

others. The lines of hydrogen and sodium, for instance, widen so easily that it is sometimes difficult to obtain them quite sharp. When a system of lines widens it is generally found that the most refrangible lines widen most easily. A line may expand equally towards both sides or chiefly towards one side; in the latter case the expansion towards the less refrangible side preponderates pretty nearly in every case. It is the almost unanimous opinion of spectroscopists that the widening is produced by an increase of pressure. If sparks are passed through gases, the lines are always broader at high than at low pressures, and the metallic lines are also broader when a spark is taken from them at higher pressures. Without altering the pressure, we may often produce a widening of lines by an increase in the intensity of the discharge, but here the pressure is indirectly increased by the rise of temperature. According to the molecular theory of gases, the following explanation might be given for the widening of lines. As long as a molecule vibrates by itself uninfluenced by any other molecule, its vibrations will take place in regular periods. The lines of its spectrum will consequently be sharp. But, if the molecule is placed in proximity with others, its vibrations will be disturbed by occasional encounters. During each encounter forces may be supposed to act between the molecules, and these forces will affect the regularity of the vibration. The question arises, whether for a given temperature and pressure a line may be of different width according as the molecule is placed in an atmosphere of similar or dissimilar molecules. Such a difference exists in all probability. If gases are mixed in different proportions, the lines are sharper when an element is present in small quantities, although the total pressure may be the same. There is one cause which limits the sharpness of spectroscopic lines: the molecules of a gas have a translatory motion. Those molecules which are moving towards us will send us light which is slightly more refrangible than those which move away from us; hence each line ought to appear as a band. In reality the width of lines generally is greater than that due to this cause.

Spectra of Different Orders.—Spectra may be classified according to their general appearance. The different classes have been called orders by Plücker and Hittorf. At the highest temperature we always obtain spectra of lines which need no further description. At a lower temperature we often get spectra of channelled spaces or fluted bands. When seen in spectroscopes of small resolving power these seem made of bands which have a sharp boundary on one side and gradually fade away on the other. With the help of more perfect instruments it is found that each band is made up of a number of lines which lie closer and closer together as the sharp edge is approached. Occasionally the bands do not present a sharp edge at all, but are made up of a number of lines of equal intensity at nearly equal distances from each other. Continuous spectra, which need not necessarily extend through the whole range of the spectrum, form a third order, and appear generally at a lower temperature than either band or line spectrum. One and the same element may at different temperatures possess spectra of different orders. A discussion has naturally arisen as to the cause of these remarkable changes of spectra, and it is generally believed that they are due to differences of molecular structure. Thus sulphur vapour when volatilized shows by absorption a continuous spectrum until its temperature is raised to 1000°, when the continuous spectrum gives way to a spectrum of bands. We know that the molecule of sulphur is decomposed as the temperature is raised, and we are thus justified in saying that the band spectrum belongs to the molecule containing two atoms, while the continuous spectrum belongs to the more complex molecule which first appears on volatilization. When a strong electric spark is passed through the vapour of sulphur a bright line spectrum is seen, and this is believed to be due to a further splitting up of the molecule into single atoms.

Long and Short Lines.—If the spectrum of a metal is taken by passing the spark between two poles in air the pressure of which is made to vary, the relative intensity of some of the lines is often seen to change. Similar variations take place if the intensity of the discharge is altered, as, for instance, by interposing or taking out a Leyden jar. It is a matter of importance to be able to use a method which in the great majority of cases will give at once a sure indication how each line will behave under different circumstances. This method we now proceed to describe. It has often been remarked, even by the earliest observers, that the metallic lines when seen in a spectroscope do not always stretch across the field of view, but are sometimes confined to the neighbourhood of the metallic poles. Some observations which Lockyer made jointly with Professor Frankland led him to conclude that the distance which each metallic line stretched away from the pole could give some clue to the behaviour of that line in the sun. In 1872 Lockyer worked out his idea. An image of the spark was formed on the slit of the spectroscope, so that the spectrum of each section of the spark could be examined. Some of the metallic lines were then seen to be confined altogether to the neighbourhood of the poles, while others stretched nearly across the whole field. The relative length of all the lines was estimated. Tables

