tion of carbonate of lime in sea-water, and on chemical changes in muds, etc.

Murray's last oceanographic expedition was a four-months' cruise in 1910 in the North Atlantic with Dr. Hjort in the *Michael Sars* when in his seventieth year. He was killed in a motor accident in March, 1914.

There is, no doubt, other Edinburgh work in connection with oceanography, such as that of the Fishery Board for Scotland, which should be mentioned, and other names of those who are still happily with us and at work, such as the indefatigable arctic and antarctic explorer, Dr. W. S.

Bruce, the leader of the *Scotia* expedition, and the founder of the Edinburgh Oceanographic Laboratory; but in this brief record of the past it has been possible only to deal simply with the historically connected work of the three great pioneers of the nineteenth century—Edward Forbes, the dredger of the shallow waters; Wyville Thomson, the explorer of the deep seas; and John Murray, who may be regarded as the founder of modern post-*Challenger* oceanography —in demonstrating the effect of Edinburgh men and ideas and work in advancing our knowledge of the science of the sea.

Absorption Spectra.

By Prof. E. C. C. Baly, C.B.E., F.R.S.

WITHOUT doubt the study of absorption spectra, more particularly those of organic compounds, has given rise to great interest, owing to the possible connection between absorption and chemical constitution. The work of Hartley, Dobbie, and others showed that in certain cases it was possible to determine the constitution of substances from observations of their absorption spectra. It is not surprising that, as the result of this work, a school of thought was founded on the basis of a direct correlation between the atomic structure of a molecule and its absorption spectrum. On the other hand, Hantzsch, who in a great number of papers has maintained the opinion that the absorption curve is an index to constitution, has travelled far beyond the original point of view. He found that changes in the absorption spectrum of a compound are observed when no change is possible in its primary valency structure, and in interpreting his results Hantzsch has invoked the aid of the secondary valencies of the atoms.

It is now known beyond any question of doubt that one and the same substance under different conditions can show different absorption spectra in the visible and ultra-violet. It is also known that, whilst a change in the primary structure of the molecule might possibly be accepted as an explanation of this in a few instances, the large majority of these variations in absorption cannot in any way be thus accounted for. Attempts were also made to interpret absorption spectra by oscillating linkages, such, for instance, as the equilibrium between the enolic and ketonic forms of ethyl acetoacetate or the oscillation that may be accepted as taking place within the benzene ring. This suggestion was very soon negatived when it was found that many substances in which no such oscillation is taking place exhibit well-marked absorption bands. For example, it might be possible to explain the ultra-violet absorption band of acetone by attributing it to the equilibrium CH_3—CO—CH_3⇌CH_3—$C(OH)$=CH_2; but hexamethylacetone, in which no such change is possible, exhibits the same absorption band as acetone.

The only other possible variable from the point of view of the chemist is the secondary valency, and this has been advanced by Hantzsch and others as the explanation of absorption in the visible and ultra-violet, the well-established differences in absorption being accounted for by different distributions of the secondary valencies. No physical explanation, however, has been offered of the assumed correlation between the secondary valency and absorptive power, a matter of great importance, since a theory cannot hold good unless some physical basis can be found for the phenomenon of the absorption of radiant energy.

In all this work the study of absorption spectra of organic compounds has been restricted to the visible and ultra-violet regions of the spectrum, and, indeed, only to that portion of the ultra-violet which is transmitted by a quartz spectrograph working in air. This is unfortunate, since the absorption bands exhibited by the compounds in that vast region known as the infra-red and in the extreme ultra-violet are ignored. Then, again, many inorganic substances show absorption bands which are exactly similar to those on which Hantzsch founds his valency formulæ of organic compounds, and obviously an identical explanation must be found for each class of compound. It is not too much to say that all the above theories have been based on insufficient data.

If the complete system of absorption bands shown by a compound over the whole spectrum is examined, it is found that the central frequency—namely, the frequency for which the absorptive power is the greatest—in any visible or ultra-violet band is always an exact multiple of the frequency of an important absorption band in the short-wave infra-red. Then, again, this infra-red frequency is itself an exact multiple of the central frequencies of well-marked bands in the long-wave infra-red. This integral relationship is of great importance, since it can readily be proved that the central frequencies are truly characteristic of the molecules, the subsidiary frequencies associated with them being probably due to the atoms and groups of atoms composing the molecules. Again, the changes in absorption ex-

hibited by one and the same substance under different conditions are restricted to the visible and ultra-violet, the fundamental short-wave infra-red frequency remaining the same.

