

**SPECIES.** In logic the term "species" is applied to any group of individuals agreeing in some common attribute or attributes, and included along with other groups in a higher category, that of "genus," which comprehends the fewer and more general attributes in which all agree and ignores those in which they differ. The application of these terms in logic is thus purely relative; any genus, however large, may be but a species of a still larger genus. But in arranging the innumerable objects of the natural sciences the naturalist finds it necessary to restrict the terms "species" and "genus" to the two lowest groupings and to distinguish the higher aggregates by special terms, as "family," "order," "class," &c. Early writers had but a loose conception of many different "kinds" of animals and plants, and spoke only of species and genus in their purely logical relations, with varying breadth of content. The term "species" was limited to its natural history usage in the end of the 17th century by John Ray. His conception of "specific characters" rested, not only on close and constant resemblance in outward form, but also on the likeness of offspring to parent, a considerable measure of variability being, however, recognized. Amongst subsequent authors this conception of common descent or parentage became more and more prominent, while the progress of successful definition of species made the limits of their variability seem always narrower and of less importance; and in this way the useful working conception of the tolerable definiteness of species gradually crystallized into the absolute dogma of their fixity. Then Linnæus in his *Philosophia Botanica* gave the aphorism "species tot sunt diversæ, quot diversæ formæ ab initio sunt creatæ" (we reckon just as many species as there were forms created at the beginning), which was generally accepted. Buffon's obstinate rejection of the Linnæan classification was associated with a belief in the modifiability of species, and showed some foresight of the doctrine elaborated soon afterwards by LAMARCK (*q.v.*). The general acceptance of this dogma was, however, effected by the influence of Cuvier; its overthrow dates only from the publication of Darwin's *Origin of Species* (1859), of which the argument need not be here repeated. (See EVOLUTION, MORPHOLOGY.) The genealogical conception of species was thus established more firmly than ever, though cleared from its former associations; in Haeckel's phrase, the species is the whole succession of organisms which exhibit the same form in the same environment. The rash generalization, that distinct species are to be recognized by their incapacity for the production of fertile hybrids, was next overthrown, while closer study has cleared away the notion of the equal definiteness of all specific forms. We now know that, while many forms, like the pearly nautilus or the Venus's fly-trap, do indeed exhibit the most perfect specific definiteness, the demarcation of equally definite species in other genera is rendered impossible by the existence of the most complete series of transitional forms, and the number of the species defined thus comes to depend simply on the personal equation of the systematist, on his predilection for "lumping" or "splitting," as the case may be. Thus, for example, the number of described German species of hawkweed (*Hieracium*) has ranged from 300 for one author, through 106 for another and 52 for a third, to less than 20 for a fourth. Similar instances of variable genera are afforded by the willows and the brambles, and many other common forms. This wide variability, as might be expected, seems to be more prevalent among the lowest forms of life, and the classical example of the relativity and variability of species has been furnished by Haeckel's beautiful monograph on the calcareous sponges (*Monographie der Kalkschwämme*, Jena, 1872), in which he offers twelve distinct arrangements of

the same set of forms from various points of view, among which the two most nearly conventional propose respectively 21 genera and 111 species and 39 genera and 289 species. All such variable forms are in fact species in the making, which become definite in proportion as certain varieties become especially adapted to their environment, and become isolated by the dying out of the intermediate forms. With these limitations, however, the working usefulness of the morphological conception of species remains undiminished. The want of any absolute standard of specific difference is largely made up by practical experience and common sense; and the evolutionary systematists are less in danger than were their predecessors of either exaggerating or understating the importance of mere varieties. (See VARIATION.)

**SPECIFIC GRAVITY.** See HYDROMETER, vol. xii. p. 536 sq.

**SPECTACLES** are flat glasses, prisms, spherical or cylindrical lenses, employed to detect and correct defects of the eyes. They are made usually of crown glass or rock crystal ("pebbles"), the latter being somewhat lighter and cooler to wear. They are mounted in the well-known rigid spectacle frame when for continuous use,—eye-glasses being preferable where they are worn intermittently, and hand-glasses or lorgnettes where they are required to supplement temporarily the spectacles usually worn, or where, as with extreme shortness of sight, no glass could be employed with comfort for any length of time.

**Preserves.**—Preserves are used to conceal deformities or to protect the eyes in the many conditions where they cannot tolerate bright light, such as ulceration and inflammation of the cornea, certain diseases of the iris, ciliary body, choroid, and retina. They are made of bluish, "smoked," or almost black coloured glass, and are of very various shapes, according to the amount of obscuration necessary.

**Prisms.**—Prisms are of great value in cases of double vision due to a slight tendency to squinting, caused by weakness or over-action of the muscular apparatus of the eyeball. Prisms deflect rays of light towards their bases. Hence, if a prism is placed in front of the eye with its base towards the nose, a ray of light falling upon it will be bent inwards, and seem to come from a point further out from the axis of vision. Conversely, if the base of the prism is turned towards the temple, the ray of light will seem to come from a point nearer the axis, and will induce the eye to turn inwards, to converge towards its fellow. In cases of myopia or short-sight owing to weakness of the internal recti muscles, the eyes in looking at a near object, instead of converging, tend to turn outwards, and so double vision results. If a suitable prism is placed in front of the eyes the double vision may be prevented. These prisms may be combined with concave lenses, which correct the myopia, or, since a concave lens may be considered as composed of two prisms united at their apices, the same effect may be obtained by making the distance between the centres of the concave lenses greater than that between the centres of the pupils. Again, to obviate the necessity for excessive convergence of the eyes so common in hypermetropia, the centre of the pupil should be placed outside the centre of the corrective convex lenses; these will then act as prisms with their bases inwards. Where, on the other hand, there is no tendency to squinting, care must be taken in selecting spectacles that the distances between the centres of the glasses and the centres of the pupils are quite equal, otherwise squinting, or at any rate great fatigue, of the eyes may be induced.

