been made use of by Becquerel in his investigations of infra-red radiations.

15. *Relationship between the Spectrum of an Element and that of its Compounds.—*In the present state of our knowledge we cannot trace any definite relationship between the spectrum of a compound body and that of its elements, and it does not even seem certain that such a relationship exists, but there is often a similarity between different compounds of the same element. The spectra, for instance, of the oxides and haloid salts of the alkaline earths show great resemblance to each other, the bands being similar and similarly placed. As the atomic weight of the haloid increases the spectrum is displaced towards the red.

It is in the case of the absorption spectra of liquids that we can most often discover some connexion between vibrations of a complex system and that of the simpler systems which form the complex. The most typical case in this respect is the effect of a solvent on thé absorption spectrum of a solution. A. Kundt,@@1 who initiated this line of investigation, came to the conclusion that the absorption spectra of certain organic substances like cyanin and fuchsin were displaced towards the red by the solvent, and that the displacement was the greater the greater the disper- sive power of the solvent. This law cannot be maintained in its generality, but nevertheless highly dispersive substances like carbon bisulphide are always found to produce a greater shift than liquids of smaller dispersion like water and alcohol. In these cases the solvent seems to act like an addition to the mass of the vibrating system, the quasi-elastic forces remaining the same.

Dr J. H. Gladstone,@@2 at an early period of spectroscopy, 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 mentioned as an important exception the case of ferric ferrocyanide, which, when dissolved in oxalic acid, transmits the rays in great abun- dancc, though the same rays be absorbed both by ferrocyanides 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 ammonium, as well as the bichromates of potassium and ammonium, 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 consider the purity of the acid sufficiently proved to allow him to draw any certain conclusions from this observation.

In many of these cases the observed facts might perhaps be explained by dissociation, the undissociated compound pro- ducing no marked effect on the spectra. In 1872 W. N. Hartley and A. K. Huntingdon examined by photographic methods the absorption spectra of a great number of organic compounds. The normal alcohols were found to be transparent to the ultra­violet 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 deriva- tives 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. Subsequently@@3 he subjected the ultra-violet absorption of the alkaloids to a careful

investigation, and 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.”

We can only briefly refer to an important investigation of Sir William Abney and Colonel E. R. Festing, who examined the infra-red absorption of a number of substances. We may quote one of the principal conclusions at which they arrived:—

“ 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 700 and 1000. Certain radicals have a distinctive absorρ- tion about 700 together with others about 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 74o, 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 nitrobenzene 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 ρres- ence of chlorine or bromine or iodine in a compound is at present undecided, and it may be well 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 cobalt and didymium salts also offer many striking examples of minor changes produced in spectra by combination and solution. (A. S.\*)

*Apparatus.—*Spectroscopes may be divided into two classes: prism spectroscopes, with angular or direct vision, and grating spectroscopes; the former acting by refraction (*q.v*.), the latter by diffraction or interference. Angular prism spectroscopes are the commonest. Such an instrument consists of a triangular prism set with its refracting edge vertical on a rigid platform attached to a massive stand. The prism may be made of a dense flint glass or of quartz if the ultra-violet is to be explored, or it may be hollow and filled with carbon bisulphide, α-bromnaphthalene or other suitable liquid. Liquid prisms, however, suffer from the fact that any change of temperature involves a change in the refractive index of the prism. The stand carries three tubes: the collimator, observing telescope and scale telescope. The colli­mator has a vertical slit at its outer end, the width of which may be regulated by a micrometer screw; in some instruments one half of the slit is covered by a small total reflection prism which permits the examination of two spectra simultaneously. At the other end of the collimator there is a condensing lens for bringing the rays into parallelism. The observing telescope is of the ordinary terrestrial form. The scale telescope contains a graduated scale which is illuminated by a small burner; the scale is viewed by reflection from the prism face opposite the first refracting face. The power may be increased, but with a diminution of intensity, by using a train of prisms. Steinheil made an instrument of four prisms, each of which had, however, to be set in the position of minimum deviation by trial. In Browning’s form the setting is automatic. The dispersion may be further increased by causing the rays to pass more than once through the prism or prisms. Thus, by means of a system of reflecting prisms, Hilger passed the dispersed rays six times through one prism, and, by similar means, Browning passed the rays first through the upper part of a train and then back through the lower part. Compound prisms are also employed. Rutherfurd devised one made of flint glass with two crown glass compensating prisms; whilst Thallon employed a hollow prism containing carbon bisulphide also compensated by flint glass prisms. In direct vision spectroscopes the refracting prisms and slit are in the observing

*@@@1 Wied. Ann.* (1878), 4, p. 34.

*@@@2 Phil. Mag.* (1857), 14, p. 418.

*@@@3 Phil. Trans.* (1885), pt. ii.