and maps are added to the memoir.¹ The longest lines (the λ those which stretch away farthest from the pole) are by no means always the strongest; and there are many instances where a faint line is seen to stretch nearly across the whole field of view, while a strong line may be confined to the neighbourhood of the pole, or is reduced sometimes to a brilliant point only. We give a few conspicuous examples of lines which are long and weak or short and strong. In lithium the blue line (4602.7) is brilliant but short. In lead 4062.5, one of the longest lines, is faint and according to Lockyer difficult to observe. In tin 5630.0 is the longest line, but it is faint, while the stronger lines near it (5588.5 and 5562.5) are shorter. The zinc lines 4923.8, 4911.2, 4809.7, 4721.4, 4679.5 are given by Thalén as of equal intensity, but the three most refrangible ones are longer. On reduction of pressure Lockyer found that some of the shorter lines rapidly decreased in length, while the longer lines remained visible and were sometimes hardly affected. When the spark was taken from a metallic salt instead of from the metal the short lines could not be seen, but only the long lines remained. An alloy behaves in the same manner as a compound, and by gradually reducing one constituent of an alloy we may gradually reduce the number of lines, which disappear in the inverse order of their length. Subsequent work has shown that the longest lines are also generally those which are most persistent on reduction of temperature, so that in the voltaic arc the longest lines seen in the spark are absent. In order to explain these facts it seems necessary in the first place to assume that the short lines are lines coming out at a high temperature only; but this explanation is not sufficient. Why should a mixture of different elements only show the longest lines of that constituent which is present in small quantities? In the case of chemical combinations we might assume that, the spark having to do the work of decomposition, the temperature of the metal is lowered, and that therefore the short lines are absent. But this cannot be if a chemical compound is replaced by a mechanical mixture. All these facts would be explained, however, if we assume that the spectrum of a molecule that is excited by molecules of another kind consists of those lines chiefly which a molecule of the same kind is already capable of bringing out at a lower temperature. It would follow from this that the effects of dilution are the same as those of a reduction of temperature,—which is the case.

Other Changes in Relative Intensity of Lines.—Besides the changes we have noticed, there are others which have not been brought under any rule as yet. Lines appear sometimes at a low temperature which behave differently from the proper low-temperature lines. These require further investigation. They may, in some cases at least, be due to some compound of the metal with other elements present. We give some examples. If a spark is taken from lead without the condenser the line 5005 appears, and Huggins has found it to be sensibly coincident with the chief line of the nebula. It is given as a strong line by Lecoq de Boisbaudran, who used feeble sparks, and in many cases it seems to behave as a low-temperature line; it ought to be a long line therefore, but it is in reality short. In line 6100 of tin, Salet noticed that when a hydrogen flame contains a compound of tin an orange line appears, which is apparently coincident with the orange line of lithium. This line does not figure on any of the maps of the tin spectrum. Lockyer found that zinc, volatilized in an iron tube, showed by absorption a green line. It is very likely the line 5184 seen by Lecoq de Boisbaudran in sparks taken from solution of zinc salts. In the absorption spectra of sodium and potassium lines appear in the green which were shown by Liveing and Dewar not to be coincident with any known line of these metals. It was suggested by them that they are due to hydrogen compounds. The wavelength of the sodium line is 5510 and that of the potassium line 5730. Lecoq de Boisbaudran mentions that an increase of temperature is often accompanied by a relatively greater increase in the brilliancy of the more refrangible rays. It is often said that such an increase is a direct consequence of the formula established by Kirchhoff. If the absorbing power of a molecule remains the same while the temperature is increased, it follows that the blue rays gain more quickly in intensity than the red ones, but the less refrangible rays ought never to decrease in intensity, the quantity of luminous matter remaining the same. Now such a decrease is actually observed in many cases when there is no reason to suppose that the quantity of luminous matter has been reduced. We must conclude, therefore, that the observed differences in the spectra are not solely regulated by Kirchhoff's law; but it is a perfectly plausible hypothesis that a higher temperature is in general accompanied by a decrease in the absorbing power of the less refrangible rays. As a stronger impact often brings out higher tones, stronger molecular shocks may bring out waves of smaller length. There are several instances of a regular increase in the relative intensity of the blue rays which may be ascribed to this cause. The most remarkable instance is perhaps seen in the spec-

¹ Phil. Trans., clxiii. p. 253 (1873).