**Spherical Lenses.**—Biconcave, biconvex, and concavo-convex (meniscus) lenses are employed in ophthalmic practice in the treatment of errors of refraction. Until recently these spherical lenses were numbered in terms of their focal

length, the inch being used as the unit. Owing principally to differences in the length of the inch in various countries, this method had great inconveniences, and is now giving place to a universal system, in which the unit is the refractive power of a lens whose focal length is one metre. This unit is called a "dioptric" (usually written "D"). A lens of twice its strength has a refractive power of 2 D, and a focal length of half a metre, and so on.

**Concave lenses** are used in the treatment of myopia or short-sight. In this condition the eye is elongated from before backwards, so that the retina lies behind the principal focus. All objects, therefore, which lie beyond a certain point (the conjugate focus of the dioptric system of the eye, the far point) are indistinctly seen; rays from them have not the necessary divergence to be focused in the retina, but may obtain it by the interposition of suitable concave lenses. Concave lenses should never be used for work within the far point; but they may be used in all cases to improve distant vision, and in very short-sighted persons to remove the far point so as to enable fine work such as sewing or reading to be done at a convenient distance. The weakest pair of concave lenses with which one can read clearly test types at a distance of 18 feet is the measure of the amount of myopia, and this fully correcting glass may be worn in the slighter forms of short-sight. In higher degrees, where full correction might increase the myopia by inducing a strain of the accommodation, somewhat weaker glasses should be used for near work. In the highest degrees the complete correction may be employed, but lorgnettes are generally preferred, as they can be removed when the eyes become fatigued. It must be remembered that short-sight tends to increase during the early, especially the school, years of life, and that hygienic treatment, good light, good type, and avoidance of stooping are important for its prevention.

**Convex Lenses.**—In hypermetropia the retina is in front of the principal focus of the eye. Hence in its condition of repose such an eye cannot distinctly see parallel rays from a distance and, still less, divergent rays from a near object. The defect may be overcome more or less completely by the use of the accommodation. In the slighter forms no inconvenience may result; but in higher degrees prolonged work is apt to give rise to aching and watering of the eyes, headache, inability to read or sew for any length of time, and even to double vision and internal strabismus. Such cases should be treated with convex lenses, which should be theoretically of such a strength as to fully correct the hypermetropia. Practically it is found that a certain amount of hypermetropia remains latent, owing to spasm of the accommodation, which relaxes only gradually. At first glasses may be given of such a strength as to relieve the troublesome symptoms; and the strength may be gradually increased till the total hypermetropia is corrected. Young adults with slighter forms of hypermetropia need glasses only for near work; elderly people should have one pair of weak glasses for distant and another stronger pair for near vision. These may be conveniently combined, as in Franklin glasses, where the upper half of the spectacle frame contains a weak lens, and the lower half, through which the eye looks when reading, a stronger one.

**Anisometropia.**—It is difficult to lay down rules for the treatment of cases where the refraction of the two eyes is unequal. If only one eye is used, its anomaly should be alone corrected; where both are used and nearly of equal strength, correction of each often gives satisfactory results.

**Presbyopia.**—Where distant vision remains unaltered, but, owing to gradual failure of the accommodative apparatus of the eye, clear vision within 8 inches becomes impossible, convex lenses should be used for reading of such

a strength as to enable the eye to see clearly about 8 inches distance. Presbyopia is arbitrarily said to commence at the age of forty, because it is then that the need of spectacles for reading is generally felt; but it appears later in myopia and earlier in hypermetropia. It advances with years, requiring from time to time spectacles of increasing strength.

**Cylindrical Lenses.**—In astigmatism, owing to differences in the refractive power of the various meridians of the eye, great defect of sight, frequently accompanied by severe headache, occurs. This condition may be cured completely, or greatly improved, by the use of lenses whose surfaces are segments of cylinders. They may be used either alone or in combination with spherical lenses. The correction of astigmatism is in many cases a matter of considerable difficulty, but the results to vision almost always reward the trouble.

Convex spectacles were invented towards the end of the 13th century, perhaps by Roger Bacon. Concave glasses were introduced soon afterwards. Airy, the astronomer, about 1827, corrected his own astigmatism by means of a cylindrical lens. Periscope glasses were introduced by Dr W. H. Wollaston. (A. BR.)

**SPECTROSCOPY.** The spectroscopy is an instrument which separates luminous vibrations of different wave-lengths, as far as is necessary for the object in view. It consists of three parts,—the collimator, the prism or grating, and the telescope. The collimator carries the slit through which the light is admitted and a lens which converts the diverging pencil of light into a parallel pencil. The pencils carrying light of different wave-lengths are turned through different angles by the prism or grating, which is therefore the essential portion of the spectroscopy. The telescope serves only to give the necessary magnifying power, and is dispensed with in small direct vision spectroscopes. For a description of the different kinds of prism used, see OPTICS; and for an explanation of the action of the grating, see UNDULATORY THEORY. The most important adjustment in the spectroscopy is that of the collimator. Especially in instruments of large resolving power it is essential for good definition that the light should enter the prism or fall on the grating as a parallel pencil. For a method allowing an easy and accurate adjustment for each kind of ray, see an article in *Phil. Mag.*, vol. vii. p. 95 (1879).

Prisms are nearly always used in the position of minimum deviation, but, if the collimator is properly adjusted, this is by no means a necessary condition for good definition. Prisms as generally cut, with an isosceles base, give the greatest resolving power in the position of minimum deviation, but the loss in resolving power is not great for a small displacement. The dispersion and magnifying power of a prism can be considerably altered by a change of its position, and a knowledge of this fact is of great value to an experienced observer. The use of a prism in a position different from that of minimum deviation is, however, a luxury which only those acquainted with the laws of optics can indulge in with safety.

