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 (that is, 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 nebnlæ. 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).