets, such as occur in the spectra of the alkali metals. In magnesium, for example, he attributed them as follows:—

λ	
2802·80	Principal series.
2795·63	
2798·07	First subordinate series.
2790·88	
2936·61	Second subordinate series.
2928·73	

This has been entirely confirmed by the behaviour of these lines in the magnetic field.[1]

Similarly in calcium the pair at 3933·83 and 3968·63 (H and K lines) is the first pair of the principal series, 3737·08 and 3706·18 the second subordinate series, and $\left\{\begin{matrix}3181\cdot40\\3179\cdot45\end{matrix}\right\}$ and 3158·98 the first member of the first subordinate series; in the last case the first line has a satellite.

In addition there occur other pairs and triplets in these spectra of constant frequency difference, but which do not belong to any known series; for example, in the spectrum of magnesium there are two pairs at $\left\{\begin{matrix}2783\cdot08\\2779\cdot94\end{matrix}\right\}$ and $\left\{\begin{matrix}2768\cdot57\\2765\cdot47\end{matrix}\right\}$ whose frequency difference is 40·5. This frequency difference

[1] See Chapter XVI., p. 547.

is half that occurring with the three pairs mentioned above. Again, there is a series of isolated lines in the magnesium spectrum at 5528·75, 4703·33, 4352·18, 4167·81, 4058·45, and 3987·08; these Rydberg[1] attributes to a new kind of series, for which he gives as formula a combination of his and Kayser and Runge's expressions—

$$\frac{10^8}{\lambda} = a - \frac{b}{(m+\mu)^2} - \frac{c}{(m+\mu)^4}$$

Fowler[2] has observed four more lines at 4511·4, 4251·0, 4106·8, and 4018·3, which apparently form an associated series with the last series. The two series have the same convergence frequency, and can both be expressed by the formula—

$$n = n_\infty - \frac{c}{(m+\mu)^2 - m_0}$$

Fowler calculates the wave-lengths of the first two lines of the new series; they are 5065 and 6674·5. The first of these is evidently the line at 5067, but the second was not observed.

Very important work has been carried out by Runge and Paschen upon the series of lines in the spectra of helium,[3] and of oxygen, sulphur, and selenium.[4] In the case of helium six series were found, two of which were principal series, two first subordinate, and two second subordinate series. One of the first subordinate series was a pair series.

The equations of the series were as follows:—

Principal ser., (1) $\frac{10^8}{\lambda} = 38455{\cdot}324 - 109891m^{-2} - 14507m^{-3}$

1st subord. „ (1) $\frac{10^8}{\lambda} = 29224{\cdot}35 - 109836{\cdot}3m^{-2} - 167m^{-3}$

2nd „ „ (1) $\frac{10^8}{\lambda} = 29197{\cdot}97 - 106152{\cdot}4m^{-2} - 86560m^{-3}$

$$\nu = 10{\cdot}07$$

[1] *Ann. der Phys.*, **50**. 625 (1893); and **52**. 119 (1894).

[2] *Proc. Roy. Soc.*, **71**. 419 (1903).

[3] *Berl. Ber.* (1895), 639; and *Brit. Ass. Report* (1895), 610; also Rydberg, *Astrophys. Journ.*, **4**. 91 (1896).

[4] *Astrophys. Journ.*, **8**. 70 (1898); and *Ann. der Phys.*, **61**. 641 (1897).

Principal ser., $(2)\frac{10^8}{\lambda} = 32029{\cdot}86 - 109537m^{-2} - 1963{\cdot}6m^{-3}$

1st subord. ,, $(2)\frac{10^8}{\lambda} = 27175{\cdot}16 - 109758{\cdot}6m^{-2} - 272{\cdot}6m^{-3}$

2nd ,, ,, $(2)\frac{10^8}{\lambda} = 27168{\cdot}595 - 108825{\cdot}6m^{-2} - 3596om^{-3}$

The general formula $\frac{1}{\lambda} = A - Bm^{-2} - Cm^{-3}$ answered better than Kayser and Runge's formula, in which m^{-4} is used. It will be seen that the first and second subordinate series form two pairs with the same convergence frequencies, and as there are two principal series Runge and Paschen concluded that helium must be a mixture of two gases, to which, following Johnstone Stoney's suggestion, they gave the names helium and parhelium; this conclusion has been, however, proved erroneous, both by the chemical and physical behaviour of helium, and also by the fact that such an occurrence of series is present in other elementary spectra.

The spectrum of oxygen has been shown by Runge and Paschen to contain two triplet series, and two series probably consisting of pairs. This spectrum of oxygen is the one called by Schuster the elementary line spectrum, *i.e.* the spectrum of the oxygen molecule in a more dissociated condition than it is in the case of the compound line spectrum. These series are also better expressed by an expression of the form—

$$\frac{1}{\lambda} = A - Bm^{-2} - Cm^{-3}.$$

Thiele[1] has come to the conclusion that the law which expresses the wave-lengths of the lines of a series must have the form—

$$\lambda = f[(n + c)^2],$$

where c is a constant and is called the phase of the series. If n be given all real integral values, it is evident that λ must have one maximum and one minimum value. In the neighbourhood of $\lambda_0 = f(o)$ a finite number of lines are crowded

[1] *Astrophys. Journ.*, 6. 65 (1897).

into an ordinary *head*, but near $\lambda_\infty = f(\infty)$ an infinite number of lines are generally crowded into a finite space which clearly occurs in line spectra, and this Thiele calls the *tail* of the series. Further, the most important consequence of the above formula is that it is necessary to take into account the lines corresponding to both positive and negative values of n; in other words, a true series should consist of two branches, each of which would be called a series. That there are two branches has been clearly established in certain band spectra; these two branches need not necessarily both be observed, for it is possible for them to coincide, *i.e.* when $c = 0$ or $\frac{1}{2}$. Thiele suggests that the two subordinate series of the metallic spectra are in reality the two branches of one series.

Thiele takes Pickering's formula (p. 582) and modifies it algebraically to the form—

$$\lambda = \frac{\lambda_0 a + \lambda_\infty (n+c)^2}{a + (n+c)^2},$$

where $\lambda = \lambda_0$ when $n + c = 0$, and $\lambda = \lambda_\infty$ when $n = \infty$.

From this we have—

$$\frac{\lambda - \lambda_0}{\lambda_\infty - \lambda} = \frac{(n+c)^2}{a}$$

and

$$\frac{\lambda^{-1} - \lambda_0^{-1}}{\lambda_\infty^{-1} - \lambda^{-1}} = \frac{\lambda_\infty}{\lambda_0} \cdot \frac{(n+c)^2}{a}.$$

Based on this formula, Thiele found a method of calculating the spectrum of helium as two branches of the same series; he found the following values, which have been selected from his list:—

−14·85	3482·509	+0·07	3·15	5877·477	0·000
−13·85	3491·868	−0·12	4·15	4472·868	+0·010
−10·85	3538·093	−0·139	7·15	3706·176	+0·009
−7·85	3653·506	−0·366	10·15	3555·574	+0·016
−4·85	4123·641	−1·526	13·15	3499·780	−0·02
−2·85	7069·532	−1·92	16·15	3472·964	0·00
−1·85	−10851·859		19·15	3457·899	0·00
−0·85	−356·046				
+0·15	+243·634				
+1·15	−1088·710				
+2·15	+61308·022				

The first lines belong to one of the second subordinate series, while the latter portion belong to the corresponding first subordinate series.[1]

More recently very valuable papers have been published by Ritz on the theory of spectral series.[2] The author starts with Rydberg's equations for the two series of hydrogen lines—

$$\pm r = N_0\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

and

$$\pm r = N_0\left(\frac{1}{n_2} - \frac{1}{(m+0{\cdot}5)^2}\right),$$

and arrives at the general equation for all substances which give spectral series—

$$\pm r = N_0\left(\frac{1}{p^2} - \frac{1}{q^2}\right),$$

where p and q are the roots of certain transcendental equations. These terms can be expressed in semi-convergent series of the form—

$$p = m + a + \frac{\beta}{m^2} + \frac{\gamma}{m^4} + \ldots$$

$$q = n + a' + \frac{\beta'}{n^2} + \frac{\gamma'}{n^4} + \ldots$$

It is clear from this that the term N_0 is absolutely the same for all substances, as Rydberg has always maintained.

If now we take the above formula, using only the first two terms of the converging series, we then obtain Rydberg's general formula—

$$\pm r = N_0\left(\frac{1}{(m+a)^2} - \frac{1}{(n+a')^2}\right);$$

this shows that the formula is only a first approximation. Further, it is clear that in order to obtain a second and better

[1] See Runge and Paschen, *loc. cit.*

[2] *Phys. Zeitschr.*, **4**. 406 (1903); and *Ann. der Phys.*, **12**. 264 (1903).

approximation we must take in a third term of the converging series, and not alter the constant N_0. We thus have for a single series (n = constant)—

$$\pm r = A - \frac{109765{\cdot}00}{\left(m + a + \frac{\beta}{m^2}\right)^2},$$

where $m = 1, 2, 3$, etc. This formula gives very striking results when applied to spectra. Further, the connection between the principal and second subordinate series is in this way mathematically proved, and the two can be united in one formula. The doublets of these two series in the spectra of the alkali metals are given by the formulæ—

$$\pm r = N_0\left\{\frac{1}{\left(n + a_1 + \frac{\beta}{n^2}\right)^2} - \frac{1}{\left(m + 0{\cdot}5 + a' + \frac{\beta'}{(m + 0{\cdot}5)^2}\right)^2}\right\}$$

$$\pm r = N_0\left\{\frac{1}{\left(n + a_2 + \frac{\beta}{n^2}\right)^2} - \frac{1}{\left(m + 0{\cdot}5 + a' + \frac{\beta'}{(m + 0{\cdot}5)^2}\right)^2}\right\}$$

In the case of sodium and potassium Ritz has calculated out the wave-lengths of the lines, and it will be seen how great an accuracy the formula gives. The values of the constants were—

Sodium.		Potassium.	
$a_1 = 0{\cdot}14595$	$\beta = -0{\cdot}1158$	$a_1 = 0{\cdot}29034$	$\beta = -0{\cdot}2239$
$a_2 = 0{\cdot}14521$		$a_2 = 0{\cdot}28750$	
$a' = 0{\cdot}15157$	$\beta' = -0{\cdot}05586$	$a' = 0{\cdot}31789$	$\beta' = -0{\cdot}1076$

In the following tables the calculated wave-lengths are not given, but only the differences between these and the observed values. The latter are given in the first column; in the second are given the differences obtained by Kayser and Runge, the asterisks meaning that the observed values were used to obtain the constants in the formula. In the third column are given the differences obtained by Ritz.

SODIUM.

Principal Series.

n		KR	R	n		KR	R
2	5896·16	+78	0·00	6	2593·98	+0·03	−0·13
	5890·19	+86	0·00			+0·09	−0·08
3	3303·07	00*	+0·03	7	2543·85	+0·10	−0·22
	3302·47	00*	00			+0·24	−0·19
4	2852·91	00*	−0·10	8	2512·23	+0·5	−0·15
			+0·07			+0·6	−0·12
5	2680·46	00*	−0·08				
			0·00				

Second Subordinate Series.

$m+\frac{1}{2}$		KR	R
1·5	5890·19	+334·0	0·00
2·5	11404·0	−1·14	+0·9
3·5	6161·15	−0·00*	0·00
4·5	5153·72	0·00*	−0·25
5·5	4752·19	0·00*	−0·23
6·5	4546·03	+1·16	+0·21
7·5	4423·7	+1·7	−0·17

Only one line of the pairs is given in this series, as they have a constant frequency difference.

POTASSIUM.

Principal Series.

n		KR	R	n		KR	R
2	7701·92	+161·3	0·00	7	3034·94	+0·23	−0·20
	7668·54	+150·6	−0·24		3034·94	+0·44	−0·05
3	4047·36	0·00*	0·00	8	2992·33	+0·68	−0·19
	4044·29	0·00*	0·00			+0·80	−0·08
4	3447·49	0·00*	+0·13	9	2963·36	+1·05	−0·13
	3446·49	0·00*	+0·12			+1·11	−0·07
5	3217·76	0·00*	0·00	10	2942·8	+1·45	−0·27
	3217·27	0·00*	+0·05			+1·60	−0·23
6	3102·37	+0·27	+0·10				
	3102·15	+0·36	+0·40				

The second subordinate series of potassium agrees with the observed values just as closely as in the case of sodium. This formula, developed by Ritz, is a great advance in our knowledge

of spectral series; by its means Rydberg's equation is shown to be a first approximation to the truth, and that Rydberg's contentions in favour of the general constancy of the term N_0 and the connection between the various series are perfectly justified. The differences between the observed and calculated values given with Ritz's equations may be quite well accounted for by experimental error in the former. It must be remembered that the measurements of the lines in the spectra of the metals were made upon photographs taken of the arc spectra; they are probably therefore liable to small errors owing to the breadth of the lines and the pressure of the atmosphere (see next chapter). In order to obtain absolute accuracy it will be necessary to observe the lines obtained in the spectra of the metals given by vacuum tubes such as were used by Hamy and Michelson, and, further, to use some form of interference apparatus for purposes of measurement of their wave-lengths.

Recently, Ritz[1] has published papers in which he shows how the use of his formula may be extended very considerably so as to derive from the known spectral series of an element new series of lines. Since Rydberg's work was published, and Ritz's original paper appeared, a number of new series and lines have been discovered by Lenard, Konen, Hagenbach, Saunders, Moll, and Bergmann. This extension also applies to other spectra, more particularly to those of helium and the alkaline earths.