There is one point about absorption spectra which has been strangely neglected in all theories —namely, the ultimate destination of the energy that is absorbed. It is obvious that when a substance exhibits an absorption band energy is being absorbed, and if no photochemical change is thereby produced the whole of the absorbed energy is again radiated in the infra-red. The integral relationship between the frequencies is in harmony with an energy quantum theory, since, if the quantum of energy is the product of the frequency into a constant, one single quantum absorbed at one frequency can be radiated as an exact number of quanta at a smaller frequency if the first frequency is an integral multiple of the second.

The usually accepted basis of all theories of absorption is the assumption that a molecule is characterised by certain definite frequencies or free periods of vibration, and that absorption of energy takes place as the result of these. There are, however, certain objections to this assumption, such, for instance, as the fact that the frequencies of a molecule are far larger than those of the atoms which it contains. These objections can at once be met by making an entirely different assumption—namely, that a molecule is characterised by an amount of energy which determines its frequency. The cardinal assumption may be made that each elementary atom is characterised by a fixed amount of energy or elementary quantum which is associated with a definite physical process such as the shift of an electron from one stationary orbit to another. These elementary quanta are related together in that they are multiples of a fundamental unit, possibly the elementary quantum of the hydrogen atom. On this hypothesis an atom can only absorb or radiate one or more of its elementary quanta.

It may readily be shown, on the grounds that when two or more atoms combine they each lose an equal amount of energy, that the resulting molecule is endowed with a molecular quantum which is a multiple of the least common integral multiple of the elementary atomic quanta of its atoms. If the physical process in the atom occupies a definite time, assumed the same for all atoms, then all atoms and molecules will have the power of absorbing or radiating energy of a definite frequency. In all probability the molecular quantum establishes the fundamental molecular frequency in the short-wave infra-red of which the visible and ultra-violet frequencies are exact multiples. On this theory, therefore, a molecule, like an atom, can lose or gain energy as a whole only in terms of its molecular quantum.

There is little doubt that the origin of the affinity between atoms which causes them to combine is to be found in their electromagnetic-force fields, and when the combination has taken place the external faces of the atoms must come into play. These cannot exist in any molecule without

mutual influence, and, indeed, the force lines must condense with the escape of energy to form a molecular-force field on which the reactivity of the molecule will depend. Obviously, this energy loss is a process in which the molecule as a whole takes part, and consequently the energy will be lost in molecular quanta. A freshly synthesised molecule, therefore, must pass into one of a number of possible phases according to the number of quanta that have been lost. It is a matter of simple proof that when a freshly synthesised molecule loses x molecular quanta in this way it becomes endowed with a new quantum which is $x + 1$ times the molecular quantum. The molecular phase, therefore, will exhibit its characteristic frequency together with a phase frequency which is an integral multiple of the molecular frequency.

The total number of molecular quanta that are evolved in the force-field condensation will depend on the nature of the external fields of the atoms. The more nearly balanced these are, the greater the number of molecular quanta that will be lost. The great majority of organic compounds have a molecular frequency of the order of 1×10^{14}, so that if four quanta are lost in the force-field condensation, the phase frequency will be 5×10^{14}, which is situated in the red; but if 10 quanta are lost, the phase frequency will be 1.1×10^{15}, which is in the ultra-violet. Again, if 17 quanta are lost, the phase frequency will be 1.8×10^{15}, which is situated in the extreme ultra-violet beyond the limit of the quartz spectrograph.

It is perfectly possible to change the phase in which a molecule exists by supplying to it or taking from it energy in an amount equal to one or more molecular quanta. This can be done in many cases by use of a suitable solvent, or even by a change of physical state, such as from liquid to gas. The change in phase is indicated by a change in the position of the absorption band in the visible or ultra-violet, and this phenomenon is frequently observed when different solvents are used. The change of molecular phase with change in physical state is well instanced by piperidine and pyridine. Liquid piperidine is diactinic to all the visible and ultra-violet rays transmitted by a quartz spectrograph, because its absorption band lies in the very extreme ultra-violet. Piperidine vapour, on the other hand, exhibits a strong absorption band in the near ultra-violet. The absorption bands of liquid and gaseous pyridine are also quite different.

The molecular-phase hypothesis clearly has a quantitative basis, since the molecular quantum evolved in the phase change is given in ergs by the product of the frequency into the time constant 6.57×10^{-27}. It applies, moreover, to inorganic substances as well as to organic, and of this a typical instance is given by sulphur. It is now accepted that the allotropes of sulphur are equilibrium mixtures of four different molecular species of sulphur, S_λ, S_π, S_ϕ, S_μ, and there is little doubt that these are in reality four molecular phases, for they exhibit absorption frequencies which are multiples of the fundamental molecular

frequency of sulphur. It is well known, too, that coloured forms can be obtained of many simple salts which normally are colourless, such as sodium chloride, by supplying energy to them.

