Problems in the Variability of Spectra.¹

By Prof. THOMAS R. MERTON, F.R.S.

T has been known for many years that the radiations which an element emits in the state of a luminous gas are not invariable but depend on the presence of other elements, the manner in which the substance is excited to luminosity, and other circumstances. It was recognised in some of the earliest investigations that many band spectra were to be associated with compounds and that a spectrum might be due partly to such compounds and partly to uncombined atoms. Thus, for example, if strontium chloride is introduced into the flame of the bunsen burner we find lines associated with the element, bands due to strontium oxide, and also bands due to the chloride, and when strontium bromide is substituted for the chloride the spectrum is the same as regards the lines due to the element and the oxide bands, but bands peculiar to the bromide are found to have replaced those due to the chloride.

Minute quantities of substances can sometimes be detected by means of these characteristic bands due to compounds, a familiar example being the blue flame which is seen when common salt is thrown onto a coal fire and is due to the copper chloride formed from the chlorine in the common salt, and the minute trace of copper which is present in the coal. A number of different elements are present in most flames, and the reactions which occur are probably very complex. In gases contained in vacuum tubes which are excited to luminosity by electrical discharges it is possible to work with pure substances, and a discussion of the spectra observed is simpler.

In the case of gases in vacuum tubes the spectrum sometimes consists of bands, and the band spectrum from the negative pole may be different from that seen in the positive column. Thus nitrogen, when excited by uncondensed discharges, shows in the visible regions two band spectra, one known as the positive band spectrum, which appears in the capillary of a vacuum tube of the conventional type, and the negative band spectrum, found in the neighbourhood of the cathode, which constitutes an important part of the spectrum of the aurora.

Both these band spectra, and indeed all band spectra, are generally attributed to molecules rather than atoms. but if a condensed discharge is passed through nitrogen the spark spectrum associated with the nitrogen atom is obtained, and this is capable of further modification when discharges of great intensity are employed. The action of the condensed discharge is almost certainly due to the greatly increased current density which obtains during the very brief periods while the discharge is passing. Its first effect is to break up the molecules into atoms, and the further stages brought about by an increase in the intensity of the discharge are generally supposed to be due to the removal of successive electrons from the atoms. There are other methods by which the current density can be increased with similar changes in the spectrum; the effect of an increase in the current density is to increase the number of charged particles in a given volume of the ¹ From a discourse delivered at the Royal Institution on Friday, March 10.

gas, with the result that a large number of the radiating atoms are subjected to intense electric fields due to neighbouring charged particles.

Similar results are observed in the spectra associated with carbon. There are at least six spectra due to compounds of carbon with hydrogen, oxygen and nitrogen, and special experimental conditions are necessary for the production of some of these spectra. In addition to these band spectra carbon shows line spectra, and with the most intense discharges which can be employed in the laboratory a number of new lines appear which are also found in the spectra of the hottest type of stars, known as the Class O, or Wolf-Rayet stars.

All these changes can be reasonably accounted for, but there are a number of other changes which are more difficult to explain. For many reasons the spectrum of hydrogen is of particular interest, because the atom of hydrogen is the simplest known atom and is supposed to consist of a positive nucleus and a single electron. There are two spectra associated with hydrogen, one of which, the Balmer series, is found in almost all celestial spectra and also in vacuum tubes in the laboratory unless the most rigorous precautions are taken to exclude all traces of hydrogen. The explanation of the origin of this spectrum has been one of the most striking successes of the quantum theory of spectra developed by Bohr and by Sommerfeld. The other spectrum of hydrogen, known as the secondary spectrum, consists of an enormous number of lines and differs in its mode of production from the Balmer series in that the secondary spectrum is characteristic of pure hydrogen. In the purest hydrogen obtainable the secondary spectrum may be as bright as the Balmer series, but if the smallest trace of impurity is present the Balmer series gains in intensity and the secondary spectrum becomes very much weaker. In a vacuum tube containing water vapour the lines of the Balmer series are extremely intense whilst those of the secondary spectrum are relatively very faint. The investigations of Michelson and Lord Rayleigh, and of Buisson and Fabry have shown that under certain conditions the masses of the atoms or molecules from which the spectrum originates may be deduced from a knowledge of the widths of the spectrum lines, and recent investigations, in which the widths of the lines of the secondary spectrum of hydrogen have been measured to a high degree of precision, have shown that the secondary spectrum is to be referred to the hydrogen molecule.

The presence of impurities in vacuum tubes containing hydrogen not only enhances the lines of the Balmer series but also brings about changes in the relative intensities of the Balmer lines themselves. Some of these changes are very striking, but there are other variations of a more subtle kind which are only discovered when accurate quantitative measurements are made of the relative intensities of the lines. A most striking effect is observed when a relatively large quantity of helium is admitted to a vacuum tube containing hydrogen. Under these conditions the

NO. 2738, VOL. 109]

relative intensities of some of the lines of the secondary spectrum alter in a surprising manner, some of the lines being greatly enhanced whilst others become very weak.