The most convenient form of Ritz's formula reads as follows:—

$$n = \mathrm{A} - \frac{\mathrm{N}}{[m + \alpha + \beta\,(\mathrm{A} - n)]^2}$$

In certain cases for small values of m, n may become negative, which must be taken into account, of course, in the term $\beta\,(\mathrm{A} - n)$. The constants α and β characterise the course of the series, and are equal to one another for two series which have constant differences.

[1] *Astrophys. Journ.*, **28**. 237 (1908); *Phys. Zeitschr.* **9**. 244 and 521 (1908).

For the sake of simplicity, in place of the term $\frac{N}{[m + \alpha + \beta(A - n)_2]^2}$ may be written the symbol (m, α, β). For the constants α and β we may put the values d and δ for the pairs of the first subordinate series (Rydberg's diffuse series); for the second subordinate series (Rydberg's sharp series) we may put the values s, σ; and for the principal series we may put p_1, π_1, and p_2, π_2; and Ritz shows that for the alkalies π_1, very approximately is equal to π_2. If the first subordinate series has a satellite, a different set of values d', δ', will apply to the second principal line, where again $\delta = \delta'$ very approximately. We may therefore express the equation of the three series as follows :—

Principal series, $\pm n = (1{\cdot}5\ s, \sigma) - (m, p_1, \pi_1)$. $m = 2, 3, 4 \ldots$ and $p_1 > p_2$.
$\pm n = (1{\cdot}5, s, \sigma) - (m, p_2, \pi_2)$.

Second subordinate series, $\pm n = (2, p_1, \pi_1) - (m, s, \sigma)$.
$m = 1{\cdot}5, 2{\cdot}5, 3{\cdot}5 \ldots$
$\pm n = (2, p_2, \pi_2) - (m, s, \sigma)$.

First subordinate series, $\pm n = (2, p_1, \pi_1) - (m, d, \delta)$.
$m = 3, 4, 5 \ldots$ (first principal line)

$\pm n = (2, p_2, \pi_2) - (m, d, \delta)$ (satellite).
$\pm n = (2, p_2, \pi_2) - (m, d, \delta')$. $m = 3, 4, 5 \ldots$ (second principal line).

It will be seen from this that the constant separation of the doublet

$$\nu = (2, p_1, \pi_1) - (2, p_2, \pi).$$

From the observed data which are now available the following points may be shown :—

(1) In the equation of a principal series if we replace the number 1·5 by the larger numbers 2·5, 3·5, etc., and further, in the equation of the subordinate series, if we replace the number 2 by the larger numbers 3, 4, 5, etc., we shall obtain new lines which have been observed in many cases. This had already been foreshadowed by Rydberg.

(2) For every value of the symbol (m, a, β) there exists a minimum value of m. This minimum is 3 for the first subordinate series, and 1·5 for the second subordinate series. It is a fundamental number, and if we assign a still smaller value to m, it will be expected that a stronger line would occur at that place; but in practice such a line has not been observed. Ritz has also shown that in the case of the first subordinate series no line is to be found in any spectrum corresponding to the value $m = 2$.

(3) We may form from the above symbols a new combination $(1{\cdot}5, s, \sigma) - (3, d, \delta)$, and we then obtain new lines which have been observed in the case of helium, potassium, and rubidium, but not, up to the present, in the cases of sodium and lithium. For the alkaline earths these lines fall in the infra-red. In the case of helium the calculated value is $n = 26244{\cdot}86$, whilst the observed value is $26244{\cdot}78$.

(4) In the cases of lithium and sodium two new combinations have been observed, viz. $(2, p_1, \pi_1) - (m, p_1, \pi_1)$ and $(2, p_2, \pi_2) - (m, p_2, \pi_2)$, where $m = 3, 4, 5$, etc.

(5) Again, we may take the combination $(3, d, \delta) - (m, p_1 - p_2, \pi_1 - \pi_2)$, where $m = 4, 5, 6$, etc.; and we then get the infra-red series found by Bergmann for potassium, rubidium, and cæsium, and the corresponding lines for lithium, sodium, and helium, which were unknown. In the case of rubidium and cæsium, the first subordinate series has a satellite so that we have further a second series $(3, d', \delta') - (m, p_1 - p_2, \pi_1 - \pi_2)$, which has a constant difference as regards the series just given, and runs along parallel to it. This was observed by Bergmann, and also earlier by Saunders in the case of cæsium. The fundamental number for the value of m in this case is $m = 4$.

(6) We may also form the following combinations:—

$$(2, p_1, \pi_1) - (m, p_1 - p_2, \pi_1 - \pi_2) \quad m = 4, 5, 6 \ldots$$
$$(2, p_2, \pi_2) - (m, p_1 - p_2, \pi_1 - \pi_2)$$
$$(4, p_1 - p_2, \pi_1 - \pi_2) - (m, p_1 - p_2, \pi_1 - \pi_2).$$

To the first two of the above correspond the pairs of lines of sodium shading towards the violet, the corresponding pair

of copper lines and the series of lines which have been found in lithium and sodium by Lenard, Konen, and Hagenbach.

(7) It is unfortunate that accurate investigations in the infra-red, such as have been made for the alkali metals, have not been carried out in the case of the alkaline earths, and the principal series have not yet been observed. As a result of this the test of the principle of combination cannot be made at present. Ritz, however, shows that the principle is valid. In the first subordinate series of the series of triplets it is necessary to introduce the new symbols (m, p_3, π_3), (m, d'', δ''), with $p_1 > p_2 > p_3$.

To a first approximation we may neglect $\pi_1 - \pi_2$, $\pi_2 - \pi_3$, and calculate $p_1 - p_2$, $p_2 - p_3$ from the limits of the subordinate series, in spite of the fact that the principal series have not been observed; $p_1 - p_2$ will be about twice as large as $p_2 - p_3$, and the two constant frequency differences will be given by—

$$\nu_1 = (2, p_2, \pi_2) - (2, p_1, \pi_1). \quad \nu_2 = (2, p_3, \pi_3) - (2, p_2, \pi_2).$$

Now, there frequently occur double lines separated by the distance ν_1, and triplets separated by the distance ν_1 and ν_2 lying outside of the series. This is to be expected from the principle of combination, and only when the symbols $(2, p_1, \pi_1)$, $(2, p_2, \pi_2)$, $(2, p_3, \pi_3)$ are associated with any quantity (m, α, β). These pairs and triplets must therefore belong to the series which end at the same point as the subordinate series already known, but of which only a few terms of sufficient intensity can be recognised.

Ritz has shown that it is also possible to find the equation of a second subordinate series of strong ultra-violet pairs for strontium, barium, and calcium, for which the constant difference ν' is twice as large as ν_1, and from the elements of these pairs to form the corresponding differences of the constants p, on the assumption that $\pi_1 = \pi_2$. The distance differs from that of the series of triplets only by about 15 per cent. If the computations were equally exact the two quantities would probably become equal to one another, which would correspond, of course, to the principle of combination.

Finally, from the limits of the subordinate series of close

triplets, which were found by Fowler and by Saunders for calcium and strontium, the differences $p_1' - p_2'$, $p_2' - p_3$ can be formed. It appears that these are the same as those calculated from the satellites and the principal lines of the first subordinate series $d - d'$, $d' - d''$, so that evidence of a new combination exists here.

The computation of a quantity (m, α, β) assumes a knowledge of the limit of a series in the formula of which it enters. It may be determined with great accuracy except when only a few diffuse lines are observed. It is also somewhat independent of the uncertainty as to the exact form of the series equation. In the cases mentioned above under (1), (3), and (4), it is necessary exclusively to calculate the differences or sums of the observed wave-lengths, and naturally here the accuracy is greater. On the other hand, the constants entering the symbol $(m, p_1 - p_2, \pi_1 - \pi_2)$ may be varied by about 20 per cent. without producing any serious effect on the difference between the calculated and observed values. Since the constants $p_1 - p_2$, $\pi_1 - \pi_2$ are small, their influence compared with that of m is relatively slight, and the series differ only a little from Balmer's series. This is especially the case for lithium, sodium, and helium, but for the elements of higher atomic weight the observations made up to the present are too inaccurate to give any certainty on this point.

In another paper Ritz[1] showed that systems of the simplest sort may be conceived of which the energy is purely electro-magnetic and which obeys Balmer's law, the laws of series, the anomalous Zeeman effect, etc. The vibration number $\pm n = N\left(\frac{1}{4} = \frac{1}{m^2}\right)$ is produced by the magnetic field of $m - 2$ elementary magnets turned towards one another which are identical among themselves. Similarly this is true for other spectra. Higher members of the series thus correspond in a certain degree to the higher magnetic polarisation which continually becomes less stable, so that with increasing values of m the lines become broader and weaker. Further, violent motions, such as occur in the electric spark, are not

[1] *Ann. der Phys.*, **25**. 660 (1908).

favourable to stability, from which it follows that the series in the spark spectra cease with smaller values of m than they do in the arc. The magnetic field in an atom may in all spectra be regarded as being produced by two poles of opposite sign, which separately may occupy different positions in the atom. Each of the two terms in the expression $(m, \alpha, \beta) - (m', \alpha', \beta')$ represent the influence of one pole, and the possible positions of the separate poles allow of the most varied combinations of the poles in pairs. In general it can be stated that the simple laws depend upon the position of these poles within the atom. As there always exists a minimum value of m in every series, a fact which occurs in no known process of vibration, this only affirms that the poles of the magnets are held by the structure of the atom at a certain minimum distance from the vibrating electron. This idea, Ritz points out, is quite plausible.

Ritz deals with the application of the above principle to the new series and the new lines which have been measured in certain specific cases, from which the following examples may be taken :—

Hydrogen.—Paschen has observed an infra-red line, $\lambda = 18751 \pm 2$, and this Ritz points out to be the fundamental of the series $\pm n = N\left(\frac{1}{3^2} - \frac{1}{m^2}\right)$, $m = 4, 5, 6, \ldots$, which when $m = 4$ gives the value of $\lambda = 18751{\cdot}7$. It can be seen that this may be looked upon as the Balmer formula $n = N\left(\frac{1}{p^2} - \frac{1}{m^2}\right)$, in which p and m are whole numbers.

Lithium.—In the case of lithium both Hagenbach and Konen and Saunders have discovered a system of new lines which together form a series. By analogy with the other alkali metals it is to be expected that the lithium lines consist of narrow pairs. Hagenbach finds, however, that the red lithium line is single, while he and Saunders agree that the line $\lambda = 4602$ of the first subordinate series is double, but the distance between the pair is twice as great as was to be expected. Although Saunders finds that the line $\lambda = 6103$ is single, Konen and Hagenbach conclude that the line is double, owing to the fact that they observed a double reversal

in it. It must be remembered that the components of this line should be still further separated than those of the line $\lambda = 4602$. Now, it may be concluded from the relation between the squares of the atomic weights mentioned below (p. 625) that $p_1 - p_2$ should be equal to 0·00005. From analogy with the other alkali metals it can only be said that $\pi_1 - \pi_2$ is of the same order, and not that it is zero. Now, Ritz has shown that $p = -0{\cdot}04815$, and $\pi = 0{\cdot}0257$, and if we put $p_1 = p$, $\pi_1 = \pi$, $p_2 = p + 0{\cdot}00005$, and $\pi_2 = \pi + 0{\cdot}0002$, it can be seen that the fundamental line $m = 2$ of the principal series, just as that of the secondary series, is not a pair. For higher values of m the lines are still only a few hundredths of an Ångström unit apart and so cannot be separated.

If we take the combination mentioned under (5) above we get the equation

$$n = 12202{\cdot}6 - \frac{N}{\left[m - 0{\cdot}00005 + \frac{0{\cdot}0002}{m^2}\right]^2}.$$

$m = 4, 5, 6$. This gives for $m = 4$, $\lambda = 18693{\cdot}7$; for $m = 5$, $\lambda = 12791{\cdot}5$.

For the first line Paschen obtained two measurements, 18694 and 18698, and for the second line he obtained the values 12784 ± 10. The higher members of this series have not yet been observed. It corresponds with the series discovered by Bergmann in the spectra of potassium, rubidium, and cæsium.[1] Again, the formula $(2, p_1, \pi_1), -(m, p_1 - p_2, \pi_1 - \pi_2)$ gives a series which runs parallel to the last-mentioned one, and the lines of which, since d, δ, $p_1 - p_2$, $p_1 - p_2$ are all very small, in the case of lithium lie exceedingly close to the lines of the first subordinate series. If we calculate the quantity $\alpha + \beta(A - n)$ for the first subordinate series, we find by analogy with the other alkali metals it must be negative. For $m = 3$ it equals $-0{\cdot}00204$, for $m = 4$; according to the measurements of Hagenbach ($\lambda = 4604{\cdot}04$) and Saunders ($\lambda = 4603{\cdot}02$), it is equal to $-0{\cdot}00243$ and $-0{\cdot}00326$ respectively. The line $\lambda = 4603$ is therefore the line of the

[1] *Zeit. Wiss. Phot.* **6**. 113 and 145 (1908).

first subordinate series. The second line situated so close to it belongs to the series $(2, p_1, \pi_1) - (m, p_1 - p_2, \pi_1 - \pi_2)$, which for $m = 4$ gives $\lambda = 4601{\cdot}32$. For this line Hagenbach gives $\lambda = 4602{\cdot}00$ and Saunders $\lambda = 4601{\cdot}6$.