trum of phosphoretted hydrogen. If a little phosphorus is introduced into an apparatus generating hydrogen, the flame will show a series of bands chiefly in the green. The spectrum gets more brilliant if the flame is cooled. This can be done, according to Salet,¹ by pressing the flame against a surface kept cool by means of a stream of water or by surrounding the tube, at the orifice of which the gas is lighted, by a wider tube through which cold air is blown. The process of cooling the flame, according to Lecoq,² changes the relative intensity of the bands in a perfectly regular manner. The almost invisible least refrangible band becomes strong, and the second band, which was weaker than the fourth, now becomes stronger. Another example of a similar change is the spectrum shown by a Bunsen burner. By charging the burner with an indifferent gas³ (N, HCl, CO₂) the flame takes a greenish colour, and, though the spectrum is not altered, the least refrangible of the bands are increased in intensity. While in these instances the changes are perfectly regular, the more refrangible rays gaining in relative intensity as the temperature is increased, there are other cases, some of which have already been mentioned, in which the changes are very irregular; such are those which take place in the spectra of tin, lithium, and magnesium. In the case of zinc the less refrangible of the group of blue rays gains in relative intensity. We cannot, therefore, formulate any general law.

Numerical Relations between the Wave-lengths of Lines belonging to the Spectrum of a Body.

It seems *a priori* probable that there is a numerical relation between the different periods of the same vibrating system. In certain sounding systems, as an organ-pipe or a stretched string, the relation is a simple one, these periods being a submultiple of one which is called the fundamental period. The harmony of a compound sound depends on the fact that the different times of vibration are in the ratio of small integer numbers, and hence two vibrations are said to be in harmonic relation when their periods are in the ratio of integers. We may with advantage extend the expression "harmonic relation" to the case of light, although the so-called harmony of colours has nothing to do with such connexions. We shall therefore define an "harmonic relation" between different lines of a spectrum to be a relation such that the wave-lengths or wave-numbers are in the ratio of integers, the integers being sufficiently small to suggest a real connexion. Some writers use the word in a wider sense and call a group of lines harmonics when they show a certain regularity in their disposition, giving evidence of some law, that law not being in general the harmonic law. We shall here use the expression in its stricter sense only. We begin by discussing the question whether there are any well-ascertained cases of harmonic relationship between the different vibrations of the same molecule. The most important set of lines exhibiting such a relationship are three of the hydrogen lines which, when properly corrected for atmospheric refraction, are, as pointed out by Johnstone Stoney, very accurately in the ratio of 20 : 27 : 32 (*Phil. Mag.*, xli. p. 291, 1871). Other elements also show such ratios; but when a spectrum has many lines pure accident will cause several to exhibit whatever numerical relations we may wish to impose on them. If we calculate the number of harmonic ratios which, with an assumed limit of accuracy, we may expect in a spectrum like that of iron, we find that there are in reality fewer than we should have if they were distributed quite at random (*Proc. Roy. Soc.*, xxxi. p. 337, 1881). With fractions having a denominator smaller than seventy the excess of the calculated over the observed values is very marked, while there are rather more coincidences than we should expect on the theory of probability if we take fractions having a denominator between seventy and a hundred. The cause of this, probably, is to be sought in the fact that the lines of an element are liable to form groups and are not spread over the whole spectrum, as they would be if they were distributed at random. This increases the probability of coincidence with fractions between high numbers, and diminishes the probability of coincidence with fractions between lower numbers. There is one point which deserves renewed investigation. When the limits of agreement between which a coincidence is assumed to exist are taken narrower, there is an increased number of observed as compared with calculated coincidences in the iron spectrum; and this would seem to point to the existence of some true harmonic ratios. With the solar maps and gratings put at our disposal by Professor Rowland, we may hope to obtain more accurate measurements, and therefore more definite information. Even if the wave-lengths of two lines are found to be occasionally in the ratio of small integer numbers, it does not follow that the vibrations of molecules are regulated by the same laws as those of an organ-pipe or of a stretched string. E. J. Balmer⁴ has indeed lately suggested a law which differs in an important manner from the laws of vibration of the organ-

¹ *Ann. Chim. Phys.*, xxviii. p. 57 (1873).
² *Spectre Lumineux*, p. 188 (1874).
³ *Op. cit.*, p. 43 (1874).
⁴ *Wied. Ann.*, xxv. p. 80 (1885).