From a theoretical point of view the spectrum of helium is second in importance only to that of hydrogen. The lines of helium are prominent in the spectrum of the chromosphere of the sun and of many stars, and their relative intensity varies under different conditions of excitation in the laboratory and in different celestial spectra. There are six chief series of lines in the spectrum of helium, three of which are usually referred to as the "helium" and three as the "parhelium" series. The helium series are the stronger in vacuum tubes containing the gas at pressures exceeding a few millimetres, whilst at very low pressures the parhelium series are predominant. Since the chief visible line of the helium series is yellow and that of the parhelium series green, the colour of the discharge is changed from yellow to green when the pressure is reduced.

There is another spectrum associated with helium which is analogous to the secondary spectrum of hydrogen in that it appears with any considerable intensity only when the gas is exceedingly pure. This spectrum is known as the band spectrum of helium, and its occurrence in a gas which is known to be incapable of forming molecules in the chemical sense of the word is very remarkable, in view of the fact that band spectra are generally attributed to molecules. It may perhaps be suspected that there is some temporary association of atoms during the passage of the electric discharge which cannot be referred to as a molecule in the chemical sense of the word. Prof. A. Fowler has shown that the arrangement of the heads of the bands in this spectrum resembles that found in series of lines which are due to atoms, though the arrangement of the lines which constitute each band is of the type usually found in band spectra.

When powerful condensed discharges are passed through helium a spark spectrum is developed. Two series in this spectrum are known as the 4686 and the T Puppis series, and their discovery by Prof. Fowler has led to some of the most important developments of theoretical spectroscopy. These spark lines of helium are found in the nebulæ and early type stars, and are attributed to helium atoms which have lost an electron.

The energy required to produce spark spectra varies widely with the nature of the gas under investigation, and for elements of the same chemical group is, as a rule, smaller the greater the atomic weight of the element. Thus in the case of helium powerful discharges are required for the production of the spark spectrum and the lines of the arc series are always bright. In the case of argon a much less intense discharge is required to produce the spark lines, and with very powerful discharges the arc lines disappear almost entirely from the spectrum. In addition to the production of these spark spectra one of the effects of powerful condensed discharges is to alter the relative intensities of the arc lines. Generally speaking, the effect of an increase of energy on a particular series of lines is to enhance relatively the more refrangible members of the series, but the effect varies in degree for different series. Experiments of this kind enable us to imitate to some extent in the laboratory the distribution of intensity amongst the lines which is found in the nebular and stellar spectra.

It will be seen that whilst many variations in spectra can be referred to different compounds, to molecules, and to uncombined atoms in successive stages of ionisation, there are a number of other changes for which there is at present no obvious theoretical explanation. The possibility of some specific influence of one gas on the spectrum of another must now be recognised apart from the formation of chemical compounds, which, in the action of helium on the spectrum of hydrogen, for example, appears to be excluded. There is also other evidence, based on a study of the broadening of spectrum lines, of a specific action on neighbouring atoms. We are still awaiting a satisfactory theoretical explanation of phenomena of this kind, though it is now forty years since what is perhaps the first known example, the action of sodium on the absorption spectrum of magnesium vapour, was observed by Prof. Liveing and Sir James Dewar at the Royal Institution.

Mathematics and Public Opinion.

PERHAPS few well-known mathematicians have escaped an experience which would be amusing if it were not so exasperating. Mr. Brown (let us say) is introduced to Prof. Smith, who teaches mathematics at a provincial college. After the usual expression of pleasure at the introduction, Brown generally adds "Of course, although I haven't had the pleasure of meeting you before, I know you well by reputation." Then, without so much as pausing to take breath, he proceeds to explain that he was always a duffer in "maths" at school, and that he has now forgotten everything about the subject they tried to teach him as a boy. Now Brown doesn't act in this way to every celebrity. If introduced to Dr. Lasker, and unaware that he is a distinguished mathematician, he does not seize the first opportunity of telling him that, although he occasionally plays draughts with his wife in the evening, chess was always beyond him,

and he could not remember the simplest openings. Still less does he act in this way if his new acquaintance is a sportsman or an epicure. Moreover, in making his lamentable confession, Brown shows no sign of regret or humiliation; on the contrary, a sort of satisfied look steals over his face, suggesting that he is glad to be free once for all from the study of such a repulsive and useless subject. England is perhaps the only country where such an occurrence is fairly frequent; and this fact suggests some very unpleasant reflections.

One thing clear from Brown's attitude is that he evidently fears lest Smith should introduce some mathematical topic during the conversation. Of course this is the thing Smith is most unlikely to do. If this were all, it would be as harmless as the caricatures of professors and policemen which we see on the stage. But there is a very serious additional

NO. 2738, VOL. 109]