Since with $m = 3$ a value of $6097{\cdot}56$ is obtained, which does not appear in the spectrum, it is clear that the fundamental value of m is 4, a fact which has been frequently noticed. Finally we have the series running parallel to the principal series given by $n = (2, p, \pi) - (m, p, \pi)$, the limit of which is equal to that of the secondary series. This series was discovered by Konen and Hagenbach, and in the accompanying table are given the calculated and observed values:—

m	λ (calc.)	λ (obs.)
3	6240·0	6240·8 (K. & H.), 6240·3 (S.).[1]
4	4636·05	4636·04 (K. & H.), 4636·3 (S.).
5	4146·8	4149·1 (K. & H.), 4148·2 (S.) very diffused.
6	3922·50	3924 (K. & H.), 3921·8 (S.).

Paschen has observed two infra-red lines of lithium, viz. $\lambda = 17563$ and $\lambda = 12209$, which, however, were not accurate. Ritz points out that these two lines may be due to the combination $(3, p, \pi), (m, d, \delta)$, which for $m = 4$ gives $\lambda = 17549$, and, for $m = 5$, $\lambda = 12236$.

It may be pointed out that, although all the observed lines have been apportioned to series, yet not a single new constant has been introduced.

Ritz[2] in his paper also gives full details of the application of his formula and his method of combination to the spectra of sodium, potassium, rubidium, cæsium, helium, and the metals of the alkaline earths. The results which he obtains are extraordinarily good, but as the methods are exactly analogous to those described above for lithium, they hardly need be dealt with in detail here.

[1] K. & H. = Konen and Hagenbach; S. = Saunders.

[2] *Phys. Zeitschr.* **9.** 521 (1908).

Mention should also be made of a paper by Halm,[1] in which he deals with the harmonic series of lines in both line and band spectra, and discusses the application of the formula

$$\frac{1}{n_\infty - n} = a_1(m + \mu)^2 + b_1 . \quad . \quad . \quad . \quad (1)$$

in which n_∞ is the value of the oscillation frequency when $m = \infty$, *i.e.* the convergence frequency or the tail of the series, n the frequency of any line of any series, m a series of integers, μ a characteristic constant representing various fractional numbers, and a_1 and b_1 constants depending on the nature of the substance. Owing to the fact that the above equation is a modification of Thiele's equation, the author speaks of equation (1) as the Rydberg-Thiele formula. Halm deals with both line series and band series, and in the former case he finds always that $\mu = \frac{p}{5q}$, p and q being integers. He calculated out 44 series, and obtained good agreements between the calculated and observed values.

It was found that out of the 44 series, 19 had $\mu = 0$, and with the exception of magnesium, calcium, and strontium, all the first subordinate series belong to this group, as also does the first hydrogen series. If in any such group we denote by ν the frequency of the line in one series, and by n that of a line of another series, we have—

$$\frac{1}{\nu_x - \nu} = \frac{a_5}{n_x - n} + b_5 . \quad . \quad . \quad . \quad (2)$$

where a_5 and b_5 are constants, and ν_x and n_x are the frequencies of the xth line of the two series. An exactly similar equation holds for wave-lengths. Equation (2) enables us to calculate one series of lines by means of another belonging to the same μ group. Halm exemplifies this by calculating the wave-lengths of all the lines of the first subordinate series of indium, thallium, zinc, and lithium, and also the third subordinate series of helium from the hydrogen series.

[1] *Trans. Roy. Soc. Edinburgh*, 41. 551 (1905).

A still closer relation is obtained if equation (1) be written in the form—

$$\frac{1}{n_\infty - n} = \frac{a_1}{(m+\mu)^2} \pm \frac{b_1^2}{a_1^2} \quad . \quad . \quad . \quad (3)$$

Halm also shows that his formula includes the Deslandres formula as a special case, as well as the Balmer and Rydberg formulæ, and thus suggests that both line and band series are comprised under the same mathematical, and probably also physical, conception. The Rydberg-Thiele formula may be written in the form—

$$\lambda = \frac{\lambda_0}{1 \pm \left(\frac{m+\mu}{\gamma}\right)^2} + \frac{\lambda_\infty}{1 \pm \left(\frac{\gamma}{m+\mu}\right)^2} \quad . \quad . \quad (4)$$

where γ is a constant. When $\lambda_0 = 0$, then

$$\lambda = \frac{\lambda_\infty}{1 \pm \left(\frac{\gamma}{m+\mu}\right)^2} \quad . \quad . \quad . \quad . \quad (5)$$

which is identical with Rydberg's equation. Although it is true that there has been found no series corresponding to the positive sign in the denominator, *i.e.* no line series is known with its head on the violet side of the spectrum, yet this equation renders possible the existence of such a series. If on the other hand $\lambda_\infty = 0$, then equation (4) becomes

$$\lambda = \frac{\lambda_0}{1 \pm \left(\frac{m+\mu}{\gamma}\right)^2} \quad . \quad . \quad . \quad . \quad (6)$$

which is identical with the Deslandres formula when $\mu = 0$. Halm points out that it appears that the wave-lengths of any line of band series appear to be made up by two terms, one satisfying the Rydberg formula (5) and the other the more general Deslandres equation (6).

An important paper has been published by Birge,[1] in which he deals with the series of the alkali metals and helium. In the first place, he calculated all his wave-lengths on the new international scale. A table of corrections to be applied in order to reduce the Rowland values to the new scale was calculated, and this table may be given here—

[1] *Astrophys. Journ.*, **32**. 112 (1910).

TABLE OF CORRECTIONS FOR REDUCTION TO FABRY AND PEROT'S SCALE.

λ in Å.	Correction Å.	λ in Å.	Correction Å.	λ in Å.	Correction Å.	λ in Å.	Correction Å.
2400	−0·08	3300	−0·12	4100	−0·15	5300	−0·16
2500	−0·08	3400	−0·13	4200	−0·16	5400	−0·18
2600	−0·08	3450	−0·14	4300	−0·16	5500	−0·20
2700	−0·09	3500	−0·15	4400	−0·17	5600	−0·21
2800	−0·10	3600	−0·15	4600	−0·17	5800	−0·21
2900	−0·11	3700	−0·15	4800	−0·17	6000	−0·21
3000	−0·11	3800	−0·15	5000	−0·17	6200	−0·20
3100	−0·11	3900	−0·14	5100	−0·16	6400	−0·21
3200	−0·11	4000	−0·15	5200	−0·15	6600	−0·22

The above corrections are calculated to reduce the wave-length on the old scale at 20° C. and 760 mm. to wave-lengths at 15° C. and 760 mm. on the Fabry and Perot scale. This reduction will, of course, necessitate the recalculation of the new constant N, and this Birge has done by means of the hydrogen lines, using Evershed's new values for the hydrogen δ and ϵ lines. The value of the constant N is found to be 109,678·6, in place of the old value given above, 109,675·0.

Birge has recalculated the series of lines in the alkali metals and helium, and he shows that the calculated differences between the observed and calculated values in the cases of lithium, sodium, and potassium lie within the estimated maximum errors of observation, as may be seen from the following tables of lithium, sodium, and helium :—

LITHIUM. PRINCIPAL SERIES.

Number of lines.	λ (air).	λ (vacuo).	Probable error.	*d*
2	6708·2	6709·83	0·2	± 0·00*
3	3232·77	3233·59	0·03	± 0·00*
4	2741·39	2742·10	0·03	− 0·07
5	2562·60	2563·27	0·03	− 0·01
6	2475·13	2475·78	0·1	− 0·23
7	2425·55	2426·19	0·1	− 0·19
8	2394·94	2395·17	0·2	− 0·15
9	2373·9	2374·52		± 0·00*
10	2359·4	2360·02		+ 0·15

The lines marked with * were used in the calculation of the constants.

SODIUM—PRINCIPAL SERIES, LESS REFRANGIBLE LINE.

Number of line.	λ (air).	λ (vacuo).	Probable error.	d
2	5896·16	5897·563	0·00	±0·00*
3	3303·07	3303·895	0·03	±0·00*
4	2852·91	2853·63	0·05	−0·04
5	2680·46	2681·17	0·10	+0·09
6	2593·98	2594·67	0·10	+0·09
7	2543·82	2544·49		−0·05
8	2512·15	2512·90		+0·07
9	2490·70	2491·36		−0·04
10	2475·60	2476·26		+0·03
11	2464·53	2465·18		+0·10
12	2456·02	2456·67		+0·05
13	2449·46	2450·11		+0·04
14	2444·24	2444·89		−0·03
15	2440·06	2440·71		+0·01
16	2436·70	2437·35		+0·06
17	2433·85	2434·50		+0·04
18	2431·43	2432·08		−0·01
19	2429·42	2430·07		−0·02
20	2427·72	2428·37		−0·01
21	2426·28	2426·93		+0·02
22	2425·00	2425·65		+0·03
23	2423·88	2424·53		+0·01
24	2422·90	2423·55		±0·00
25	2422·04	2422·69		±0·00*
26	2421·29	2421·93		+0·02
27	2420·60	2421·25		+0·01
28	2420·02	2420·67		+0·04
29	2419·50	2420·15		+0·07
30	2419·00	2419·65		+0·06
31	2418·44	2419·09		−0·05
32	2418·09	2418·74		±0·00
33	2417·71	2418·36		−0·01
34	2417·38	2418·03		+0·01
35	2417·10	2417·75		+0·02
36	2416·80	2417·45		±0·00
37	2416·56	2417·21		+0·03
38	2416·33	2416·98		+0·04
39	2416·11	2416·76		+0·03
40	2415·89	2416·54		+0·02
41	2415·70	2416·35		+0·03
42	2415·52	2416·17		+0·02
43	2415·37	2416·02		+0·03
44	2415·21	2415·86		+0·04
45	2415·06	2415·71		+0·03
46	2414·94	2415·59		+0·05
47	2414·78	2415·43		+0·01
48	2414·64	2415·29		−0·01
49	2414·50	2415·15		−0·04

HELIUM.

No. of line.	λ (air).	μ (vacuo).	Probable error.	γ
2	20400		?	−20
3	5015·732	5016·996	0·02	±0·00*
4	3964·875	3965·848	0·02	±0·00*
5	3613·785	3614·662	0·02	+0·01
6	3447·734	3448·575	0·02	+0·025
7	3354·667	3355·499	0·02	+0·01
8	3296·900	3297·726	0·02	+0·03
9	3258·336	3259·152	0·02	−0·04
10	3231·327	3232·139	0·02	−0·04
11	3211·626	3212·437	0·02	−0·04
12	3196·81	3197·62	0·02	−0·03

The first column in the above tables contains the number of the line in the series, the second column contains the wave-length in air (Rowland), while the third column contains the wave-lengths in vacuo on the Fabry and Perot scale. The fourth column contains the estimated maximum experimental error, while the last column contains the differences between the calculated values and the observed values given in the third column.

On the other hand, in the case of cæsium the differences are far too large to be attributed to observational errors, but Birge points out that the Ritz formula is theoretically an infinite series. How many terms of the series must be used depends, of course, on the size of the coefficients. These coefficients are found to increase with increasing atomic weight, so that the higher terms become less negligible as the atomic weight increases. This increase in coefficients is shown in the following table:—

Substance.	Atomic weight.	α	β
Hydrogen . . .	1	0	0
Helium . . .	4	+0·011131	−0·004767
Lithium . . .	7	−0·047423	+0·025801
Sodium . . .	23	+0·144335	−0·1130286
Potassium . . .	39	+0·286917	−0·22083
Rubidium . . .	85	+0·345595	−0·265769
Caesium . . .	133	+0·411966	−0·33269

Again, in the cases of sodium, potassium, rubidium, and cæsium, the coefficients α and β are directly proportional to the atomic volumes, a fact that has also been noticed by Hicks.[1] These relations as given by Birge are shown in the following table:—

Substance.	α	β	$\frac{\beta}{\alpha}$	Atomic volume.	$\frac{\alpha}{\text{A.V.}}$	$\frac{\beta}{\omega}$
Sodium .	0·14433	−0·11302	0·784	23·606	615×10^{-5}	480×10^{-5}
Potassium	0·28692	−0·22083	0·770	44·617	643×10^{-5}	495×10^{-5}
Rubidium	0·34559	−0·26577	0·768	56·05	616×10^{-5}	473×10^{-5}
Cæsium .	0·41196	−0·33269	0·807	70·584	584×10^{-5}	472×10^{-5}

The Second Type of Regularity.—There remains now to be described the second type of regularity in spectra; for the discovery of this type we are indebted to Kayser,[2] and to Kayser and Runge.[3] In these spectra the regularity consists in the recurring of certain constant frequency differences between the lines; nothing further at present is known concerning the structure of the spectra; no series have been found similar to those previously described. The elements whose spectra belong to this group are tin and lead, arsenic, antimony, and bismuth, ruthenium, palladium, and platinum; further, also, Rydberg has shown similar differences in the spectra of copper[4] and argon.[5] The occurrence of constant frequency differences can best be shown by the two examples of tin and antimony (Kayser and Runge).

[1] *Proc. Roy. Soc.*, **83**. 226 (1910).
[2] *Abh. d. Berl. Akad.* (1897).
[3] *Ibid.* (1894).
[4] *Astrophys. Journ.*, **6**. 239 (1897)
[5] *Ibid.*, **6**. 338 (1897).

TIN.

1	2	3	4	5
3801·16	3175·13	−0·01	3009·24	0·00
3330·71	2840·05	+0·01	2706·59	+0·02
2850·72	2483·49	+0·01	2380·83	−0·01
2813·66	2455·32	−0·02	2354·93	+0·01
2785·14	2433·57	−0·04	2334·93	−0·04
2779·92	2429·59	−0·01	—	—
2594·49	2286·75	+0·04	2199·42	+0·04
2571·67	2269·00	+0·03	—	—
2524·05	2231·85	+0·05	2148·59	+0·11
2495·80	2209·73	+0·05	—	—
2408·27	2140·84	+0·26	2064·12	−0·32
2359·05	2101·06	−0·16	—	—
2317·32	2068·67	+0·03	—	—

In this table the first column contains a number of lines whose oscillation frequencies when increased by 5187·03 give the lines in the second column, the errors being shown in column 3; again, if we add 6923·26 to the frequencies of the lines in the first column, the frequencies of the lines in the fourth column are obtained with the differences given in the fifth column. In this way the lines in the horizontal rows form triplets of constant frequency difference.