Lord Rayleigh has given the theory of the spectroscopy under OPTICS, and shown on what its resolving power depends. There is no connexion between resolving power and dispersion, any value of resolving power being consistent with any value of dispersion. To obtain large resolving power with small dispersion requires, however, the use of inconveniently large telescopes and prisms or gratings. It is easy, on the other hand, to obtain small resolving power together with large dispersion.

The following definitions would be found of general use if adopted. **Resolving Power.**—The unit resolving power of a spectroscopy in any part of the spectrum is that resolving power which allows the separation of two lines differing by the thousandth part of their own wave-length or wave-number,—the wave-number being the number

of waves in unit length. *Purity.*—The unit purity of a spectrum is that purity which allows the separation of two lines differing by the thousandth part of their own wave-length or wave-number. We speak of the resolving power of a spectroscopy and of the purity of a spectrum. The resolving power is a constant for each spectroscopy, and independent of the width of the slit. The purity of a spectrum, on the other hand, depends on the width of the slit, unless that width is small compared to a certain quantity presently to be mentioned. The resolving power of a spectroscopy is numerically equal to the greatest purity of spectrum obtainable by it.

Adopting these definitions, we get from Lord Rayleigh's equations for the resolving power  $R$  of a grating

$$1000 R = mn,$$

where  $n$  is the total number of lines used on the grating and  $m$  the order of the spectrum. For a spectroscopy with simple prisms we get

$$1000 R = - (t_2 - t_1) \frac{\delta\mu}{\delta\lambda},$$

where  $t_2$  and  $t_1$  are the greatest and smallest lengths of paths in the dispersive medium. If we put for the refractive index of the medium  $\mu = A + B/\lambda^2$  we may write

$$1000 R = 2B(t_2 - t_1)/\lambda^3.$$

It will be seen that, while the resolving power of a spectroscopy with grating depends only on the order of the spectrum and is independent of the wave-length for each order, the resolving power of a spectroscopy with prism will vary inversely as the third power of the wave-length  $\lambda$ , so that the resolving power will be about eight times as great in the violet as in the red (see OPTICS). If compound prisms are used we must write

$$1000 R = 2(B_2 t_2 - B_1 t_1)/\lambda^3,$$

where  $t_2$  is the greatest effective length of path in one medium,  $t_1$  in the other medium,  $B_2$  and  $B_1$  being the dispersive constants for the two media.

The purity  $P$  of a spectrum is given by the equation

$$P = \frac{\lambda}{d\psi + \lambda} R,$$

where  $d$  denotes the width of slit and  $\psi$  is the angle subtended by the collimator lens at the slit. If the slit is sufficiently narrowed,  $d\psi$  may be made small compared to  $\lambda$ , and in that case the purity of the spectrum is independent of the width of slit and equal to the resolving power. If, on the other hand, a wide slit is used, so that  $d\psi$  is large compared to  $\lambda$ , the purity becomes inversely proportional to the width of slit. In actual work the slit is generally of such width that neither term in the denominator of the expression for purity can be neglected.

There is a necessary limit to the resolving power of all optical instruments, depending on the fact that light consists of a series of groups of waves incapable of interfering with each other. If it is true, as is generally believed, but without sufficient reason, that a retardation of 50,000 wave-lengths is sufficient to destroy the capability of interference—that is to say, that the groups consist on the average of approximately 50,000 waves—the maximum purity obtainable in any spectroscopy is 50. The closest line resolved with a grating, as far as the present writer is aware, requires a resolving power of about 100. Professor Piazzi Smyth has with prisms realized a purity of 50. It would seem, therefore, that the theoretical limit of purity has very nearly been reached, for, though the estimate of 50,000 waves to the group is in all probability too small, there are other considerations which render it highly improbable that the total number of waves to the group should, for sunlight at any rate, be more than two or three times larger. The limit of possible purity will very likely depend on the temperature of the luminous body.

Almost the greatest practical difficulty which the spectroscopist has to contend with generally is the want of sufficient light. The following remarks apply to line spectra principally, but they hold also almost entirely for the spectra of fluted bands, which break up into lines under high resolving power. The maximum illumination for any line is obtained when the angular width of the slit is equal to the angle subtended by one wave-length at a distance equal to the collimator aperture. In that case  $d\psi = \lambda$  and the purity is half the resolving power. Hence when light is a consideration we shall not, as a rule, realize more than half the resolving power of the spectroscopy. If the visual impression depended only on the intensity of illumination, a further widening of the slit should not increase the visibility of a line. As a matter of fact spectroscopists generally work with slits wider than that which theoretically gives full illumination. The explanation of the fact is physiological, visibility depending on the apparent width of the object. If different spectroscopies have their slits of such width that the apparent width of a line as seen by the eye is the same, and if the magnifying power is such that the pupil is just filled with light, the purity of the spectrum is directly proportional to the resolving power. We come to the conclusion, therefore, that for both narrow and wide slits the efficiency of a spectroscopy depends exclusively on its resolving power. It has been pointed out by Lord Rayleigh that, owing to the want of definition in the optical images on the retina when the full aperture of the pupil is used, the pencil must be contracted to a third or a quarter of its natural width, if full resolving power is to be obtained. This is accompanied with a serious loss of light, which can be partly obviated by contracting the horizontal aperture only (the refracting edge being supposed vertical). There are two ways of doing this. One consists in the use of magnifying half prisms. But the loss of light by reflexion in simple half prisms more than counterbalances the advantage; compound half prisms like those used by Christie may, however, be employed. We may also use prisms of three or four times the height of the effective horizontal aperture, with correspondingly large telescopes, and then by the eye-piece contract the beam until its vertical section fills the pupil. The latter plan, though theoretically best, involves more expensive apparatus and prisms of very homogeneous material.

