|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Zine Triplets. | | | Calcium Triplets. | | |
| A. | B. | C. | A. | B. | C. |
| 2992 | 37 | 19 | 2245 | 10 | 5 |
| 3257 | 38 | 20 | 2517 | 11 | 5 |
| 3571 | 40 | 18 | 2744 | 10 | 6 |
| 3686 | 40 | 19 | 2868 | 10 | 6 |
| 3833 | 40 | 18 | 2977 | 10 | 5 |
| 3975 | 38 | 19 | 3044 | 11 | G |
| 4057 | 41 | 17 | 3101 | 11 | 5 |
|  |  |  | 3174 | 10 | 5 |
|  |  |  | 3208 | 10 | .. |

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Magnesium Triplets. | | | | | |
| Cornu. | | | Hartley and Adeney. | | |
| A. | B. | C. | A. | B. | C. |
| 1929·3@@1 | 4∙2 | 1∙9 | 2605·6 | 3∙9 | 2∙0 |
| 2605∙8 | 4·1 | 1·7 | 2997∙4 | 4·0 | 2∙4 |
| 2999∙2 | 3∙8 | 2·7 | 3229∙8 | 4∙5 | 2∙l |
| 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

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 recently@@4 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 Festing@@5 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

@@@1 Measured by Thalén.

@@@2 Measured by Liveing and Dewar.

@@@3 *Phil. Mαg.,* xiv. p. 418 (1857).

@@@4 Phil. Trans., part ii. (1885).

@@@5 Phil. Trans., iii. p. 887 (1881).