A similar arrangement is found in the case of antimony.

ANTIMONY.

1	2	3	4	5	6
4033·70	3722·92	—	—	—	—
3637·94	3383·23	2770·03	2670·73	2395·30	2352·32
3232·61	3029·91	2528·61	2445·61	2212·63	2175·90
2851·20	2962·34	2289·09	2220·85	—	—
2719·00	2574·15	2203·09	2139·81	—	—
2652·70	2514·65	2159·36	2098·53	—	—
2614·74	2480·51	—	—	—	—
2554·72	2426·44	—	—	—	—
2481·81	2360·57	—	—	—	—
2373·78	2262·63	—	—	—	—
2329·19	2222·08	—	—	—	—
2306·56	2201·47	—	—	—	—

By adding to the frequencies of the lines in the first column 2069·49, 8612·61, 9954·87, 14260·29, and 15023·19, the lines in the columns 2, 3, 4, 5, and 6 are obtained, the errors being exceedingly small in every case.

The spectrum of copper is very interesting, because it shows on the one hand close analogies with the alkali metals, and on the other Rydberg has found similar series of lines with constant frequency differences like the heavy metals just mentioned, which cannot be arranged in series. Rydberg finds a series of six triplets, for which $\nu_1 = 129{\cdot}50$ and $\nu_2 = 50{\cdot}58$, also two series of pairs with these frequency differences; also a series of triplets with $\nu_1 = 680{\cdot}19$ and $\nu_2 = 212{\cdot}21$, and again one series of pairs for which $\nu = 680{\cdot}19$, and another with $\nu = 212{\cdot}21$. Rydberg also shows that these triplets and doublets can be sometimes arranged like the complex triplets of the alkaline earth metals. This is shown in the table—

I	ν_1		ν_2	
26599·07	129·46	26728·53	50·47	26779·00
679·73		679·84		680·02
27278·80	129·57	27408·37	50·65	27459·02
		212·35		212·22
		27620·72	50·52	27671·24

It will be seen that all four values of the constant frequency difference are to be found in the triplet. The red spectrum of argon contains a regularity quite similar to that of tin and antimony, etc.; the constant differences are 846·47, 1649·68, and 2256·71, these being supposed to be added to the lines in the first column as in tin and antimony above.

Band Spectra.—By a band spectrum is meant a fluted spectrum, or channelled-space spectrum, which, under higher dispersion, is resolved into groups of fine lines. These lines always get closer towards the red or blue, until they run together to a single line called the head. A single band thus consists of a single line or head, from which starts a series of lines, which become more and more separated the further they

are away from the head. A number of these heads with their attendant series form a group of bands, and a complete band spectrum may contain several of these groups. Such banded spectra are given by nitrogen in a vacuum tube; we have here two banded spectra, one in the positive column of the electric discharge and the other in the negative glow. We have also amongst others the cyanogen bands, and the two-band spectra of carbon.

For our knowledge of the structure of these bands we are indebted to Deslandres, whose work may be briefly described.[1] The first point noted by him was that the oscillation frequencies of the lines starting from one head form arithmetical series; we may call this, with Kayser,[2] Deslandres's first law. Deslandres noted that more than one such arithmetical series of lines can proceed from the same head; in the band spectrum, due to one particular substance, all the bands resemble one another, and comprise the same number of series all arranged in the same way.

A band spectrum thus consists of repetitions of similar groups of lines, *e.g.* pairs, triplets, quartets, etc., the number and distribution of the lines in the groups being connected with the number and distribution of the atoms in the vibrating molecule. This regular distribution of the lines may be to a small extent upset by certain irregularities and disturbances.

If now the heads of the bands forming a group be examined, it will be found that these again are regularly distributed in the same manner as the lines in each band. The differences in frequency of the heads of the bands in each group form an arithmetical series, but the arrangement of the heads is reversed from that of the lines forming each band; that is to say, if the bands themselves are degraded towards the blue, then the heads of the bands form sub-groups, which

[1] See the following papers: *Comptes Rendus*, **100.** 1259 (1885); **103.** 375 (1886); **104.** 972 (1887); **106.** 842 (1888); **112.** 661 (1891); **134.** 747 (1902); **138.** 317 (1904); *Ann. Chim. et Phys.*, **15.** 5 (1888); *Jour. d. Phys.*, **10.** 276 (1891).

[2] *Handbuch der Spectroscopie*, II, 475.

are degraded towards the red. Two further points of interest may be noted: first, that if we examine the successive sub-groups of a band spectrum in the direction in which the bands are degraded, it will be found that usually the number of bands in each sub-group is one less than in the previous sub-group; the second point is that while the head of each band is the brightest line in the band, the opposite is the case with the heads of the bands forming one sub-group, counting from the opposite end of the spectrum from the one to which the bands are degraded, the first head is the brightest in each sub-group, the second one next brightest, and so on.

The arrangement of the heads in a group of bands, so that they form an arithmetical series, may be called Deslandres's second law.

We may consider these laws of Deslandres more fully. The several series of lines forming each band are so arranged that the frequency differences between successive lines form an arithmetical series. Deslandres pointed this out first for the band with its head at 3914·6 in the negative pole spectrum of nitrogen. Such a series of lines can be expressed by a formula of the type—

$$\frac{1}{\lambda} = A + bn^2,$$

where n is a series of positive integers, 1, 2, 3, etc.

In the case of the band with its head at 3914·6, it can be very closely expressed by the formula—

$$\frac{1}{\lambda} = 25\text{5}\cdot454 + 0\cdot0015335(n - 1)^2,$$

as is shown by the following table :—

Number of the lines.	$\frac{1}{\lambda}$ observed.	$\frac{1}{\lambda}$ calculated.	Differences.
0	255·454	255·454	0·000
10	255·578	255·578	0·000
15	255·758	255·755	+0·003
23	256·197	256·196	+0·001
31	256·832	256·834	−0·002
39	257·672	257·668	+0·004
47	258·692	258·699	−0·007
55	259·916	259·926	−0·010
63	261·308	261·349	−0·041

Kayser and Runge[1] have proved this law also in the case of the great cyanogen band at $\lambda = 3883{\cdot}55$; they have shown that the law is not accurate when the series is exceptionally long, as, for example, in the case of this band. The results are shown in the following table, in which the wave-lengths are given:—

n	λ observed.	Calculated by Deslandres's formula.	Differences.	Calculated by Kayser and Runge.
0	3883·55	3883·55	0·00	3883·48
10	3882·50	3882·51	−0·01	3882·10
20	3879·36	3879·41	−0·05	3879·30
30	3874·16	3874·25	−0·09	3874·13
40	3866·95	3867·04	−0·09	3866·96
50	3857·82	3857·82	+0·00	3857·83
60	3846·79	3846·61	+0·18	3846·81
70	3833·93	3833·44	+0·49	3833·95
80	3819·36	3818·35	+1·01	3819·37
90	3803·16	3801·40	+1·76	3803·17
100	3785·42	3882·63	+2·79	3785·43
110	3766·39	3762·10	+4·29	3766·36
120	3746·15	3739·87	+6·28	3746·11
130	3724·91	3716·00	+8·91	3724·90
140	3702·92	3690·56	+12·36	3702·97
150	3680·51	3663·62	+16·89	3680·58
160	3658·05	3635·25	+22·80	3658·05

[1] *Abhand. Berl. Akad.* (1889).

The formula used for the third column was—

$$\frac{1}{\lambda} = 3883{\cdot}55 + 0{\cdot}0687n^2.$$

The figures in the fifth column were obtained by Kayser and Runge with a pure interpolation formula—

$$\frac{1}{\lambda} = a + be^{cn} \sin (dn)^2.$$

The Deslandres formula gives excellent results up to the seventieth line, but after that the intervals decrease rapidly in relation to the series.

Deslandres also points out that when there are more than one series in a band, these series are identical, and may be obtained one from the other by simple addition or subtraction of a constant; each series differs only in the value of the constant A.

Turning now to the second law of Deslandres, we have exactly the same arrangement of the heads of the bands in a group[1] as in the case of the lines in each band. Each group contains several series of heads of bands; each series is so arranged that the intervals between the frequencies of successive heads form an arithmetical progression, and, further, all the series in each group are exactly similar, and may be obtained one from the other by adding or subtracting a constant. This was first proved by Deslandres in the case of the second group of the positive nitrogen spectrum (λ 5000 – λ 2800). The heads of bands in one series can, therefore, be expressed by a formula of the same type as in the case of the line series—

$$\frac{1}{\lambda} = \mathrm{C} + \mathrm{B}n\,.$$

The five series in the second group of the nitrogen spectrum may be quoted.

[1] By a group of bands is meant the whole set of bands whose heads form associated series; such groups contain sub-groupings, in which the heads of bands are arranged very similarly to the lines in each band, but in the reversed sense, as explained on p. 613.

Series 1.	Series 2.	Series 3.	Series 4.	Series 5.	Intervals (calculated).
—	—	—	183·251	201·045	
					14·136
—	—	—	197·360	215·179	
					14·428
—	—	193·162	211·792	229·578	
					14·719
—	188·372	207·770	226·517	244·279	
					15·010
—	203·388	222·787	241·518	259·316	
					15·302
198·776	218·685	238·080	256·837	274·664	
					15·593
214·352	234·256	253·714	272·444	290·247	
					15·885
230·247	250·117	269·587	288·337	306·077	
					16·176
246·374	266·350	285·791	304·492	322·247	
					16·468
262·872	282·831	302·230	320·946	338·707	
					16·759
279·636	299·569	318·990	337·723	355·479	
					17·051
296·664	316·628	336·020	354·772	—	

The mean difference between series 1 and 2 is 19·9307, between series 2 and 3 is 19·419, between series 3 and 4 is 18·7247, and between series 4 and 5 is 17·782.

The differences between the consecutive terms are given in the last column; they form, as can at once be seen, an arithmetical series. The five series are, therefore, absolutely similarly constituted, and only differ from one another by a constant amount in each case.

Cuthbertson[1] was the first to point out that the first group in the positive spectrum of nitrogen could be arranged in the same way; he arranged the heads of the bands in thirteen series, some of which contain only two members.

This table may be given here on account of the interesting way in which it confirms Deslandres's law:—

[1] *Phil. Mag.*, **3**. 348 (1902).

1	2	3	4	5	6	7	8	9	10	11	12	13
150·96												
15·31												
166·27	152·78											
15·02	15·01											
181·29	167·79	154·58										
14·78	14·72	14·73										
196·07	182·51	169·31	156·37									
		14·42	14·43	158·15								
		183·73	170·80	14·13								
		14·09	14·11	172·28	159·91							
		197·82	184·91	13·83	13·84							
		13·86	13·82	186·11	173·75	161·65						
		211·68	198·72		13·51	13·54	163·19					
			13·53		187·26	175·19	13·46	164·74				
			212·25(?)			13·23	176·65	13·34	179·51			
						188·42	12·90	178·08	12·27	180·93		
							189·55	12·59	191·78	11·93	182·32	
								190·67		192·86	11·63	183·73
											193·95	11·29
												195·02

All the bands except 163·19 and 164·74 conform to this scheme very well; one band, 183·73, is used twice. Cuthbertson points out that the last member of the thirteenth series, 195·02, is consecutive to the last member of the first series.

Deslandres[1] pointed out that if fifteen series were adopted in place of the thirteen which Cuthbertson recognises, then the two heads at 163·19 and 164·74 at once conform to the scheme, as well as a new head measured by Thalen at 147·29. Further, it is interesting to note that in addition to the fact the intervals between the horizontal rows form an arithmetical series, the intervals between the vertical columns also form an arithmetical series, which Deslandres has called the second progression.