The question of illumination is important also when photography is used for spectroscopic analysis. For a given intensity of the source of light the intensity of the image on the sensitive film will be directly proportional to the solid angle of the cone of light forming the last image, and will be independent of the arrangement of intermediate lenses. Hence lenses with as short a focus compared to aperture as is consistent with good definition should be used in the camera.

The methods of recording and reducing spectroscopic observations are described in all books and treatises on the subject and may therefore be passed over here.

A lens is often used to concentrate the light of the source on the slit. There is some loss of light due to reflexion from the surface of the lens, but its position, aperture, and focal length do not affect the luminosity of the spectrum seen as long as the whole collimator is filled with light.

Bodies are rendered luminous for spectroscopic investigation either by being placed in the Bunsen flame or by the help of the electric current. A little difficulty may arise where the body is given in solution and does not show its characteristic lines in the flame. Lecoq de Boisbaudran takes the spark from the surface of the solution. The present writer has found the tube sketched in the figure on the next page a great improvement on those commonly used, if a sufficient quantity of the solution is at

hand; otherwise the method is too wasteful. The current is brought into the solution by a platinum wire, sealed into a small glass tube; the platinum wire reaches about to the level of the open end of the tube. A capillary of thick-walled glass tubing is placed over the platinum wire; the liquid rises in the capillary and sparks can be taken as from a solid. The lines due to the glass are easily eliminated. If a small quantity of material only is available, the plan adopted by Bunsen and extensively used by Hartley<sup>1</sup> seems the most successful. Pointed pieces of charcoal (Bunsen) or pieces of graphite pointed to a knife edge (Hartley) are impregnated with the liquid, and the spark is taken from them. Some substances, when introduced into a vacuum tube, especially near the negative pole, and under great exhaustion, show a characteristic phosphorescence. Becquerel was the first to examine the spectra shown under these circumstances, and Crookes has lately used the same method with great success.



*Spectra of Metalloids.*

A good deal of discussion has taken place on the spectra of the metalloids, owing to the fact that they seem to be able to give different spectra under different circumstances. Spectra have occasionally been assigned to the elements which on further investigation were found to belong to some compound present. According to the general opinion of spectroscopists at present, different spectra of the same elements are always due to different allotropic conditions. If a complex molecule breaks up into simpler molecules the breaking up is always accompanied by a change of spectrum.

*Nitrogen.*—(a) The line spectrum appears whenever a strong spark (jar discharge) is taken in nitrogen gas. It is always present when metallic spectra are examined by the ordinary method of allowing the jar discharge to pass between metallic poles.<sup>2</sup> Hartley (*Phil. Trans.*, 1884, part i.) has measured the ultra-violet lines of the air spectrum, but has not separated the oxygen from the nitrogen lines. (b) The band spectrum of the positive discharge, which is generally called the band spectrum of nitrogen, always appears when the discharge is sufficiently reduced in intensity. The spectrum consists of two sets of bands of different appearance, one in the less refrangible part and one in the more refrangible part of the spectrum, — the two sets of bands overlapping in the green. Hence some observers believe the spectrum to be made up of two distinct spectra. Plücker and Hittorf (*Phil. Trans.*, 1865) give a coloured drawing of this spectrum, which is one of the most beautiful that can be observed. The most complete drawing of it is given by Piazzi Smyth (*Trans. Roy. Soc. Edin.*, vol. xxxii. part iii.), and there is also a good drawing by Hasselberg (*Mém. Acad. Imp. de St. Pétersb.*, vol. xxxii.). (c) The glow which surrounds the negative electrode in an exhausted tube shows in many cases a spectrum which, as a rule, is not seen in any other part of the tube. The memoir of Hasselberg contains a drawing of it. The spectrum seen when a weak spark is taken in a current of ammonia is neither that of nitrogen nor that of hydrogen, but must be due to a compound of these gases. When the pressure of the gas is reduced, a single band is seen having a wave-length from 5686 to 5627 Xth metres (*Nature*, vi. p. 359). When a spark is taken from a liquid solution of ammonia a more complicated spectrum appears (Lecoq de Boisbaudran), and, if ammonia and hydrogen are burnt together either in air or oxygen, a complicated spectrum is obtained the chemical origin of which has not been satisfactorily explained. Drawings of it are given by Dibbits (*Pogg. Ann.*, cxxii. p. 518) and by Hofmann (*Pogg. Ann.*, cxlvii. p. 95). The absorption spectrum of the red fumes of nitrogen tetroxide has often been mapped; the most perfect drawing is given by Dr B. Hasselberg (*Mém. Acad. Imp. de St. Pé.*, xxvi.). According to Moser (*Pogg. Ann.*, cx. p. 177), three bands close to the solar line C disappear when the vapour is heated. Recently Deslandes has obtained in vacuum tubes some ultra-violet bands which seem to be due to a compound of nitrogen and oxygen (*C. R.*, chap. i. p. 1256, 1885).

*Oxygen.*—(a) The elementary line spectrum of oxygen is that which appears at the highest temperature to which we can subject oxygen, that is, whenever the jar and air break are introduced into the electric circuit. It consists of a great number of lines, especially in the more refrangible part of the spectrum. (b) The compound

<sup>1</sup> *Phil. Trans.*, clxxv. p. 49 (1884).

<sup>2</sup> We may refer once for all to Watts, *Index of Spectra*, for a list of wave-lengths of the different spectra.

line spectrum of oxygen appears at lower temperatures than the first. It consists, according to Piazzi Smyth, of six triplets and a number of single lines. This spectrum corresponds to the band spectrum of nitrogen. (c) The continuous spectrum of oxygen appears at the lowest temperature at which oxygen is luminous. The wide part of a Plücker tube, for instance, filled with pure oxygen generally shines with a faint yellow light, which gives a continuous spectrum. Even at atmospheric pressure this spectrum can be obtained by putting the contact breaker of the induction coil out of adjustment, so that the spark is weaker ed. (d) The spectrum of the negative glow was first accurately described by Wüllner, and is always seen in the glow surrounding the negative electrode in oxygen. It consists of five bands, three in the red and two in the green. For further information respecting these spectra, see Schuster (*Phil. Trans.*, clxx. p. 37, 1879) and Piazzi Smyth (*Trans. Roy. Soc. Edin.*, vol. xxxii. part iii.). According to Egoroff, the A and B lines of the solar spectrum are due to absorption by oxygen in our atmosphere, and some recent observations of Janssen seem to support this view.