pipe and which still leaves the ratios of the periods of vibration integer numbers. According to him, the hydrogen spectrum can be represented by the equation

$$\frac{m^2}{m^2 - 4} \lambda_0 = \lambda,$$

where λ_0 is some wave-length and m an integer number greater than 2. The following table (I.) shows the agreement between the calculated and observed hydrogen lines. And the agreement is a very remarkable one, for the whole of the hydrogen spectrum is represented by giving to m successive integer values up to sixteen.

| $\lambda_0 = 3645.$ | | Observed Hydrogen Spectrum. | $\lambda_0 = 3645.$ | | Observed Hydrogen Spectrum. |
|---------------------|-------------------------------|-----------------------------|---------------------|-------------------------------|-----------------------------|
| m . | $m^2 \lambda_0 / (m^2 - 4)$. | | m . | $m^2 \lambda_0 / (m^2 - 4)$. | |
| 3 | 6561.0 | 6562.1 | 10 | 3796.9 | 3795.0 |
| 4 | 4860.0 | 4860.7 | 11 | 3769.6 | 3767.5 |
| 5 | 4320.0 | 4340.1 | 12 | 3749.1 | 3745.5 |
| 6 | 4100.6 | 4101.2 | 13 | 3733.3 | 3730.0 |
| 7 | 3969.0 | 3968.1 | 14 | 3729.9 | 3717.5 |
| 8 | 3885.0 | 3887.5 | 15 | 3711.0 | 3707.5 |
| 9 | 3834.3 | 3834.0 | 16 | 3702.0 | 3699.0 |

The differences between the observed and the calculated numbers show a regular increase towards the ultra-violet. It might be thought that a better agreement could be obtained by taking a number slightly different from four in the denominator; but this is not the case. On the contrary, the agreement in the visible part is at once destroyed if we make the ultra-violet lines fit better. The agreement is not improved but rendered slightly worse if we take account of atmospheric refraction.

As a first approximation Balmer's expression gives a very good account of the hydrogen spectrum. If the law was general we should find that in the iron spectrum, for instance, which is the only spectrum carefully examined, those fractions would occur more frequently than others which can be put into the form $m^2/(m^2 - n^2)$, that is to say, $\frac{3}{2}$ and $\frac{4}{3}$ for fractions made up of numbers smaller than 10. A reference to the table in *Proc. Roy. Soc.*, vol. xxxi. p. 337, shows that these fractions do not occur more frequently than others. But, if we change the sign of n^2 in the denominator, we find $\frac{3}{2}$ and $\frac{4}{3}$ as the only fractions falling within the range of spectrum examined, and these two fractions are indeed those which occur more frequently than any others made up of numbers smaller than 10.

It might be worth trying to see whether the wave-lengths of lines making up a fluted band can be put into the form $\frac{m^2}{m^2 \pm n^2} \lambda_0$; according to the sign chosen in the denominator, the band would shade off towards the blue or red. The form of expression seems at first sight well adapted, for it shows how by giving m gradually increasing numbers the lines come closer and closer together towards what appears in the spectrum as the sharp edge of the band. If we take periods of vibration instead of wave-lengths Balmer's expression would reduce to

$$T = T_0 \left[1 - \left(\frac{n}{m} \right)^2 \right],$$

where T_0 is a fixed period of vibration, n a constant integer, and m an integer to which successive values are given from n upwards.

It is often observed, and has already been mentioned, that the spectrum of some elements contains in close proximity two or three lines forming a characteristic group. Such doublets or triplets are often repeated, and if the harmonic law was a general one we should expect the wave-lengths of these groups to be ruled by it; but such is not the case. The sodium lines which lie in the visible part of the spectrum are all double, the components being the closer together the more refrangible the group. But neither are the lines themselves in any simple ratios of integers, nor do the distances between the lines show much regularity. The ultra-violet lines of sodium as photographed by Liveing and Dewar are single, with the exception of the least refrangible of them (3301). But this line is a very close double, and it may be that the others will ultimately be resolved. Some elements, such as magnesium, calcium, zinc, cadmium, show remarkable series of triplets; and the relative distances of the three lines seem well maintained in each of them. Even the distances when mapped on the wave-number scale are so nearly the same for each element that it would be a matter of great importance to settle definitively whether the slight variations which are found to exist are real or due to errors of measurement. In the following table (II.) we give the position of the least refrangible line of each triplet together with the distances between the first and second (column B) and between the second and third line of each triplet (column C). The figures in column A represent the number of waves in one millimetre. For the zinc and calcium triplets the measurements of Liveing and Dewar are given; the magnesium triplets are put down as measured by Cornu as well as by Hartley and Adeney. The differences in these measurements will give an idea of the degree of uncertainty. The triplets of cadmium are farther apart and are mixed up with a greater number of single lines.