Now, it has been shown that both the heads of the bands and the lines in the bands can be expressed by formulæ of the type—

$$\frac{1}{\lambda} = A + Bn^2.$$

The two formulæ can be united into one—

$$\frac{1}{\lambda} = Am^2 + Bn^2 + C.$$

Deslandres calculated back by means of this formula to the origins of the five series in the second group of the nitrogen spectrum given above; he then found that the squares of the numbers so obtained formed a series, the intervals between whose terms formed an arithmetic series. The term C can therefore be replaced by $\sqrt{Cp^2 + \gamma}$, where p is a series of integers. Again, the term A is not a constant for all the series; it appears to be a simple function of the parameters n^2 and p^2 which define the originating line of the band. Deslandres thus arrives at the general formula—

$$\frac{1}{\lambda} = f(n^2, p^2) \times m^2 + Bn^2 + \phi(p^2),$$

m^2, n^2, p^2 being the squares of successive whole numbers, B a constant, and f and ϕ special functions to be determined. In general the variations of m give the rays of one band, and those of n and p the heads of the different bands. By means

[1] *Comptes Rendus*, **134**. 747 (1903).

of this formula the heads of the bands given by Cuthbertson above can be calculated as follows :—

$$\frac{1}{\lambda} = 22785{\cdot}1 - \frac{30{\cdot}319}{8}(2n)^2 + \frac{29{\cdot}363}{8}(2p+1)^2.$$

$\frac{1}{\lambda}$

n	p	Calculated.	Observed.	Differences.
53	48	14737·3	14729	−8·3
52	48	16329·0	16319	−10·0
52	47	14919·6	14915	−4·6
51	47	16481·0	16474	−7·0
51	46	15100·9	15096	−4·9
50	46	16632·0	16627	−5·0
49	46	18132·8	18129	−3·8
48	46	19603·2	19607	+3·8
50	45	15281·3	15278	−3·3
49	45	16782·1	16779	−3·1
48	45	18252·5	18251	−1·5
49	44	15460·8	15458	−2·8
48	44	16931·2	16391	−0·2
47	44	18371·9	18373	+1·1
46	44	19781·1	19782	+0·9
45	44	21760·6	21168	+7·4
48	43	15639·2	15637	−2·2
47	43	17079·4	17080	+0·6
46	43	18489·2	18491	+1·8
45	43	19868·6	19872	+3·4
44	43	21217·8	21225	+7·2
47	42	15816·7	15815	−1·7
46	42	17226·6	17228	+1·4
45	42	18606·7	18611	+4·3
46	41	15993·5	15991	−2·3
45	41	17372·8	17375	+2·2
44	41	18722·0	18726	+4·0
45	40	16168·9	16165	−3·9
44	40	17518·1	17519	+0·9
43	40	18836·9	18842	+5·1
43	39	17662·4	17665	+2·6
42	39	18950·9	18955	+4·1
42	38	17805·8	17808	+2·2
41	38	19064·0	19067	+3·0
41	37	17948·2	17951	+2·8
40	37	19176·1	19178	+1·9
40	36	18089·7	18093	+3·3
39	36	19287·3	19286	−1·3
39	35	18230·2	18232	+1·8
38	35	19397·5	19395	−2·5
38	34	18369·8	18373	+3·2
37	34	19506·7	19502	−4·7

Deslandres has also investigated very fully the series of lines in the band with head at $\lambda = 3577$ in the second group of the nitrogen spectrum. He finds that there are six series of lines, one series containing pairs. They can all be expressed by the formula—

$$\frac{1}{\lambda} = A\left(m + \frac{p}{q}\right)^2 + C.$$

Thus—

Series 1: $\frac{1}{\lambda} = 27946{\cdot}046 + 0{\cdot}1967023(m + \frac{3}{4})^2,$

and so on.

On page 592 it was pointed out that Thiele has brought forward the formula for all spectra—

$$\lambda = f[(n + c)^2],$$

and that as a result there must be a head and a tail to every series. If that were so, we should expect to find such tails in band spectra with the bands degraded the opposite way to the "head" bands. If that were so, we should also expect to find that the intervals between the successive lines in a series in a band should not form an arithmetic series for all the terms, but that they should increase more and more slowly until they reach a point where they begin to decrease. Both these facts have actually been noted. If we take the cyanogen band with its head at $\lambda = 3883{\cdot}55$, and note the successive intervals as measured by Kayser and Runge—

n	λ	Difference.	n	λ	Difference.
10	3882·50	0·23	120	3746·15	2·08
11	3882·27	0·22	121	3744·07	2·11
12	3882·05		122	3741·96	
20	3879·36	0·45	140	3702·92	2·21
21	3878·91	0·45	141	3700·71	2·23
22	3878·46		142	3698·48	
40	3866·95	0·82	150	3680·51	2·25
41	3866·13	0·83	151	3678·26	2·26
42	3865·30		152	3676·01	
60	3846·79	1·21	160	3659·05	2·23
61	3845·58	1·23	161	3655·82	2·20
62	3844·35		162	3653·62	
80	3819·36	1·57	167	3642·63	2·17
81	3817·79	1·55	168	3640·46	2·17
82	3816·24		169	3648·29	
100	3785·42	1·82			
101	3783·60	1·85			
102	3781·75				

Clearly the differences mount to a maximum and then begin to decrease.

The tails of the cyanogen bands have apparently been discovered by King,[1] who obtained them by photographing the

[1] *Astrophys. Journ.*, **14**. 323 (1901).

cyanogen spectrum with a very long exposure. They were found at—

$\lambda = 3160{\cdot}32$ and $3405{\cdot}04$	$\lambda = 3658{\cdot}34$ and $3984{\cdot}93$
$= 3180{\cdot}58$ „ $3433{\cdot}17$	$= 3629{\cdot}06$ „ $3944{\cdot}91$
$= 3203{\cdot}84$ „ $3465{\cdot}69$	$= 3603{\cdot}12$ „ $3910{\cdot}45$

and must be the tails corresponding to the heads as follows :—

Head.	Tail.	Ratio $\frac{\text{head}}{\text{tail}}$.	Head.	Tail.	Ratio $\frac{\text{head}}{\text{tail}}$.
3883·60 3590·52	3465·69 3203·84	1·12059 1·12069	4165·54 4532·06	3658·34 3984·93	1·13864 1·13730
3871·59 3585·99	3433·17 3180·58	1·12770 1·12746	4158·22 4514·95	3629·06 3944·91	1·14581 1·14450
3861·91 3584·10	3405·04 3160·32	1·13417 1·13409	4152·93 4502·35	3603·12 3910·45	1·15259 1·15136

These facts go strongly to corroborate Thiele's theory, and at the same time they limit the applicability of Deslandres's laws. Deslandres, however, knew that his formula does not express the lines in a series beyond about the sixtieth line; as he then pointed out, the intervals do not increase in the right proportion. In all probability, when the lines in the tails of these band spectra have been properly mapped, we shall find that Deslandres's laws apply equally well to these, but at present nothing is known except the wave-lengths given above.

The Relations between the Spectra of the Elements of one Family.—Certain observations have been made upon the relations between analogous spectra, amongst which is much that is worthless. Amongst the earliest information we have on this matter is that given by Lecoq de Boisboudran, who stated that in the spectra of the alkali metals and of the alkaline earths the lines, considered according to their refrangibilities, are placed according to their atomic weights. He found that

with increase of atomic weight in metals of the same family the lines were shifted to the red. Our present knowledge is based upon the measurements made by Kayser and Runge, and by others, and upon the arrangement of the lines in series according to these observers' and Rydberg's formulæ. Certain facts have been pointed out by Kayser and Runge, and one of the most important is the fact that in the case of the elements of the same family the constant frequency difference of the pairs or the triplets are very nearly proportional to the squares of the atomic weights. In order to show this we may, with Rydberg,[1] compare the values of $\frac{1000\nu_1}{P^2}$, where P is the atomic weight; the following table contains the results :—

	Na = 23·06	Mg = 24·38	Al = 27·08	O = 16
ν_1	17·19	40·91	112·02	3·70
$\frac{10^3\nu}{P^2}$	32·3	68·8	152·8	14·5
	K = 39·14	Ca = 40·00	Ga = 69·9	S = 32·06
ν_1	57·85	105·82	823·6	18·15
$\frac{10^3\nu_1}{P^2}$	37·8	66·1	168·6	17·7
	Rb = 85·44	Sr = 87·52	In = 113·4	Se = 79·07
ν_1	235·98	394·22	2212·54	103·7
$\frac{10^3\nu_1}{P^2}$	32·3	51·5	172·1	16·6
	Cs = 132·88	Ba = 137·04	Tl = 204·15	
ν_1	553·87	878·5	7792·63	
$\frac{10^3\nu_1}{P^2}$	31·6	46·8	187·0	

Another interesting point Rydberg mentions in the same paper is, that if all the values of the expression $\frac{10^3\nu_1}{P^2}$ are plotted against the atomic weights P, a periodic curve is obtained and also an identically shaped periodic curve is obtained if the values of the common convergence frequencies

[1] *International Reports*, **2**. 217 (Paris, 1900).

of the first and second subordinate series are plotted instead of the expression $\frac{10^3 \nu_1}{P^2}$.

Ritz[1] has shown that much closer values than the above are obtained if in place of $\frac{1000\nu_1}{P^2}$ we introduce $\frac{p_2 - p_1}{P^2}$;[2] the discrepancies which still remain are probably due in part to the incompleteness of the series equations, but more especially to the fact that $(\pi_1 - \pi_2)^2$ is neglected, which is certainly not admissible in the case of aluminium, indium, and thallium. If we knew the principal series of these elements it would be possible to decide about this. Ritz gives the following values for $\frac{p_2 + p_1}{P^2} \times 10$:

Sodium	14·2	Rubidium	18·0
Copper	18·6	Magnesium	14·6
Strontium	15·7	Cadmium	18·6
Aluminium	24·8	Thallium	32·7
Potassium	18·9	Cæsium	18·6
Silver	24·2	Calcium	17·7
Zinc	17·2	Mercury	22·3
Indium	29·2	Helium	20·4

As the atomic weight increases it is known that the series fall off with increasing rapidity, so that only those lines are observed which correspond to the lowest numbers of the order. At the same time the number of the different series and the number of combinations increase. Thus, finally, a spectrum is reached in which there exist a large number of characteristic constant differences but no series. Ritz puts forward the view that the so-called spectra of the second class are those with very many combinations and with very slightly developed series.

Ramage[3] has published two papers on this subject, in the first of which he discusses the relations of the spectra, densities, and melting-points to atomic mass. Ramage carefully selects the lines which correspond in the spectra of analogous elements, that is to say, lines which have the same value of

[1] *Phys. Zeitschr.*, **9**. 521 (1908).

[2] For the meaning of $p_2 - p_1$ and $\pi_1 - \pi_2$, see p. 598.

[3] *Proc. Roy. Soc.*, **70**. 1, and 303 (1902).

m in the equations to the series; the frequencies of these lines are then plotted against the squares of the atomic masses. When the corresponding points are joined together by lines, it will be found that these lines are mostly straight; there are, however, breaks in certain places, *e.g.* between sodium and potassium, and between magnesium and zinc. The diagram shows very clearly what was stated above, that ν varies with the square of the atomic weight; the lines connecting the corresponding members of homologous triplets and doublets intersect on the line of zero atomic mass. It is also interesting to note that curves of exactly the same shape, that is to say, curves with the same breaks, are obtained by plotting the absorption maxima found with the lakes formed with metallic salts and alkannin (see p. 456) against the squares of the atomic weights.

Ramage gives an equation based on that deduced by Rydberg, by which can be calculated the frequencies of the principal series of potassium, rubidium, and cæsium; in Rydberg's equation he puts—

$$n_0 + 35349 - 0{\cdot}2233\mathrm{W}^2,$$

where W is the atomic weight and

$$\mu = \{1{\cdot}19126 + 0{\cdot}00103\mathrm{W} + (0{\cdot}04377 + 13\mathrm{W}^2 \times 10^{-7})(1 - 3^{1-m})\}.$$

The last factor $(1 - 3^{1-m})$ is inserted to correct for a small variation in μ, which, he considers, occurs throughout the series. The frequencies obtained with this formula agree very closely with the observed values. In his second paper, Ramage gives similar equations for the subordinate series of these metals; the two convergence points of the first subordinate series are obtained from the equation—

$$n_0 = 22830 - 21{\cdot}633\mathrm{W} \pm \frac{\mathrm{A}}{2},$$

where W is the atomic weight and A is the average distance between the doublets. This distance he takes to be 57·8, 236·4, and 547·6 for potassium, rubidium, and cæsium respectively. The frequency of the lines of the series can be obtained from the equation of Rydberg by putting $\mu = 0{\cdot}7869$

$-(1466W^2 \times 10^{-8})$; the results calculated in this way are very near the observed values. For the second subordinate series Ramage finds—

$$n_0 = 22850 - 21{\cdot}812W \pm \frac{B}{2}$$

and $$\mu = 0{\cdot}7990 + 7784W^2 \times 10^{-9},$$

where B = 57·8, 238·0, and 553·6 for potassium, rubidium, and cæsium respectively. The following comparison of the values of the convergence frequencies of the two series as obtained by the various methods is given by Ramage :—

Element.	From above formulæ.			By calculation from observed lines.	From formula for principal series.	Rydberg's[1] values.
	First series.	Second series.	Mean of two series.			
				mean.		
Potassium (1)	21953·9	21968·0	21960·95	21960	21969·4	21955·46
,, (2)	22011·7	22025·8	22018·75	22018	22024·3	22013·31
Rubidium (1)	20861·8	20868·3	20865·65	20865	20868·6	20869·15
,, (2)	21098·2	21106·3	21102·25	22101	21112·3	21098·83
Cæsium (1)	19677·2	19674·2	19675·7	19672	19686·7	—
,, (2)	20224·8	20228·0	20226·4	20226	20234·2	—

The numbers in the sixth column were obtained by the Rydberg-Schuster law,[2] which connects the principal and subordinate series.

Marshall Watts[3] has drawn attention to interesting relationships between the spectra of analogous metals and the squares of their atomic weights. He finds that there are two distinct kinds of connection between the spectra of allied elements. In one class, to which zinc, cadmium, and mercury, and gallium and indium belong, the differences between the oscillation frequencies of certain lines of the one element are to the differences between the oscillation frequencies of the corresponding lines of the other element as the squares of their atomic weights. It is thus possible to calculate the atomic weight of one element from the atomic weight of another of the same family by means of their spectra. In

[1] *Paris Reports*, **2.** 212 (1900). [2] See p. 576.

[3] *Phil. Mag.*, **5.** 203 (1903).

the other class of cases to which the alkali metals and those of the alkaline earths belong, the element of greater atomic weight has the smaller oscillation frequency; three elements are so related that the frequency differences between the elements, in comparing corresponding lines in their spectra, are proportional to the differences between the squares of the atomic weights. It is thus possible in this case to calculate the atomic weight of one element from the atomic weights of two other elements in the same series.

An example may be given from the two classes in order to show the accuracy.

Example 1.—Determination of the atomic weight of zinc (64·9) from that of cadmium (111·83).