*Carbon.*—(a) The line spectrum appears when a very strong spark is sent through carbonic oxide or carbonic acid. The ultra-violet lines observed by Hartley when sparks are taken from graphite electrodes also belong probably to this spectrum. (b) Considerable discussion has taken place as to the origin of the spectrum seen at the base of a candle or a gas flame. At first observations seemed to point to the fact that it was due to a hydrocarbon. It has been ascertained, however, that sparks taken in cyanogen gas, even when dried with all care, show the spectrum, and a flame of cyanogen and oxygen gives the same bands brilliantly. These facts have convinced the majority of observers that the spectrum is a true carbon spectrum. The best drawing is given by Piazzi Smyth, who ascribes the spectrum, however, to a hydrocarbon. The flame of cyanogen, which had already been examined by Faraday and Draper before the days of spectrum analysis, shows a series of bands in the red, reaching into the green. There is no doubt that they are due to a compound of nitrogen and oxygen. Another series of bands in the blue, violet, and ultra-violet have been also proved by Liveing and Dewar to be due to a compound of nitrogen and carbon. If the discharge is passed at low pressure through carbonic acid or carbonic oxide a spectrum is seen which seems to belong to carbonic oxide. A very beautiful and remarkable drawing of this spectrum, especially of its most brilliant band, has been published by Piazzi Smyth.

Very little need be said of the remaining metalloids, as we do not possess a sufficiently careful examination of their spectra. Chlorine, bromine, and iodine show bands by absorption. If a spark is passed through the gases line spectra appear. Sulphur volatilized in a vacuum tube may show either a line or a band spectrum under the influence of the electric discharge. The absorption through the vapour of sulphur is continuous at first on volatilization, but as the vapour is heated to 1000° the continuous spectrum gives way to a band spectrum. A spark through the vapour of phosphorus gives a line spectrum. We may obtain the spectra of fluorine, silicon, and boron by comparing the spectra given by sparks taken in atmospheres of fluoride of boron and fluoride of silicon.

*Spectra of Metals and their Compounds.*

*Hydrogen.*—If sparks are taken through hydrogen, four well-known lines appear in the visible region of the spectrum. The remarkable series of ultra-violet lines photographed by Dr Huggins in the spectra of some stars which in their visible part show hydrogen chiefly has suggested the question whether the whole series is not due to that gas. This has now been proved to be the case by Cornu, who has recently examined the hydrogen spectrum with great care. In vacuum tubes filled with hydrogen a complicated spectrum often appears which is so persistent that nearly all observers have ascribed it to hydrogen (though Salet had given reasons against that conclusion). According to Cornu, the purer the gas the feebler does this spectrum become, so that the above-mentioned line spectrum seems to be the only true hydrogen spectrum. A flame of hydrogen in air or oxygen shows a number of lines in the ultra-violet belonging apparently to an oxide of hydrogen (Liveing and Dewar, Huggins). Aqueous vapour gives an absorption spectrum principally in the yellow.

*Alkali Metals.*—The metals of the alkali group are distinguished by the fact that their salts give the true metal spectra when rendered luminous in the Bunsen burner; that is to say, their salts are decomposed and the radiation of their metallic base is sufficiently powerful to be visible at the temperature of the flame. Their spectra are not so easily seen if sparks are taken from the liquid solution, but Lecoq de Boisbaudran has obtained fine spectra of sodium and potassium by taking the spark from a semi-fluid bead of the sulphates. The most complete description of the spectra of sodium and potassium seen when the metals are heated up in the voltaic arc is given by Liveing and Dewar (*Proc. Roy. Soc.*, xxix. p. 378, 1879), who have also mapped their ultra-violet lines (*Phil. Trans.*, 1883, pt. i.). Abney has found a pair of infra-red lines

belonging to sodium, with wave-lengths 8187 and 8199 (*Proc. Roy. Soc.*, xxxii. p. 443, 1881). Becquerel finds lines in the infra-red at 11,420. The vapour of sodium and potassium heated up in a tube is coloured and shows a spectrum of fluted band; but in the case of sodium the yellow line is always present at the same time. It is probable that the band spectrum belongs to the vapour, containing two atoms in each molecule, and that at higher temperatures the molecules are split up, the single atoms showing the line spectra. Both potassium and sodium show an additional absorption line (5510 for Na and 5730 for Ka) at the temperature at which the fluted bands appear. According to a suggestion of Liveing and Dewar, these lines may depend on the presence of hydrogen, which it is very difficult to exclude. These experimenters have also described interesting but complicated absorption phenomena depending on the simultaneous presence of two or more metals. Thus sodium and magnesium show a band in the green ( $\lambda=5300$ ), which does not appear when sodium alone or magnesium alone is volatilized. Potassium and magnesium show similarly two lines in the red (*Proc. Roy. Soc.*, xxvii. p. 350, 1878). If a spark is taken from potassium in an atmosphere of carbonic oxide a band appears (5700) depending probably on a combination between the potassium and the carbonic oxide. Lockyer has observed certain curious phenomena (*Proc. Roy. Soc.*, vol. xxii. p. 378) taking place at the temperature at which the band spectrum of sodium changes into the line spectrum; these phenomena deserve a fuller investigation. Lithium furnishes a good example of a change in the relative intensity of lines at different temperatures. At the temperature of the flame the red line is the most powerful, an orange line being also seen. When a spark is taken from a liquid solution the orange line is far the strongest, and a blue line is seen, which in its turn rapidly gains in intensity as the temperature is raised. When the spark is taken from solutions of different strengths the more concentrated solution shows a change in relative intensity of lines in the direction in which an increase of temperature would act. Combination of the metals with transparent acids does not when in solution show any appreciable absorption in the visible part of the spectrum; but Sorét has mapped their ultra-violet absorption.