| Zinc Triplets. | | | Calcium Triplets. | | |
|----------------|----|----|-------------------|----|----|
| A. | B. | C. | A. | B. | C. |
| 2992 | 37 | 19 | 2245 | 10 | 5 |
| 3257 | 38 | 20 | 2517 | 11 | 5 |
| 3371 | 40 | 18 | 2744 | 10 | 6 |
| 3656 | 40 | 19 | 2868 | 10 | 6 |
| 3833 | 40 | 18 | 2977 | 10 | 5 |
| 3975 | 38 | 19 | 3044 | 11 | 6 |
| 4097 | 41 | 17 | 3101 | 11 | 5 |
| | | | 3174 | 10 | 5 |
| | | | 3208 | 10 | .. |

| Magnesium Triplets. | | | Hartley and Adeney. | | |
|---------------------|-----|-----|---------------------|-----|-----|
| A. | B. | C. | A. | B. | C. |
| 1929.3 ¹ | 4.2 | 1.9 | 2605.6 | 2.9 | 2.0 |
| 2005.8 | 4.1 | 1.7 | 2997.4 | 4.0 | 2.4 |
| 2999.2 | 3.8 | 2.7 | 3229.8 | 4.5 | 2.1 |
| 3230.4 | 3.9 | 1.9 | | | |
| 3399.0 ² | 4.1 | 1.2 | | | |

Relation between Spectrum of a Body and Spectra of its Compounds.

The spectrum of a body is due to periodic motion within the molecules. If we are justified in believing that the molecule of mercury vapour contains a single atom, it follows that atoms are capable of vibration under the action of internal forces, for mercury vapour has a definite spectrum. We may consider, then, the spectrum to be determined in the first place by forces within the atom, but to be affected by the forces which hold together the different atoms within the molecule. The closer the bond of union the greater the dependence of the vibrations on the forces acting between the different atoms. Experimental evidence seems to favour these views, for we observe that whenever elements are loosely bound together we can recognize the influence of each constituent, while in the compounds which are sufficiently stable to resist the temperature of incandescence the spectrum of the compound is perfectly distinct from the spectra of the elements. The oxides and haloid salts of the alkaline earths, for instance, have spectra in which we cannot trace the vibrations of the component atoms; but the spectra of the different salts of the same metal show a great resemblance, the bands being similar and similarly placed. The spectrum seems displaced towards the red as the atomic weight of the haloid increases. No satisfactory numerical relationship has, however, been traced between the bands. The number of compounds which will endure incandescence without decomposition is very small, and this renders an exhaustive investigation of the relationship between their spectra very difficult.

The compounds whose absorption spectra have been investigated have often been of a more unstable nature, and, moreover, dissociation seems going on in liquid solutions to a large extent; the influence of the component radicals in the molecule is more marked in consequence. Dr Gladstone,³ at an early period in the history of spectrum analysis, examined the absorption spectra of the solution of salts, each constituent of which was coloured. He concluded that generally, but not invariably, the following law held good: "When an acid and a base combine each of which has a different influence on the rays of light a solution of the resulting salt will transmit only those rays which are not absorbed by either, or, in other words, which are transmitted by both." He mentions as an important exception the case of ferric ferro-cyanide, which, when dissolved in oxalic acid, transmits blue rays in great abundance, though the same rays are absorbed both by ferro-cyanides and by ferric salts. Soret has confirmed, for the ultra-violet rays, Dr Gladstone's conclusions with regard to the identity of the absorption spectra of different chromates. The chromates of sodium, potassium, and ammonia, as well as the bichromates of potassium and ammonia, were found to give the same absorption spectrum. Nor is the effect of these chromates confined to the blocking out simply of one end of the spectrum, as in the visible part, but two distinct absorption bands are seen, which seem unchanged in position if one of the above-mentioned chromates is replaced by another. Chromic acid itself showed the bands, but less distinctly, and Soret does not