The following are the oscillation frequencies of the lines assumed to correspond :—

	Cadmium.		Zinc.	
(*a*)	30654·4	10*r*	32500·0	8*r*
(*b*)	30734·9	8*b*	32540·1	10*r*
(*c*)	31905·5	8*b*	32928·7	10*b*
(*d*)	32446·8	6*b*	33118·6	8*b*
(*e*)	36023·7	6*b*	34310·8	4
(*f*)	37334·5	8	34791·3	6
(*g*)	38851·1	4	35285·7	8*r*
(*h*)	39280·5	2*n*	35408·9	6
(*i*)	43690·5	10*r*	36934·7	6
(*j*)	44086·7	4*r*	37059·2	2*b*
(*k*)	44630·0	6*r*	37242·2	8*b*
(*l*)	45550·6	1	37548·1	8

From these numbers we get for the atomic weight of zinc by combining—

(*a*)	and	(*c*)	65·44	
(*a*)	„	(*d*)	65·69	
(*a*)	„	(*f*)	65·48	
(*a*)	„	(*g*)	65·17	
(*a*)	„	(*h*)	64·93	
(*a*)	„	(*i*)	65·28	
(*a*)	„	(*j*)	65·15	
(*a*)	„	(*k*)	65·12	
(*a*)	„	(*l*)	65·16	
(*b*)	„	(*e*)	64·69	
(*c*)	„	(*e*)	64·77	and so on.

	Cadmium.		Zinc.	
(*m*)	19655·8	10*r*	21170·0	10*r*
(*n*)	20826·7	10*r*	21591·6	8*b*
(*o*)	28840·2	10*r*	24371·4	2
(*p*)	30301·9	4	24869·7	4

(*m*) and (*n*) 67·08
(*n*) „ (*o*) 65·38
(*n*) „ (*p*) 65·76
(*m*) „ (*p*) 65·98

	Cadmium.		Zinc.	
(*q*)	27669·1	8*r*	29885·1	10*r*
(*r*)	29370·4	10*r*	30456·0	8*r*

(*q*) and (*r*) give 64·78 for the atomic weight of zinc.

Example 2.—From the atomic weight of cæsium, 132·7, and that of potassium to calculate the atomic weight of rubidium (85·2).

The following lines are assumed to correspond:—

	Cæsium.		Rubidium.		Potassium.	
(*a*)	12469	6	13742	4	14465	7
(*b*)	21764	6*r*	23714	6*r*	24700	6*r*
(*c*)	21945	8*r*	23791	8*r*	24719	8*r*
(*d*)	25707	4*r*	27833	4*r*	28998	6*r*
(*e*)	25787	6*r*	27868	6*r*	29006	8*r*
(*f*)	27638	2*r*	29832	2*r*	31068	4*r*
(*g*)	27678	4*r*	29852	4*r*	31073	6*r*

(*a*) gives 86·87
(*b*) „ 83·24
(*c*) „ 83·11
(*d*) „ 84·51
(*e*) „ 84·93
(*f*) „ 85·52
(*g*) „ 85·51

Runge and Precht[1] have determined the atomic weight of radium by comparing the constant frequency difference of the pairs in the first and second subordinate series with those in the cases of magnesium, calcium, strontium, and barium. It has been stated before that this constant frequency difference, which is the same as in the first pair of

[1] *Phys. Zeitschr.*, **4**. 285 (1903).

the principal series, is proportional to the squares of the atomic weights of the elements in one family. This, however, according to Runge and Precht, is not strictly true, but the atomic weight is proportional to a power of the frequency difference, or the logarithms of the atomic weights are a linear function of the logarithms of the frequency differences. Now, radium belongs to the same family as magnesium, calcium, strontium, and barium, whose constant frequency differences are 9·17, 223, 801, and 1691 respectively. On plotting the logarithms of these numbers against the logarithms of the atomic weights, a straight line was drawn through the points and extrapolated to find the atomic weight of radium, taking its frequency difference as 4858·6. The atomic weight in this way was found to be 257·8. Against this, however, is the experimentally determined number 225, which fits in the periodic classification much better than the value 257·8.

On the other hand, Marshall Watts [1] has drawn the curves for four different families, and finds that the lines are not straight but are slightly curved; the effect of this curvature being especially noticeable in the case of the elements of the highest atomic weight. From the curve of the alkaline earths he has calculated an interpolation formula which gives the atomic weights as follows:—Magnesium, 24·52; calcium, 40·08; strontium, 87·62; barium, 137·41; and radium, 226·56, from which latter number it may be concluded that the spectrum data are quite consistent with the atomic weight found for radium by chemical methods.

In conclusion, a few words may be said in regard to the apportioning of lines in series. In this connection the properties and behaviour common to the lines of one series should be carefully observed.

First, we have the character of the lines, whether they are sharp or nebulous or whether they are easily self-reversed, or whether they are long or short lines; for example, the lines belonging to the principal series in the alkali metals are easily self-reversed. The lines in a spectrum may be sorted into series and groups by comparing their characters.

[1] *Phil. Mag.*, **18**. 411 (1909).

Secondly, we have the Zeeman effect, which gives us the same types of resolution for all lines of the same series even in different elements.

Thirdly, Humphreys' pressure effect, by means of which all the lines of one series suffer proportional shifts with equa pressure changes (see Chapter XVIII.).

Fourthly, the comparison between flame, arc, and spark spectra.

Fifthly, the existence of constant frequency differences in the spectra.

Sixthly, the influence of self-induction.

In addition to the papers discussed in this chapter reference may be made to the following:—

Barnes, "New Lines in the Spectrum of Calcium," *Astrophys. Journ.*, **30**. 14 (1909).

Conway, "Series in Spectra," *Proc. Roy. Soc., Dublin*, **11**. 181 (1907).

Derichsweiler, "Band Spectra of Copper Halogen Salts," *Zeit. wiss. Phot.*, **4**. 401 (1906).

Deslandres, "Negative Band Spectrum of Nitrogen," *Comptes Rendus*, **139**. 1174 (1904).

Deslandres and d'Azambuja, "New Band Spectrum of Carbon," *Comptes Rendus*, **140**. 917 (1905).

Fabry, "Arc Spectra of the Fluorides of the Alkaline Earths," *Comptes Rendus*, **140**. 578 (1905).

Fowler, "New Triplets in the Arc Spectrum of Strontium," *Astrophys. Journ.*, **21**. 81 (1905).

Fowler, "Fluted Spectrum of Titanium Oxide," *Proc. Roy. Soc.*, **79**. 509 (1907).

Hicks, "Critical Study of the Spectral Series of the Alkalies, Helium, and Hydrogen," *Phil. Trans.*, **210**. 57 (1910).

Hoeller, "The Red Portion of the Spectrum of Barium," *Zeit. wiss. Phot.*, **6**. 217 (1908).

Jungbluth, "Regularities in the Structure of the third Cyanogen Band," *Astrophys. Journ.*, **20**. 237 (1904).

Kien, "Flame Spectrum of Copper Chloride," *Zeit. wiss. Phot.*, **6**. 337 (1908).

Kretzer, "Series in the Antimony Spectrum," *Zeit. wiss. Phot.*, **8**. 45 (1910).

Lohmeyer, "Band Spectra of Mercury Halogen Salts," *Zeit. wiss. Phot.*, **4**. 367 (1906).

Meisenbach, "Arc Spectrum of Calcium Chloride," *Zeit. wiss. Phot.*, **6.** 658 (1908).

Milner, "Series Spectrum of Mercury," *Phil. Mag.*, **20.** 636 (1910).

Mogendorff, "A new Empirical Spectrum Formula," *Konink. Akad. Wetensch. Amsterdam, Versl.*, **15.** 429 (1906).

Olmsted, "Band Spectra of closely allied Compounds," *Zeit. wiss. Phot.*, **4.** 255 (1906).

Paschen, "Infra-red Line Spectra," *Ann. der Phys.*, **27.** 537 (1908); **29.** 625 (1909); and **33.** 717 (1910).

Paschen, "Series Systems in the Spectra of Zinc, Cadmium, and Mercury," *Ann. der Phys.*, **30.** 746 (1909).

Randall, "Infra-red Line Spectra," *Ann. der Phys.*, **33.** 739 (1910).

Riecke, "Series of Lines in Potassium," *Phys. Zeit. Schr.*, **9.** 241 (1908).

Ritz, "Origin of Spectral Series," *Comptes Rendus*, **144.** 634 (1907), and **145.** 178 (1907).

Rösch, "Band Spectra of the Fluorides of the Alkali Metals," *Zeit. wiss. Phot.*, **4.** 384 (1906).

Rudorf, "Spectral Series and the Atomic Weight of Radium," *Zeit. Phys. Chem.*, **50.** 110 (1904).

Runge, "Spectra of the Alkali Metals," *Phys. Zeitschr.*, **9.** 1 (1908).

Saunders, "Arc Spectra of the Alkali Metals," *Astrophys. Journ.*, **20.** 188 (1904).

Saunders, "Narrow Triplets in the Spectra of Calcium and Strontium," *Astrophys. Journ.*, **21.** 195 (1905).

Saunders, "Series in the Arc Spectra of Magnesium, Zinc, and Cadmium," *Phys. Rev.*, **20.** 117 (1905).

Saunders, "Series in the Alkali Metal Spectra," *Astrophys. Journ.*, **28.** 71 (1908).

Saunders, "Series in the Spectrum of Barium," *Astrophys. Journ.*, **28.** 223 (1908).

Saunders, "Series in the Spectra of Calcium, Strontium, and Barium," *Astrophys. Journ.*, **32.** 153 (1910).

Schott, "Kinematical Explanation of Groups of Spectrum. Lines with Constant Frequency Difference," *Phil. Mag.*, **12.** 579 (1906).

Von der Helm, "Investigation of the Long Wave Regions of the Nitrogen Band Spectrum," *Zeit. wiss. Phot.*, **8.** 405 (1910).

Watson, "Regularities in the Spectrum of Neon," *Astrophys. Journ.*, **33.** 399 (1911).

Wolter, "Ultra-violet Bands in the Spectrum of Carbon Monoxide," *Zeit. wiss. Phot.*, **9.** 361 (1911).

Wood, "An Extension of the Principal Series of the Sodium Spectrum," *Phil. Mag.*, **16.** 945 (1908).

Wood, "The Complete Balmer Series in the Sodium Spectrum," *Astrophys. Journ.*, **29.** 97 (1909).

Zickendraht, "The Spectrum of Sodium," *Ann. der Phys.*, **31.** 233 (1910).

CHAPTER XVIII

CHANGE OF WAVE-LENGTH

Change of Wave-length by Pressure.—A series of investigations on this subject have been carried out by Humphreys and Mohler, and their results have been published by them conjointly and separately.[1] In 1897 Humphreys published a very complete account of the work, which contained some very interesting relations that had been discovered in the measurements. The experimental method was as follows: an electric arc was enclosed in an iron cylinder 14 inches high and 7 inches in diameter, with a stuffing box at each end, through which rods passed carrying the poles. This cylinder was air-tight, and air was pumped into it, the pressure being read upon a Bourdon pressure gauge; the greatest pressure used was about 15 atmospheres. The poles of the arc were vertical, and the light from the arc passed out through a quartz window in the side of the iron cylinder; in general two carbon poles were used, and the lower one (positive) was bored with a $\frac{1}{8}$-inch hole, into which the required substance was placed; sometimes the lower or both carbons were replaced by metal rods. A Rowland grating of 21 feet 6 inches focus and 20,000 lines to the inch was used, and comparison photographs were taken of the spectra at various pressures. Shifts of the lines were then observed, always towards the red, and these shifts were found to be due to the external pressure of the air; they were not in the nature of an unsymmetrical broadening, but were a

[1] *Astrophys. Journ.*, **3.** 114 (1896); **4.** 175 (1896); **4.** 249 (1896); **6.** 169 (1897).

definite change of position of the line in the spectrum. It was found that a change of temperature alone produced no shift in the lines, as the wave-lengths of lines were found to be the same at both poles, although the positive pole is the hotter, nor was any change observed when the current was increased from 3 to 180 amperes. An increase in the density or partial pressure of the vapour of the substance produces a broadening, as is well known from the thickening of the lines in the centre of the spectrum of a horizontal arc. It was found that the shifts were proportional to the absolute pressure, because experiments were made at the same external pressure, but with gradually increasing amounts of substance in the arc; the shift was the same in all cases.

The displacement of any line is directly proportional to the excess of pressure above 1 atmosphere (the position of the line at atmospheric pressure being considered as its normal position), and is always towards the red end of the spectrum.

This is also true for pressures below 1 atmosphere. Further, the shift is proportional to the wave-lengths of the lines; it is possible therefore to make comparisons of the shifts of lines with different substances, by reduction of those observed to some chosen standard of pressure and wave-length. Measurements were made of the wave-lengths of a number of lines in each of forty-eight metals, and from the values obtained the following conclusions were drawn.

Any harmonic series of lines of an element give shifts (reduced to the same standards) which are approximately equal, while the shifts of the principal, first subordinate, and second subordinate series have very nearly the ratio 1 : 2 : 4. In general we may say, therefore, that lines of the same character of any element give equal shifts.

The product of the cube root of the atomic volume (atomic weight divided by density) and the coefficient of linear expansion of an element is approximately the same as the shifts of the lines. Further, the shift of the lines is inversely proportional to the absolute temperature of the melting-point. This follows from Pictet's observation that the product of the absolute

temperature of the melting-point, the coefficient of linear expansion, and the cube root of the atomic volume, is nearly the same for all metals except antimony and bismuth.