**Metals of Alkaline Earths.**—Calcium, strontium, and barium are distinguished by the fact that their volatile compounds give fine spectra in the Bunsen flame. The more stable salts, as the phosphates and silicates, give the reaction only feebly or not at all. When a salt like the chloride of barium is introduced into the flame the spectrum is seen to change gradually; the spectrum seen at first is different according as the chloride, bromide, or iodide is used, while the spectrum which finally establishes itself is the same for the different salts of the same metal. Mitscherlich, who was the first to investigate carefully these phenomena (*Pogg. Ann.*, cxxi. p. 459, 1864), ascribes the spectra seen at first to the compound placed in the flame, while gradually the oxide spectrum gets the upper hand. This explanation has always been accepted, and receives support from the fact that the bromide spectrum is strengthened by introducing bromine vapour into the flame, and the other compound spectra can be similarly strengthened by introducing suitable vapours. There is an observation, however, made by Professors Liveing and Dewar which in one case is not compatible with Mitscherlich's explanation. "A mixture of barium carbonate, aluminium filings, and lamp-black heated in a porcelain tube gave two absorption lines in the green, corresponding in position to bright lines seen when sparks are taken from a solution of barium chloride, at wave-lengths 5242 and 5136, marked  $\alpha$  and  $\beta$  by Lecoq de Boisbaudran." These two lines, or rather bands, are the brightest in the spectrum commonly ascribed to barium chloride. In addition to the compound spectra the brightest of the metallic lines seen at a low temperature appear in the flame. The metallic line is in the violet with calcium, in the blue with strontium, and in the green with barium. Sparks taken from a solution of the metallic salts show the compound spectra well, and in addition more of the true metallic lines than the flame. The best drawings of the compound spectra are those given in Lecoq de Boisbaudran's *Atlas*; but measurements with higher resolving powers are much wanted. When the salts are introduced into the voltaic arc numerous metallic lines appear which have been mapped by Thalén. Liveing and Dewar have investigated those lines which can be reversed and have also mapped the ultra-violet spectra. Captain Abney has mapped a pair of infra-red lines belonging to calcium between 8500 and 8600, and, according to Becquerel, with the help of a phosphorescent screen bands or lines appear of still lower refrangibility (8830 to 8880). Lockyer (*Phil. Trans.*, clxiii. p. 253, 1878, and clxiv. p. 805, 1874) has measured and mapped as regards their length the lines of these as well as of many of the other metals.

**Metals of Magnesium Group.**—Beryllium presents comparatively simple spectroscopic phenomena, as far as it has hitherto been investigated. Two green lines were mapped by Thalén and five in the ultra-violet by Hartley (*Jour. Chem. Soc.*, June 1883). The spectrum of magnesium is well known from its green triplet; but the vibrations of the metal seem very sensitive to a change of

conditions. Full details are given by Liveing and Dewar in *Proc. Roy. Soc.*, xxxii. p. 189. These authors have found that some of the bands seen occasionally, when magnesium wire is burned in air, are due to a compound of magnesium and hydrogen. The spectrum appears when sparks are taken from magnesium poles in an atmosphere containing hydrogen. For a description of the peculiarities of the flame, arc, and spark spectrum, the reader is referred to the original paper. The ultra-violet spectrum, which contains several repetitions of the green triplet, has also been mapped and measured by Hartley and Adeney (*Phil. Trans.*, clxxv., 1874, pt. i.). The spectra of zinc and cadmium are obtained either by sparks from liquid solution or by the spark, with Leyden jar, from the metal poles. The ultra-violet spectra show for both elements a remarkable series of triplets, the lines of the cadmium triplet being about three times as far apart as those of the zinc triplets. The least refrangible of the series is in the blue with wave-lengths 5085.1, 4799.1, 4677.0 for cadmium, and 4809.7, 4721.4, 4679.5 for zinc.

**Lead Group.**—The spectrum of lead is best obtained by taking the spark from the metallic poles. Care must be taken, however, to renew the surface frequently, otherwise the oxide spectrum will gradually make its appearance. The oxide itself shows its spectrum, according to Lecoq de Boisbaudran, in the Bunsen burner. The salts of thallium show the principal metal line at the temperature of the flame. The spark spectrum is more complicated. The ultra-violet spectra of both lead and thallium have been mapped.

**Copper Group.**—The spectra of the metals belonging to this group are easily obtained in the ordinary way. When copper chloride is introduced into the Bunsen flame a fine spectrum of bands is seen. It is the same spectrum which is found when common salt is thrown upon white hot coals. This reaction for copper chloride is very sensitive, but it has never been satisfactorily decided whether the presence of copper is really necessary for its production or whether the spectrum belongs to a peculiar condition of chlorine vapour. Silver when first volatilized gives a green vapour, which at a low temperature shows continuous absorption, but at a higher temperature a spectrum of fluted bands (Lockyer). Mercury shows its lines with great brilliancy if introduced and heated in a vacuum tube. Some of the lines widen easily, and at higher pressures a continuous spectrum completely covers the background. The copper salts in aqueous solution absorb principally the red end of the spectrum, the green salts also the violet end. The glass, coloured green with oxide of copper, transmits through sufficient thickness exclusively the yellow and green rays between D and E (H. W. Vogel).