¹ Measured by Thalén. ² Measured by Liveing and Dewar. ³ *Phil. Mag.*, xiv. p. 419 (1857).

consider the purity of the acid sufficiently proved to allow him to draw any certain conclusion from this observation. Erhard's work on the absorption spectra of the salts in which chromium plays the part of base has already been mentioned. Nitric acid and the nitrates of transparent bases, such as potassium, sodium, and ammonia, show spectra, according to Soret, which are not only qualitatively but also quantitatively identical; that is to say, a given quantity of nitric acid in solution gives a characteristic absorption band of exactly the same width and darkness, whether by itself alone or combined with a transparent base. It also shows a continuous absorption at the most refrangible side, beginning with each of the salts mentioned at exactly the same point. The ethereal nitrates, however, give different results. In 1872 Hartley and Huntington examined by photographic methods the absorption spectra of a great number of organic compounds. The normal alcohols were found to be transparent to the ultra-violet rays, the normal fatty acids less so. In both cases an increased number of carbon atoms increases the absorption at the most refrangible end. The fact that benzene and its derivatives are remarkable for their powerful absorption of the most refrangible rays, and for some characteristic absorption bands appearing on dilution, led Hartley to a more extended examination of some of the more complicated organic substances. He determined that definite absorption bands are only produced by substances in which three pairs of carbon atoms are doubly linked together, as in the benzene ring. More recently⁴ he has subjected the ultra-violet absorption of the alkaloids to a careful investigation, and has arrived at the conclusion that the spectra are sufficiently characteristic to "offer a ready and valuable means of ascertaining the purity of the alkaloids and particularly of establishing their identity." "In comparing the spectra of substances of similar constitution it is observed that in such as are derived from bases by the substitution of an alkyl radical for hydrogen, or of an acid radical for hydroxyl, the curve is not altered in character, but may vary in length when equal weights are examined. This is explained by the absorption bands being caused by the compactness of structure of the nucleus of the molecule, and that equal weights are not molecular weights, so that by substituting for the hydrogen of the nucleus radicals which exert no selective absorption the result is a reduction in the absorptive power of a given weight of the substance. . . . Bases which contain oxydized radicals, as hydroxyl, methoxyl, and carboxyl, increase in absorptive power in proportion to the amount of oxygen they contain."

It would seem, however, by comparing the above results with those obtained by Captain Abney and Colonel Festing⁵ that the absorption of a great number of organic substances is more characteristic in the infra-red than in the ultra-violet. Some of the conclusions arrived at by these experimentalists are of great importance, as the following quotations will show:—"Regarding the general absorption we have nothing very noteworthy to remark, beyond the fact that, as a rule, in the hydrocarbons of the same series those of heavier molecular constitution seem to have less than those of lighter." This effect agrees with the observations made by Hartley and Huntington in the ultra-violet, in so far as a general shifting of the absorption towards the red seems to take place as the number of carbon atoms is increased. Such a shifting would increase the general absorption in the ultra-violet as observed by Hartley and Huntington, and decrease it in the infra-red as observed by Abney and Festing. Turning their attention next to the sharply defined lines, the last named, by a series of systematic experiments, concluded that these must be due to the hydrogen atoms in the molecule. "A crucial test was to observe spectra containing hydrogen and chlorine, hydrogen and oxygen, and hydrogen and nitrogen. We therefore tried hydrochloric acid and obtained a spectrum containing some few lines. Water gave lines, together with bands, two lines being coincident with those in the spectrum of hydrochloric acid. In ammonia, nitric acid, and sulphuric acid we also obtained sharply marked lines, coincidences in the different spectra being observed, and nearly every line mapped found its analogue in the chloroform spectrum, and usually in that of ethyl iodide. Benzene, again, gave a spectrum consisting principally of lines, and these were coincident with some lines also to be found in chloroform. It seems, then, that the hydrogen, which is common to all these different compounds, must be the cause of the linear spectrum. In what manner the hydrogen annihilates the waves of radiation at these particular points is a question which is, at present at all events, an open one, but that the linear absorptions, common to the hydrocarbons and to those bodies in which hydrogen is in combination with other elements, such as oxygen and nitrogen, are due to hydrogen, there can be no manner of doubt. The next point that required solution was the effect of the presence of oxygen on the body under examination. . . . It appears that in every case where oxygen is present, otherwise than as a part of the radical, it is attached to some hydrogen atom in such a way that