Some of these comparisons are given in the following table:—

Element.	Atomic volume V.	Coefficient of linear expansion α.	Melting-point (absolute) T.	$\frac{48600}{T}$	Shift.	$\alpha\sqrt[3]{V}$.
Aluminium	10·6	0·00002313	1123°	43·3	55	50·6
Antimony .	17·9	0·00001692	710°	68·0	49	43·0
Bismuth. .	21·1	0·00001621	538°	90·3	49	44·7
Cadmium .	12·9	0·00003069	593°	82·0	76	75·6
Cobalt . .	6·9	0·00001236	2070°	24·0	24	23·6
Copper . .	7·1	0·00001678	1330°	36·5	33	32·5
Gold . .	10·1	0·00001443	1310°	37·0	40	67·0
Iron . . .	7·2	0·00001210	2080°	23·3	25	23·3
Lead . .	18·1	0·00002924	605°	80·3	60	76·9
Magnesium	13·9	0·00002694	1023°	47·0	{62} {44}	65·0
Potassium .	45·4	0·00008415	335°	145·0	132	300·0
Sodium . .	23·7	0·00007105	369°	132·0	108	204·0
Tin . . .	16·3	0·00002234	503°	96·6	55	50·6
Zinc . . .	9·1	0·00002918	676°	71·9	57	61·2

In this table are given a few examples selected for which all the data are known; in the column headed $\frac{48600}{T}$ the constant 48600 was so chosen as to bring the value of $\frac{48600}{T}$ the same as the value of $\alpha\sqrt[3]{V}$ for iron. In the column headed "shift" are given the shifts in thousandths of an Ångström unit reduced to $\lambda = 4000$ and a pressure of 12 atmospheres. In the last column are given the products of the coefficient of expansion and the cube root of the atomic volume, multiplied by 10^6.

In the case of magnesium, where two values of the linear shift are given, the upper and lower values are for the second and first subordinate series respectively; the values given for potassium and sodium are for the principal series.

The shift of the lines is a periodic function of the atomic weight, like the atomic volume and other properties. If a curve be drawn with linear shifts on the ordinates and atomic weights on the abscissæ, the shape of the curve is very similar to the atomic volume curve.

Further, it was also found that the shifts of lines of the same series belonging to elements in the same sub-group of the periodic table are proportional to the cube of the atomic weight of the elements; there are certain exceptions to this, for if the shifts of the uranium, neodymium, platinum, osmium, yttrium, thorium, tantalum, and tungsten lines be calculated from this rule they will be found to be about twice what have been actually observed. It is very probable that comparable lines have not been observed in these cases; doubtless they are only apparent exceptions. The following table gives a few results of comparison of the observed shifts and those calculated from the cube root of the atomic weight; the shifts again are reduced to $\lambda = 4000$ and $p = 12$ A.

Standard.		Calculated.		Observed.
Cæsium . . .	161	Lithium	60	85
		Sodium	90	108
		Potassium	109	132
		Rubidium	139	132
Copper . . .	33	Silver	39	39
		Gold	48	40
Calcium—				
(1st subordinate series)	54	Magnesium	46	44
			23	30
(Principal series)	52	Strontium	70	65
			35	37
		Barium	81	58
			40	34
Zinc.	57	Beryllium	30	36
		Cadmium	68	76
		Mercury	83	81
Aluminium . .	55	Boron	40	49
		Indium	89	88
		Thallium	106	102

Standard.		Calculated.		Observed.
Tin	55	Carbon	26	50 (only one line)
		Silicon	34	43
		Germanium	47	44
		Lead	66	60
Bismuth . . .	49	Arsenic	35	38
		Antimony	41	49
		Erbium	45	47
Chromium . .	26	Molybdenum	32	40

Humphreys sums up the results as follows:—

1. Increase of pressure causes all isolated lines to shift towards the red end of the spectrum.

2. This shift is directly proportional to the increase of pressure.

3. It does not depend upon the partial pressure of the luminescent gas or vapour, but upon the total pressure.

4. The shift is nearly or quite independent of the temperature.

5. The lines of bands are not shifted (aluminium oxide and cyanogen bands).

6. The shifts of the similar lines of an element are proportional to the wave-lengths of the lines.

7. Different series of lines are shifted to different extents. Kayser and Runge's principal, first, and second subordinate series shift at the same wave-length and pressure in the ratio of 1 : 2 : 4.

8. The similar lines of an element (though not belonging to a recognised series) are shifted equally, but to a different extent from those lines unlike them.

9. The shifts of the similar lines of different metals are to each other, in most cases, as the absolute temperatures of the melting-points of the metals.

10. The shifts of the similar lines of different elements are to each other approximately as the product of the coefficients of linear expansion, and the cube roots of the atomic volumes of the elements in the solid state.

11. Analogous or similar lines of elements belonging to the

same sub-group of the periodic table shift proportionately to the cube root of the atomic weights.

12. The lines of those substances which have in the solid state the greatest coefficients of linear expansion have the greatest shifts. The converse is also true.

13. The shift of similar lines is a periodic function of the atomic weight.

Since Humphreys' original papers, a number of investigations have been made in this field, amongst which may be mentioned the following. The effect of pressure upon the arc spectrum of iron, copper, silver, and gold by Duffield.[1] The effect of pressure on the band spectrum of the fluorides of the alkaline earth metals and upon the arc spectrum of titanium by Rossi.[2] Duffield has found that although the iron lines have never yet been arranged in series, yet from their displacements they can be divided into three groups, and the shifts of these three groups bear to one another the approximate ratio 1 : 2 : 4. Moreover, as the pressure is increased, the self-reversed lines become more numerous, the tendency to reverse reaching a maximum in the neighbourhood of 20 to 25 atmospheres. Some changes were also noticed in the relative intensity of the lines, some being enhanced and some being weakened.

In the case of copper which was investigated between the limits $\lambda = 4000$ and $\lambda = 4600$, no tendency to reverse was noticed.

In his paper on the effect of pressure on the band spectra of the alkaline earth fluorides, Rossi has shown that these bands are shifted towards the red. This result is of great importance, because it has already been shown by Dufour[3] that these bands show the Zeeman effect.

A very important paper has been published by Humphreys,[4] dealing with the cause of the change in width, and the shift of the lines produced by pressure. He assumes the conception

[1] *Phil. Trans.*, **208**. 111 (1908); **209**. 205 (1908); **211**. 33 (1911).
[2] *Proc. Roy. Soc.*, **82**. 518 (1909); **83**. 414 (1910).
[3] *Comptes Rendus*, **146**. 118, 229 (1908).
[4] *Astrophys. Journ.*, **23**. 233 (1906).

of J. J. Thompson that an atom consists of negative electrons in a sphere of uniformly distributed positive electricity. If the electrons are moving in circular orbits, each ring will produce its own magnetic field, and therefore the system will possess minimum potential energy when the planes of the rings are parallel and all the electrons are rotating in the same direction. He then considers the mutual action of this type of atom when in a gaseous state, taking the specific case of iron atoms in the electric arc. He thus arrives at certain general deductions, and shows that all the observations upon the width and pressure shift of the lines can be satisfactorily accounted for. He finds that amongst the spectroscopic phenomena, therefore, which a dense gas may be expected to give, are the following, which are taken from his paper:—

1. All lines should increase in width when the pressure about their source is increased.

2. With increase of pressure the maxima of all lines should shift toward the red end of the spectrum. (This is a general statement; possible exceptions will be mentioned below.)

3. Ordinarily the spreading of a line should be much greater than its pressure displacement, though with a short exposure it may appear on a negative as a displaced narrow line.

4. Since the intensity of a magnetic field due to a circular current varies inversely as the cube of the distance from it, while the average distance between the molecules of a gas (supposed monatomic in the electric arc) varies directly as the cube root of the pressure, therefore the spreading and the shift both should be roughly linear functions of the pressure. That is, they should increase approximately as the average mutual disturbing influence of the atoms, or as the intensities of those parts of each other's magnetic fields in which they exist.

5. For lines of a given element, similar in their nature, the shifts should be proportional to the wave-length.

6. The spreading and the shifting both should obtain whatever the nature of the surrounding gas, as all atoms present are supposed to be magnetic. The shift, however,

should increase as the atomic weight of the surrounding medium is increased—heavier atoms possessing stronger magnetic fields.

7. The shift of analogous lines, due to different elements of the same general nature, elements of the same Mendeléeff group, should increase with increase of atomic weight, since the strength of an atom's magnetic field probably is an increasing function of atomic weight.

8. Any group of lines due to a given element, such as a series, that gives Zeeman effects proportional to the wave-length, should shift under pressure in the same ratio.

9. Generally speaking, lines of large Zeeman effects should show large pressure displacements, while those of small Zeeman effects should be little shifted.

10. Any lines, such as those of band spectra, that do not show the Zeeman effect, should not be displaced.

The Doppler Effect.—The Doppler effect is the apparent change in the wave-length of light produced by the motion in the line of sight of either the observer or the source of light. That an apparent change should take place is readily understood if we consider the oscillation frequency of a ray; let us consider a source at a great distance to be emitting homogeneous light which produces Z vibrations per second; then, further, in 1 kilometre of the path traversed by the light there are, let us say, γ complete waves. If we observe the light at rest, then, we receive of course Z vibrations per second, but if we approach the source at the rate of 1 kilometre per second we will receive $Z + \gamma$ vibrations per second, and $Z - \gamma$ vibrations if we recede at the same rate. This is true of all vibrations, and was first propounded scientifically by Doppler[1] in 1843, who sought to explain the colours of stars by means of the theory. The theoretical proof of the principle is very complex, so we must content ourselves with the elementary aspect of it.

Doppler's actual method of reasoning is rather cumbersome, and we may arrive at the same results in an easier manner as

[1] *Abh. d. K. Böhmischen, Gesell. d. Wissenchaften.* (5), **2**. 465 (1843); and *Pogg. Ann.*, **68**. 1 (1846).

follows. We can with Doppler differentiate between two cases.

Case 1. With the source at rest and the observer in motion. Let us call the velocity of light v, that is to say, a wave travels a length v in one second, and the oscillation frequency n, that is to say, the number of waves reaching a source at rest in a second or the number of waves in the length v. Then, of course, if λ be the wave-length of the light we shall have—

$$\lambda = \frac{v}{n}.$$

Now, if the observer were still, he would receive n oscillations in each second; but if he move towards the light at the rate of a length a per second, he will receive more than n oscillations in each second. When he was still the relative velocity of the light waves and observer was v, but when he moves it increases to $v + a$, and thus the number of oscillations is increased to $n\left(\frac{v + a}{v}\right)$. Conversely, the number of oscillations would be $n\left(\frac{v - a}{v}\right)$ if the observer were moving away from the source.

Thus, generally $$n' = n\frac{v \pm a}{v}$$

and $$\lambda' = \lambda\frac{v}{v \pm a}$$

Case 2. The observer at rest, but the source in motion. If both were still, a train of n waves of length v would reach the observer in one second; but if the source approach the observer at the rate of a length b in each second, the waves will be more crowded together, so to speak; in other words, n waves will occupy a length $v - b$. If, therefore, a length $v - b$ contain n waves, then a length v will contain $n\frac{v}{v - b}$ waves; and thus, as a train of waves of length v reach the observer in each second, the number of oscillations received is $n\frac{v}{v - b}$ in each second, or for the general case—

$$n' = n\frac{v}{v \mp b}$$

and

$$\lambda' = \lambda\frac{v \mp b}{v}$$

From the equations deduced for the two cases it is easy to deduce that for the case of both observer and source in motion—

$$N = n\frac{v \pm a}{v \mp b},$$

$$\Lambda = \lambda\frac{v \mp b}{v \pm a},$$

the upper sign in each case being used in case of the two approaching one another.

From these equations it is clear that when the observer and the source of light are approaching one another the apparent wave-length of a definite radiation will become shortened, and *vice versa*. Doppler sought to explain the colours of the stars by this theory, on the assumption that all stars not approaching or receding from us gave a white light, then he said that rapidly approaching stars should look blue, and those rapidly receding should appear red. This, however, is false reasoning, because a white star means the emission of a continuous spectrum, which naturally extends into the infra-red and ultra-violet, so that an approach of the star would shorten the wave-lengths of all the rays in proportion, the extreme visible blue would become ultra-violet, and just as much infra-red would become visible, so that the net amount of light rays would be the same and no change of colour would ensue. In discontinuous spectra, on the other hand, the shifts of lines due to motions of the observer or source can be measured, and from these the motions can be calculated.

Doppler's principle can be very strikingly observed in the case of sound waves, because of the slow velocity with which they travel; it is perfectly easy to produce experimentally velocities of translation of the sounding body or the observer which are more nearly comparable with the velocity of sound than we can in the case of light. This was first done by

Buÿs-Ballot,[1] in 1845, who made observations with locomotives on the Netherlands railway. Probably most people are familiar with the change in pitch which takes place in the whistle of an engine as they pass in a fast travelling railway train, especially if when in a fast train an engine is passed moving in the opposite direction and whose whistle is sounding; the same may be noticed in the flattening of the pitch of a bicycle bell as it passes in the street. Since the velocity of light is so great very great speeds are necessary to produce a measurable change in the oscillation frequency of a spectrum line. The motion necessary to produce a particular change in the frequency may be found from the equations given above. In Case 2, of observer at rest and source in motion, we have—

$$\lambda' = \lambda \frac{v \mp b}{v},$$

and thus $$\lambda v \mp b\lambda = v\lambda',$$

thence $$b = \frac{v}{\lambda}(\lambda - \lambda') \text{ for approach when } \lambda \text{ is less than } \lambda,$$

and $$b = \frac{v}{\lambda}(\lambda' - \lambda) \text{ for recession when } \lambda \text{ is less than } \lambda'.$$

Generally, therefore, $$\mp b = \frac{v\Delta\lambda}{\lambda},$$

where $\Delta\lambda$ is the change in wave-length observed.