**Cerium Group.**—Yttrium gives a good spark spectrum from the solution of the chloride; the salts show no absorption bands. Crookes has found, however, that a certain substance yields brilliant phosphorescent bands under the influence of the negative pole in a vacuum tube. These bands he has, after a lengthy investigation, put down to yttrium compounds, and explained the changes they undergo in different compounds and the sensitiveness of the reaction. Lecoq de Boisbaudran, who obtains the same spectrum by taking a spark (without Leyden jar) from solutions, making the solution the positive pole, has expressed an opinion that the bands are not due to yttrium but to two substances provisionally called by him  $Z\alpha$  and  $Z\beta$ . He has also under certain conditions seen a higher temperature spectrum, which he ascribes to  $Z\gamma$ , leaving it undecided whether  $Z\gamma$  is a new substance or identical with  $Z\alpha$  (*Phil. Trans.*, 1883, p. 891, and *C.R.*, ci. p. 552, cii. p. 153).—**Lanthanum** is easily recognized by a strong spark spectrum.—**Cerium**, like yttrium and lanthanum, has no peculiar absorption spectrum when in combination and solution; although the salts are strongly coloured yellow, its line spectrum has characteristic lines in the blue.—**Didymium** is characterized spectroscopically by the fine absorption spectra of its salts. Different salts show slightly different spectra, but they can be recognized at first sight as didymium spectra. The crystals of didymium salts show remarkable differences in the absorption spectra according to the direction in which the ray traverses the crystal. Light reflected from the powdered salts shows the characteristic spectrum. According to Auer von Welsbach (*Monatsschr. f. Chemie*, vi. p. 477), didymium has lived up to its name  $\delta\delta\upsilon\mu\omicron\varsigma$ , "twins," for by fractional crystallization he has found it to be an intimate mixture of two substances, each of them giving half the absorption spectrum and half the emission spectrum of didymium.—**Terbium** has a characteristic line spectrum when the spark is taken from a solution of the salts.—The salts of **erbium** give a characteristic absorption spectrum, but till recently the drawings of it contained also absorption bands due to thulium and holmium. The spectrum of erbium, as previously mapped by Thalén, belongs almost exclusively to ytterbium; but he has recently mapped the lines belonging to what is now known as erbium (*C.R.*, xci. p. 326). Erbium salts heated in the Bunsen burner show a spectrum of bright bands without apparent volatilization.—**Ytterbium**, discovered by Marignac (atomic weight 17.3, Nilson), gives an absorption band in the ultra-violet. Its luminous spectrum is rich in lines (Thalén, *C.R.*, xci. p. 326).—**Samarium**, also discovered by

Marignac and called by him originally  $Y\beta$ , gives absorption bands in the visible part and in the ultra-violet (Sorét, *C.R.*, xc. p. 212). It frequently occurs with didymium, and most of the maps of the didymium spectrum contain the samarium bands. When precipitated with another metal it shows a brilliant phosphorescent spectrum (Crookes), which, however, is slightly different according to the metal. The peculiar yttrium spectrum is very weak even when it is mixed in considerable quantities with samarium. But when the quantity of yttrium is increased to about 60 per cent. a very rapid change takes place, and afterwards it is the samarium spectrum which is very weak. A band in the orange peculiar to the mixture, weak in pure samarium and absent in yttrium, is strongest in a mixture containing about 80 per cent. of samarium and 20 per cent. of yttrium.—**Holmium**, identified as a separate element by Sorét (*C.R.*, xci. p. 378), has absorption bands in the visible part of the spectrum (6405, 5363, 4855 on Lecoq's map of chloride of erbium), and also a strongly marked ultra-violet absorption spectrum.—**Thulium**, likewise first recognized by Sorét, is band 6840 on Lecoq's drawing of chloride of erbium, and also possesses a band at 4645. Thalén has measured the bright line spectrum (*C.R.*, xci. p. 376, 1880).—**Scandium** is characterized by a bright line spectrum (Thalén, *C.R.*, xci. p. 48, 1880).—**Gadolinium** (Marignac's  $Y\alpha$ ) has a weak absorption spectrum in the ultra-violet and a characteristic phosphorescent spectrum (*Proc. Roy. Soc.*, February 1886); but the latest researches of Crookes have rendered it probable that it is a mixture of several new elements (*Proc. Roy. Soc.*, 10th June 1886).—The **mosandrium** of Lawrence Smith seems a mixture of gadolinium and terbium. The **philippium** of De la Fontaine was a mixture of yttrium and terbium; and the latest decision of the same chemist is probably holmium.

**Aluminium Group.**—The spectra of the metals belonging to this group can be obtained in the ordinary way by means of the electric spark. The chloride of indium shows the two strongest metallic lines, one in the indigo and one in the violet, when introduced into the Bunsen flame. According to Claydon and Heycock, a number of other lines appear when the spark is taken from the metal electrodes. When a weak spark is taken from aluminium electrodes in air a band spectrum is often seen belonging apparently to the oxide, for it disappears when the spark is taken in hydrogen. Gallium, another metal belonging to this group, was first discovered by means of its spectroscopic reaction. The chloride shows two violet lines feebly in the Bunsen flame, but strongly if a spark is taken from the liquid solution. The ultra-violet lines of indium and of aluminium have been photographed by Hartley and Adeney, as well as by Liveing and Dewar. Some of the lines had been previously mapped by Cornu, whose researches extend furthest into the ultra-violet. According to Stokes, aluminium shows lines more refrangible than those of any other metal, and the wave-lengths of their lines as measured by Cornu are for one double line 1934, 1929, and for another 1860, 1852.