⁴ *Phil. Trans.*, part ii. (1885). ⁵ *Phil. Trans.*, iii. p. 887 (1881).

it obliterates the radiation between two of the lines which are due to that hydrogen. . . . If more than one hydroxyl group be present, we doubt if any direct effect is produced beyond that produced by one hydroxyl group, except a possible greater general absorption; a good example of this will be found in cinnamic alcohol and phenyl-propyl alcohol, which give the same spectra as far as the special absorptions are concerned. . . . Hitherto we have only taken into account oxygen which is not contained in the radical; when it is so contained it appears to act differently, always supposing hydrogen to be present as well. We need only refer to the spectrum of aldehyde, which is inclined to be linear rather than banded, or rather the bands are bounded by absolute lines; and are more defined than when oxygen is more loosely bonded."

"An inspection of our maps will show that the radical of a body is represented by certain well-marked bands, some differing in position according as it is bonded with hydrogen, or a halogen, or with carbon, oxygen, or nitrogen. There seem to be characteristic bands, however, of any one series of radicals between 1000 and about 1100, which would indicate what may be called the central hydrocarbon group, to which other radicals may be bonded. The clue to the composition of a body, however, would seem to lie between λ 700 and λ 1000. Certain radicals have a distinctive absorption about λ 700 together with others about λ 900, and if the first be visible it almost follows that the distinctive mark of the radical with which it is connected will be found. Thus in the ethyl series we find an absorption at 740, and a characteristic band, one edge of which is at 892 and the other at 920. If we find a body containing the 740 absorption and a band with the most refrangible edge commencing at 892, or with the least refrangible edge terminating at 920, we may be pretty sure that we have an ethyl radical present. So with any of the aromatic group; the crucial line is at 867. If that line be connected with a band we may feel certain that some derivative of benzene is present. The benzyl group shows this remarkably well, since we see that phenyl is present, as is also methyl. It will be advantageous if the spectra of ammonia, benzene, aniline, and dimethyl aniline be compared, when the remarkable coincidences will at once become apparent, as also the different weighting of the molecule. The spectrum of nitro-benzene is also worth comparing with benzene and nitric acid. . . . In our own minds there lingers no doubt as to the easy detection of any radical which we have examined, . . . and it seems highly probable by this delicate mode of analysis that the hypothetical position of any hydrogen which is replaced may be identified, a point which is of prime importance in organic chemistry. The detection of the presence of chlorine or bromine or iodine in a compound is at present undecided, and it may well be that we may have to look for its effects in a different part of the spectrum. The only trace we can find at present is in ethyl bromide, in which the radical band about 900 is curtailed in one wing. The difference between amyl iodide and amyl bromide is not sufficiently marked to be of any value."

The absorption spectra of the didymium and cobalt salts afford many striking examples of the complicated effects of solution and combination in the spectra. It is impossible to explain these without the help of illustrations, and we must refer the reader, therefore, to the original papers.¹ Some very interesting changes have been noticed in the position of absorption bands when certain colouring matters are dissolved in different liquids. Characteristic absorption bands appear for each colouring matter in slightly different positions according to the solvent. Hagenbach, Kraus, Kundt,² and Claes³ have studied the question. In a preliminary examination Professor Kundt had come to the conclusion that solvents displaced absorption bands towards the red in the order of their dispersive powers; but the examination of a greater number of cases has led him to recognize that no generally valid rule can be laid down. At the same time highly dispersive media, like bisulphide of carbon, always displace a band most towards the red end, while with liquids of small dispersion, like water, alcohol, and ether, the band always appears more refrangible than with other solvents; and as a general rule the order of displacement is approximately that of dispersive power.

Relations of the Spectra of Different Elements.

Various efforts have been made to connect together the spectra of different elements. In these attempts it is generally assumed that certain lines in one spectrum correspond to certain lines in another spectrum, and the question is raised whether the atom with the higher atomic weight has its corresponding lines more or less refrangible.