Taking v as equal to 299,860 kilometres a second, it is seen from this equation that a velocity of about 6 kilometres per second is necessary to produce a change of 0·1 A.U. in the wave-length of the F line of hydrogen ($\lambda = 4861$ A.U.).

In astronomy the application of Doppler's principle has met with great success, some extraordinarily interesting observations having been made in connection with it. It is difficult to pass some of these by, although this book does not aspire in any way to the wonderful fields of astronomical spectroscopy. First, in the case of the sun, Vogel, in 1871, succeeded in

[1] *Pogg. Ann.*, **66**. 321 (1845).

showing the displacement of the Fraunhofer lines owing to the rotation of the sun by comparing observations made of the two ends of the solar equator. Then also the velocity of the prominences in the line of sight has been measured from the displacement of the lines produced, and, further, the tremendous gas currents in the neighbourhood of the solar spots. On the stars and nebulæ a great number of observations have been made, and their velocities calculated, and here considerable corrections must be introduced for the earth's motion round the sun. Perhaps the most interesting discovery made in this direction is that of spectroscopic binary stars, as they are called. The well-known variable star Algol was found to vary in its velocity in the line of sight, both positive and negative motions being obtained at different times, and, further, the period of these motions was found to agree with the period in the variable luminosity. In this way Algol was found to be a binary system of one bright and one dark component rotating round a common centre of gravity. Before the minimum Algol is receding from the sun, and after the minimum it is approaching the sun, and Vogel calculated from the first series of measurements that the diameters of the bright and dark components were 1,700,000 and 1,330,000 kilometres respectively, their orbital velocities 42 and 89 kilometres, and their masses four-ninths and two-ninths that of the sun respectively, and, further, that their centres are 5,180,000 kilometres apart. Other stars of this type have also been observed, both bright and giving the same spectra, the lines of the spectra of such binaries appear single when one is seen behind the other, but the lines double themselves when the two components are presented side by side, with one approaching and the other receding from us. It must, of course, be understood that such systems are quite unresolvable by the most powerful telescopes. Evidence has also been recently discovered of unequal velocities in different parts of the same nebula.[1]

[1] For further imformation on these points see Scheiner's *Astronomical Spectroscopy*, translated by E. B. Frost. Gime & Co., London and Boston, U.S., 1898.

As an example of a spectroscopic binary star, that of o Persei may be taken, which has recently been observed by Vogel.[1] The calculations were based on measurements of the lines H, $\lambda = 4388$, and $\lambda = 4472$; it was found that the velocities were, on—

Nov.	7·0,	1902	+100	km. per second
„	8·0	„	+70	„ „
„	8·5	„	±0	„ „
„	9·0	„	−75	„ „
„	9·5	„	−110	„ „
„	10·0	„	−90	„ „
„	10·5	„	−30	„ „
„	11·0	„	+45	„ „
„	11·5	„	+100	„ „

The measurements show that the period was 4·39 days, and that the distance between the two stars was 6,940,000 kilometres.

Canal Rays.—On page 411 mention was made of the application of Doppler's principle to the measurement of the moving particles in the electric spark; and more recently this application to terrestrial problems has been considerably extended. Some years ago Goldstein[2] found that if in a cylindrical vacuum tube a flat metallic plate is used as cathode, and mounted at right angles to the axis of the tube, and if, moreover, this cathode is perforated with small holes, then, when the discharge is passed at very low pressures, rays pass out through these holes away from the anode, and to these he gave the name of Canal Rays. Such rays are apparently due to positively charged particles of the gas, that is to say atoms which have lost one or more negative electrons, and which are travelling with considerable velocity.

Stark pointed out that if these canal rays are luminous, and are travelling with a great velocity, the Doppler effect must be exhibited, that is, if the canal rays were examined end-on the spectrum lines should be displaced towards the blue or red end of the spectrum, according as to whether the particles are

[1] *Berl. Ber.* (1902), 1113.
[2] *Ann. der Phys.*, **64**. 38 (1898).

moving towards or away from the slit. Stark first of all proved that this was so in the case of hydrogen, the hydrogen lines being displaced towards the violet when the rays are travelling towards the spectroscope. As a result of a long series of experiments, Stark has developed a theory that the line-emission spectra of the elements are due to the positive ions, that is to the atoms which have lost the electrons, and that the band spectra are due to the recombining of the positive ions with the necessary electrons to reproduce the neutral atoms. Now, it is generally found in observations of the Doppler effect of canal rays that each spectrum line is doubled, one component having the theoretical wave-length, and the other component being displaced according to the Doppler principle. Stark explains this by saying that the true emitter of the line spectrum is the positive ion, which is travelling with great velocity, and also that these canal rays ionise the neutral atoms as they strike them in their path. The result of these collisions and subsequent ionisation is the appearance of the component with the theoretical wave-length. Again, it has been shown by Stark that band spectra do not show the Doppler effect at all, in which fact, of course, he finds support to his theory that the band spectra are due to the recombination of the positive ion and negative electrons. It may perhaps be added that if the spectrum of the discharge be examined at right angles to the path of the canal rays, no displacement of the lines will be seen. I cannot give in detail an account of the great number of investigations made by Stark in support of his theory, or, indeed, of the numerous papers describing the Doppler effect with canal rays in various gases, but at foot will be found references to the more important papers dealing with this subject.

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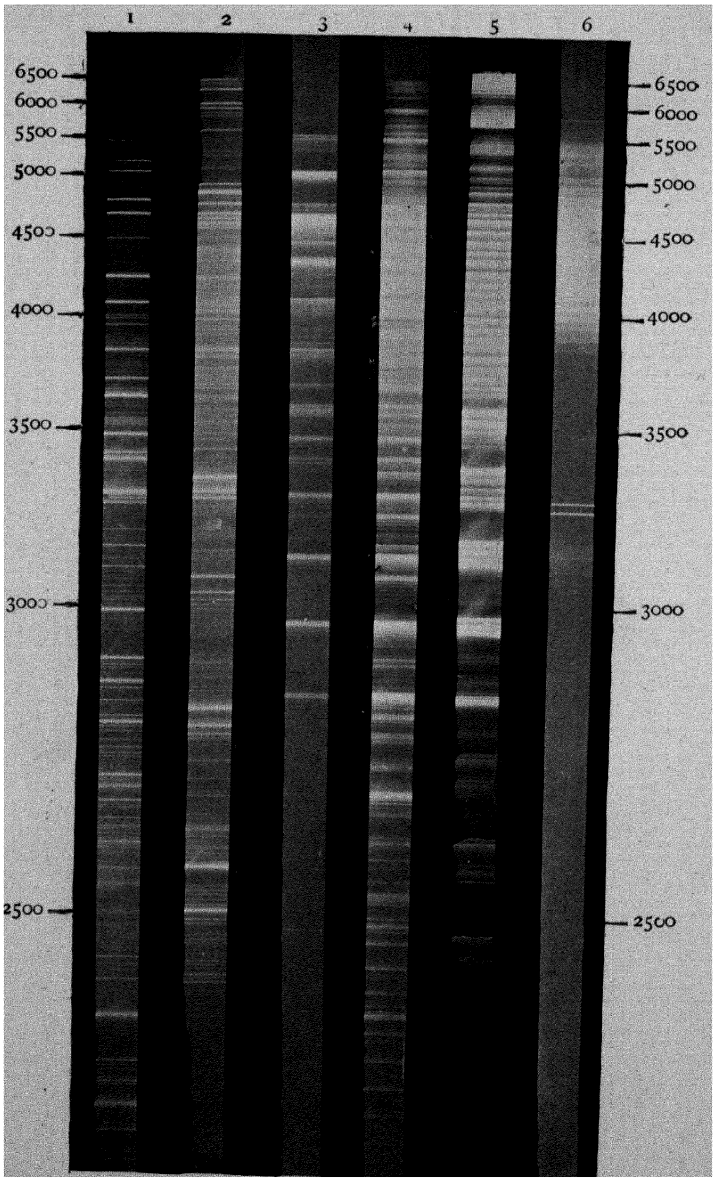
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PLATE III.



On Plate III. are shown half-tone reproductions of six spectra, which, although they do not show the fine detail of the originals, yet may serve as illustrations of various spectral types.

The spectra are as follows:—

1. Arc spectrum of silver.
2. Spark spectrum of zinc.
3. Spectrum given by a vacuum tube containing carbon monoxide, usually called the Swan spectrum.
4. Spectrum given by a vacuum tube containing carbon dioxide, usually known as the carbon oxide spectrum.
5. Positive band spectrum of nitrogen as given by the capillary portion of a vacuum tube containing nitrogen.
6. Flame spectrum of copper as obtained with copper chloride in a Mecke burner fed with coal gas containing chloroform vapour.

APPENDIX

THE following recipes may be given for making solutions for silvering glass. The first one may be recommended in cases where a dense deposit is required for mirrors, and the second and third for purposes of half-silvering.

The first process is the one used by Brashear, and the directions have been given for its use by Wadsworth.[1] The great advantage in its use lies in the firm silver coating produced, which may be rubbed when wet with the hand or with a pad of cotton-wool without injury.

The reducing solution is made as follows:—

Loaf sugar or rock candy	90 grms.
Strong nitric acid	4 c.c.
Alcohol	175 c.c.
Distilled water	1000 c.c.

The sugar is dissolved in the water, and then the alcohol and nitric acid are added. This solution should be prepared at least a week before it is wanted; the longer it is kept the better it gets.

The silver solution is an ammoniacal solution of silver oxide, to which, just before using, is added a solution of potassium hydroxide containing a weight of this compound equal to half the weight of the silver nitrate used. The silver solution must be made as it is required.

[1] *Astrophys. Journ.*, 1. 252 (1895); also published in the *English Mechanic* in 1883.

AMOUNT OF SUBSTANCES REQUIRED CALCULATED FOR ROUND MIRRORS.

Diameter of mirror.	Area.	Silver nitrate.	Potassium hydroxide.	Ammonia (sp. g., 0·880).	Reducing solution.
cms.	sq. cms.	grms.	grms.	cc.	cc.
30	707·0	15·0	7·5	12·0	85
25	491·0	11·0	5·5	9·0	65
20	314·0	7·0	3·5	6·0	40
15	177·0	4·0	2·0	3·0	25
10	78·5	1·8	0·9	1·5	10
5	19·6	0·5	0·25	0·5	3

The silver solution is made as follows: the silver nitrate and the potassium hydroxide required are dissolved separately to make 1 per cent. solutions. To about nine-tenths of the silver solution the ammonia solution is added until the precipitate which first appears is just redissolved, and then some more silver solution until the precipitate reappears. The potash solution is then added, which will probably produce more of the precipitate; ammonia is then again added until the precipitate is dissolved, and then more silver solution, this being done alternately until all the silver nitrate has been added, taking care that the last addition is one of silver. In this way a solution is obtained which looks opalescent from the presence of a slight excess of silver oxide; this opalescence is absolutely necessary. If there are any floating particles, the solution is filtered; the necessary amount of reducing solution is added, the whole is mixed thoroughly, and then the mirror is immediately immersed. The mirror may be put with its face up or down, but best with its face up, as the depositing of the silver can then be watched; in this case it is necessary to keep the solution in constant motion in order to prevent any precipitated silver particles from settling on to the face. The best temperature is 21° C.

When the silvering is complete, the mirror is lifted out and placed in an inclined position under a stream of clean water, and the whole surface is rubbed vigorously with a pad of clean absorbent cotton-wool until the white film on the surface of

the silver is removed and the whole deposit is bright and clear. No further polishing is required. This process is not so good for half-silvering purposes as the older processes, because the deposit given by it is not so uniform although more durable.

The following recipe is given by Edser and Stansfield,[1] and gives very good results for half-silvering. One grm. of silver nitrate is dissolved in 20 c.c. distilled water, and strong ammonia (0·880 sp. g.) is added until the precipitate is just redissolved. A solution of 1·5 grm. potassium hydroxide in 40 c.c. water and again ammonia until the precipitate re-dissolves; 80 c.c. distilled water are next added, and then silver nitrate solution (any strength), until there is a faint permanent precipitate. Make up to 300 c.c.

For the reducing solution 1·8 grm. of milk sugar is dissolved with the aid of heat in 20 c.c. distilled water. The two solutions are mixed just before silvering, and the mirror is put in with its face down. At 15° ten minutes are usually required for half-silvering, and one hour for full silvering. A thick silver surface obtained with this process may be rubbed with cotton-wool in running water.

Martin's process, which was used by Fabry and Perot for half-silvering the mirrors in their interference apparatus (see Chapter IX.), is as follows. Four solutions are made up:—

A. Silver nitrate	40 grms.
Distilled water	1000 c.c.
B. Ammonium nitrate	60 grms.
Distilled water	1000 c.c.
C. Potassium hydroxide (pure by alcohol) .	100 grms.
Distilled water	1000 c.c.

To make solution D, 100 grms. pure sugar candy are dissolved in 1000 c.c. distilled water, and then 23 grms. tartaric acid are added, after which the solution is boiled for ten minutes. When cool, 200 c.c. alcohol are added, and then, lastly, distilled water to make it up to 2000 c.c.

Equal parts of A and B are mixed together, and similarly

[1] *Nature*, **56**. 504 (1897).

equal parts of C and D. Both these mixtures are mixed in the silvering vessel, and the mirror is at once suspended face downwards in the solution.

It is needless to point out the absolute necessity for perfectly clean surfaces for the silver to deposit upon; these may be obtained by rubbing them with a cotton-wool pad dipped in warm nitric acid and then thoroughly rinsing with water. A further treatment with alcohol, followed again by water, is also advisable.

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PRINTED IN GREAT BRITAIN BY WILLIAM CLOWES AND SONS, LIMITED, BECCLES.