The phenomena of fluorescence and phosphorescence are also due to molecular phases. If a molecule absorbs a phase quantum which, for instance, is ten times the molecular quantum, this energy can be radiated in two ways. It may either be radiated as 10 molecular quanta, when the fluorescence will be in the infra-red, or it may be radiated partly as one quantum characteristic of a lower phase—say, that phase with frequency five times the molecular frequency—and partly as molecular quanta. In the second case the fluorescence will be visible.

Since the essential characteristic of the phases of a molecule from the chemical point of view is their force fields, the variation in which causes their different reactivities, it might be argued that this theory is only a re-statement of the secondary valency hypothesis. Such an argument would not, however, be sound, for the secondary valency hypothesis does not explain absorption. At best it only succeeds in showing that different distributions of secondary valency can generally be written where the same molecule has been found to exhibit different absorption under different conditions. The present theory establishes the existence of different phases of any inorganic or organic molecule, each of which has its own energy content, its own reactivity, its own frequency and power of absorbing light. The theory attempts to correlate all the phenomena of absorption and to place them on a quantitative basis, and in this attempt it would seem to meet with some success. Although in this article we are not concerned with the chemical aspect of the differences in the force fields of the phases, it may also be claimed that this theory offers a quantitative explanation of the phenomena of reaction and reactivity.

Artificial Production of Rain.

By Dr. Harold Jeffreys.

IN an article in the *Times* of October 17 an account is given of the achievements of Mr. Charles M. Hatfield in producing rain. The method used is not described in any detail. A tank filled with certain unspecified "chemicals" was exposed at a height of 25 ft. above the ground, and it is claimed that this had the effect of producing 8 in. of rain in three months at Medicine Hat, 22 miles away. The theory of the method is that the apparatus draws clouds from other parts to the Medicine Hat district and causes them to precipitate their moisture there. No direct observations of the motions of clouds are mentioned in confirmation of this theory, though they should not have been difficult to obtain.

The official raingauge at Medicine Hat during May, June, and July, the period of the contract, recorded 4·8 in., which was 1·3 in. below the normal for the station for those months. Further comment on the success of the experiments is unnecessary.

The financial side of Mr. Hatfield's contract with the United States Agricultural Association of Medicine Hat is interesting, for the association was apparently prepared to pay Mr. Hatfield as if 8 in. of rain had fallen. Still more interesting is the fact that he was promised 4000 dollars for 4 in., and 6000 dollars for 6 in. Since the normal rainfall is 6·1 in., Mr. Hatfield would have been much more likely than not to make a substantial profit even if he had done nothing at all.

It may be mentioned that at Calgary, Alberta, the rainfall was 3·0 in. below normal; at Edmonton it was 3·1 in. above; and at Qu'Appelle (Sask.), 300 miles to the east, it was 3·85 in. above normal.

It is also stated that at Los Angeles, in the first four months of 1905, Mr. Hatfield guaranteed 18 in. of rain, and that his own raingauge showed 29·49 in. If this is correct the rainfall must have been extremely local, for the official raingauge at Los Angeles in those months showed only 14·98 in. Still, this was 4·4 in. above normal. At San Diego, however, which is 200 miles away, the excess was 4·6 in., and it appears likely that the abnormality at both stations was due to more widespread causes than Mr. Hatfield's chemicals.

Attempts have on many previous occasions been made to produce rain by artificial means, but the results have been uniformly unsuccessful. The reason is not difficult to see. To make the water vapour in the air condense it is necessary to cool the air in some way to a temperature below the dew point. This may be done in two ways. One may cool the air directly, for instance by the evaporation of liquid carbon dioxide or liquid air. This certainly would produce a little condensation; the fatal objection to it is that it would be thousands of times cheaper to distil sea water. The other method is to raise the air. The pressure decreases with height, and to reduce the pressure on a particular mass of air is known to cool it. The difficulty is to raise it enough. To produce an inch of rain over an area of 100 square miles requires the condensation of 6 million tons of vapour, and to achieve this some hundreds of millions of tons of air must be lifted up. The distance it must be raised depends on how nearly saturated it was originally, but it could not be less than a kilometre in ordinary fine weather conditions. We have no source of energy at our command great enough to achieve this.

It is often suggested that rain may be produced