¹ Bunsen, "On the Inversion of the Bands in the Didymium Absorption Spectra," *Phil. Mag.*, xxviii. p. 246 (1864), and xxxii. p. 177 (1866); Russell, "On the Absorption Spectra of Cobalt Salts," *Proc. Roy. Soc.*, xxxii. p. 258 (1881). ² *Wied. Ann.*, iv. p. 34 (1878). ³ *Wied. Ann.*, iii. p. 339 (1878).

No definite judgment can as yet be given as to the success of these efforts. Lecoq de Boisbaudran has led the way in these speculations, and some of the similarities in different spectra pointed out by him are certainly of value. But whether his conclusion, that "the spectra of the alkalis and alkaline earths when classed according to their refrangibilities are placed as their chemical properties in the order of their atomic weight," will stand the test of further research remains to be seen. Ciamician⁴ has also published a number of suggestive speculations on the question, and Hartley⁵ has extended the comparison to the ultra-violet rays.

When metallic spectra are examined it is often found that some line appears to belong to more than one metal. This is often due to a common impurity of the metals; but such impurities do not account for all coincidences. The question has been raised whether these coincidences do not point to a common constituent in the different elements which show the same line. If this view is correct, we should have to assume that the electric spark decomposes the metals, and that the spectrum we observe is not the spectrum of the metal but that of its constituents. Further investigation has shown, however, that in nearly all cases the assumed coincidences were apparent only. With higher resolving powers it was found that the lines did not occupy exactly the same place. With the large numbers of lines shown by the spectra of most of the metals some very close coincidences must be expected by the doctrine of chances. The few coincidences which our most powerful spectroscopes have not been able to resolve are in all probability accidental only. (A. S*.)

SPEECH-SOUNDS, the sounds actually used for the conveyance of thought by speech. See PHONETICS.

1. *Symbolization*.—It is necessary to have some system of writing speech-sounds, in order to talk of them. The system used in the present article is the palaeotype of the present writer's *Early English Pronunciation*. All letters or words thus written will be enclosed in (). The following preliminary list of the ordinary sounds, with examples, will render what follows intelligible. For an alphabetical list, see art. 20.

English.—1. beet bait baa bought boat boet (biit beet baa baat boot buot). 2. knit net gnat knot nut nook (nit net net not not nuk). 3. file foil foul fuel (fa'il fo'il fa'ul fiuu'il). 4. hay (hee). 5. pea bee, toe doe, cape gape (pii bii, too doo, keep geep). 6. whey way, feel veal, thin then, seal zeal, rush rouge, hue you (whee wee, fiil viil, th'in dhen, siil ziil, rosh ruuzh, zhiuu jun). 7. ear ring, gull little (iir riq, goll li'l). 8. sum chasm, sun open, sung (sam kœz'm, sœn oop'n, sq). 9. chest jest (tjœst djœst).

Foreign.—F French, G German, I Italian. 10. bête F, lèche F, no IT, dâ F, feu F, veuf F, vin F, vent F, vont F, un F, soûn F, sol F, lui F (bœt, laash, no, dy, œ, vœf, vea, va, voa, œa, siœa, siœa, ly). 11. dach teich, tage siege, wahl, all G (dakh tœikjh, taagh, ziigjh, bhaal). 12. paglia IT, besogne F (pœ'ljœ, bœzœn).

2. *Nature of Speech-Sounds*.—Speech-sounds result from shocks given to the air by the organs of speech, received by the drumskin of the ear, and transmitted to the auditory nerves in the cochlea. The apparatus is explained by Helmholtz, who deals with musical sounds. But speech is not musical, and its sounds are much obliterated when rendered musical.⁶ An original quality of tone generated by the vocal chords is modified by the cavities through which it passes, as explained by Helmholtz (*Sensations of Tone*) on the principle of resonance. There are three ways in which speech-sounds may be produced—(1) by the air in the mouth, without additional breathing, by smacks and clicks; (2) by drawing in air, as orally in chirps, whistles, sobs, gasps, and nasally in snuffles, snores; (3) by expelling air, as in the greater number of speech-sounds. The last are

⁴ *Wien. Ber.*, lxxviii. (1878).

⁵ *Journal Chem. Soc.*, September 1883.

⁶ Ellis, *Speech in Song*, sect. iv.