**Metals of the Iron Group.**—The spectroscopic phenomena of this group are somewhat complicated. The line spectra can be obtained either by taking sparks from the metal or from the solution of a salt, and also by placing the metal in the voltaic arc. The lines are very numerous and very liable to alter in relative intensity under different circumstances. The great difference, shown, for instance, between the arc and spark spectra of iron in the ultra-violet region is shown in the map by Liveing and Dewar in *Phil. Trans.*, 1885, pt. i. The visible part has also been investigated by the same authors and by Lockyer, and much information has thus been added to the knowledge previously obtained by Kirchhoff, Ångström, and Thalén. That part of the iron spectrum lying between a wave-length of 4071 and 2947 has been mapped by Cornu; Liveing and Dewar's observations refer chiefly to the more refrangible region. Considering the very important part which the iron spectrum plays in solar observations, a full investigation of its changes by a variation of temperature would at the present time be of great value. If observations with the method adopted by Lecoq de Boisbaudran were repeated with higher resolving powers they would add much to our knowledge. Some of the manganese salts, such as the chloride or carbonate, seem to be the only salts belonging to this group which show a characteristic spectrum when heated in the Bunsen burner or the oxyhydrogen flame. The spectrum observed in these cases is, according to Watts, the characteristic spectrum of the Bessemer flame, which disappears at the right moment for stopping the blast; it is probably due to an oxide of manganese. When a spark spectrum is taken from a solution of the chloride the same spectrum is seen, but the relative intensity of the lines depends on the length and the strength of the spark. The green-coloured manganates show a continuous absorption at the two ends of the spectrum, transmitting in concentrated solutions almost exclusively the green part of the spectrum. The absorption bands of permanganate of potassium are well known and seem to be due to the permanganic acid, as they appear also with other permanganates. The green salts of nickel show a continuous absorption at the two ends of the spectrum. The cobalt salts show well-defined absorption bands. Their careful

investigation by Dr W. J. Russell deserves special notice (*Proc. Roy. Soc.*, xxxii. p. 258, 1881).

**Metals of Chromium Group.**—The metallic spectra of this group have been measured principally by Thalén in the usual way. Lockyer and Roberts have obtained a channelled spectrum of chromium by absorption. As regards the spectra of compounds of chromium, the absorption of the vapour of chloro-chromic anhydride has been measured by Emerson and Reynolds (*Phil. Mag.*, xlii. p. 41, 1871), and consists of a series of regularly distributed bands. The chromium salts all possess a decided colour and show interesting absorption phenomena. The chromates absorb the violet and blue completely, also the extreme red, and transmit only the orange, yellow, and in dilute solutions part of the green. The most complete investigation of the salts in which chromium plays the part of a base is due to Erhard in a dissertation published at Freiburg. Potassium chrom-alum, ammonia chrom-alum, sulphate of chromium, when in solution, give an identical absorption for the same amount of chromium. The extreme red is freely transmitted by the violet solution, but the absorption grows rapidly towards the yellow. An indistinct absorption band ( $\lambda=6790$  to  $\lambda=6740$ ) is seen when the layer is thick or the solution concentrated. The strongest absorption takes place for a wave-length of 5800. The green is transmitted again more freely, the minimum absorption taking place for a wave-length 4880; the absorption then grows rapidly towards the violet. When the solutions are heated the colour changes to green, the absorption is increased throughout the spectrum, except in the green, where it remains nearly unchanged, and the minimum of absorption shifts to a wave-length of 5090. The solution, which remains green on cooling, has, when compared with its original state, an increased absorption in the red and blue and a slightly diminished absorption in the green. When light is sent through plates cut out of crystals of potassium chrom-alum or ammonia chrom-alum, three absorption bands (6860, 6700, 6620) are seen in the red. The green and blue show the same absorption as the solution. The chloride in solution gives the same absorption as the chrom-alums,—transmitting, however, slightly more light for the same quantity of chromium. The hot solution also shows the same changes, but with this difference that colour and absorption phenomena are almost entirely recovered on cooling. The nitrate (solution of chromic hydroxide in nitric acid) agrees with chrom-alum, but transmits more light. Red crystals of potassic chromic oxalate only transmit the red with an absorption band slightly less refrangible than B ( $\lambda=6867$ ). The blue salt has the absorption band at a wave-length of 7040 and transmits part of the light in the green and blue. The solutions of the salts show the same absorption as the crystals, with the position of the absorption band apparently unchanged. The warm solutions absorb more than the cold ones. The oxalate of chromium gives an absorption band of 6910 to 6860 and transmits the green and blue more freely than the double salt. The tartrate only shows the absorption band in the red very weakly and absorbs more red than the previously mentioned solutions. The acetate transmits more yellow than the other salts and has some broad absorption bands near a wave-length of 7170. When the solution is heated it becomes green, absorbing the red more than when cold, but leaving the green and blue absorption unchanged. The absorption phenomena shown by uranium salts are more complicated than those of the chromium salts, but they are at the same time more characteristic, as the spectra are more definitely broken up into bands. According to Vogel, the uranic and uranous salts behave differently (*Praktische Spectral-Analyse*, p. 247), but a more careful investigation is desirable. Sorby finds that a mixture of zirconium and uranium dissolved in a borax bead shows characteristic bands, which are visible neither with uranium nor with zirconium alone.

There is little to be said as regards the remaining groups of metals (tin, antimony, gold). Their spectra are best obtained by taking the spark from metallic electrodes or by volatilization in the voltaic arc.

#### Influence of Temperature and Pressure on Spectra of Gases.

If the spectrum of an element is examined under different conditions of temperature or pressure, it is often found to differ considerably. The change may be small—that is to say, the lines or bands may only show a different distribution of relative intensity—or it may be so large that no relationship at all can be discovered between the spectra. It has been pointed out by Kirchhoff that a change in the thickness of the luminous layer may produce a change in the appearance of the spectrum, and Zöllner and Wüller have endeavoured to explain in this way a number of important variations of spectra. But their explanation does not stand the test of close examination. The thickness of layer cannot be neglected in the discussion of solar and stellar spectra, or in the comparison of absorption spectra of liquids; but none of the phenomena which we shall notice here are affected by it.

**Widening of Lines.**—The lines of a spectrum are found to widen under certain conditions, and, although probably all spectra are subject to this change, some are much more affected by it than