Chemiluminescence.¹

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IN attempting to make the subject matter of this discourse as experimental as possible, it will be impossible to delve in great detail into the molecular mechanism of the reactions. This, I think, is as well, because many of the reactions which should be shown on account of their great beauty are certainly extremely complicated and have not, in fact, been subjected to any but a very superficial examination.

Chemiluminescence may be regarded as the counterpart of photochemical processes. By the absorption of light of suitable frequencies, atoms and molecules may be raised to states of higher initial energy. These excited entities may now undergo a series of changes, the nature of which will depend on a variety of circumstances. They may liberate their absorbed energy in the form of fluorescent light, impart part or all of their energy to a neighbour of another species by a collision, become converted into a metastable more permanent and energy-rich molecule which may afterward revert to the normal form, or suffer some species of chemical reaction such as ionisation, dissociation, or combination.

By suitable modification of conditions one can affect the velocities of chemical reactions over relatively wide ranges, and it is found that in many strongly exothermic reactions there exists a narrow range of relatively high velocities which is chemiluminescent. Closer examination indicates that practically all these reactions are complex in that they are accompanied not only by the emission of radiation localised in some portion of the spectrum but also by a rise in temperature. It is by a study of the chemiluminescent portion of such composite reactions that we may hope to gain a further insight into the molecular mechanism and the operation of the process of chemical activation.

We may with some degree of assurance assume that chemiluminescence is in many cases the result of liberation of chemical energy in a form similar to that of fluorescent energy, and we have noted that fluorescence is the result of decay of a number of excited molecules, the excitation being produced in this case by the absorption of radiation. Thus conditions suitable for chemiluminescence result in reactions in which large numbers of excited molecules are produced by chemical reaction, under conditions such that at least a fraction of the excited molecules can revert to the normal form with the emission of radiation. Excluding thermally accelerated exothermic reactions, a large group of auto accelerating reactions exhibit chemiluminescence; these are usually designated as branching chain reactions, and we shall observe that there are several hypotheses as to the nature of such reactions and at least two distinct light-producing processes.

A typical reaction of this type is the oxidation of phosphorus—one of the oldest chemiluminescent reactions observed with a definite substance, although the chemiluminescence of fireflies, decay-

ing wood and certain bacteria and fish have long been commented on and were formerly attributed to the action of vital forces. The name phosphorus arose from a confusion of chemiluminescence with the phosphorescence of the impure barium sulphide, the so-called lapis Bologniensis. We may symbolise the fact that the reactions proceed in branching chains in a number of ways: thus, denoting the reactants by A_2 and B_2 and the molecules in the excited state by A'_2 we might postulate as the mechanism

In both cases the conditions that one elementary reaction shall produce at least two reacting molecules so as to effect an auto accelerated reaction are fulfilled, but whilst in the first the chemiluminescence is imagined to result from the return of the excited species AB' or A'_2 to the normal, in the second it is supposed to take place through some type of atomic combination; for example, $2A \rightarrow A_2$ or $A + B \rightarrow AB$, a mechanism which has been more fully investigated in a series of reactions which will be discussed later.

We may note that, in addition to these types of chain mechanism, there exists a third in which it is imagined that a certain number of reaction centres are formed, by some identified as ions; around these reaction centres reaction takes place and more reaction centres are formed. As a hypothetical case we might imagine that in a hydrogen chlorine mixture a positive ion is formed, and around this ion a number of hydrogen and chlorine molecules are held by electrostatic forces. On neutralisation of the ion, the energy set free effects the combination of the small group of molecules around the ion and chemiluminescence and the formation of a few more ions result.

That in the oxidation of phosphorus, sulphur, and probably many other substances, the chemiluminescence is the result of some such type of chain mechanism can scarcely be doubted, but it is difficult in fact to state to which of these three possible types any one reaction definitely belongs. It is perhaps significant that in the oxidation of phosphorus a number of the lines in the complex band spectrum of the emitted light are identical with those of ionised oxygen. A typical phenomenon observable in the chain or cluster reactions is that of inhibition by small quantities of inhibitors. We may note the ease with which inhibitors such as benzene and ether inhibit the glow of phosphorus, a confirmation of the nature of the chemical process at work. Many other vapours exhibit chemiluminescence on oxidation, a fact noted by Sir Humphry Davy; thus the vapours of ether and carbon disulphide can readily be caused to undergo cold luminous combustion. Under more restricted

¹ From a lecture, with experiments, delivered at the Royal Institution on Friday, Feb. 15.

conditions, the union of acetylene and chlorine and the oxidation of the hydrocarbons can be made to exhibit chemiluminescence, and although in these reactions the thermal changes are relatively large, yet since the light emitted is definitely chemiluminescent, it seems almost certain that, contrary to the views of several investigators in these reactions, one cannot be dealing exclusively with thermally accelerated as opposed to branching chain or cluster accelerated reactions; excited molecules, atoms, or reactive clusters must be taking part in the reaction.

Far more complicated, but equally beautiful, are a number of chemiluminescent reactions taking place in solution. The well-known Wedekind reaction, the interaction of chlorpicrin and phenyl magnesium iodide exhibiting a green chemiluminescence, requires the use of a draught chamber, but the cold oxidation of pyrogallol formaldehyde mixture exhibiting an orange-red light, due to Trautz and Schorigin, blue luminescence in the oxidation of 3-aminophthalic hydrazide and the green of triphenyl glyoxalin (Lophin) are all brilliant and readily demonstrated. These reactions are characterised by a high temperature coefficient—some 2.3 for a rise of 10° C.—an indication of the chemical origin of the light-emitting system.

It is somewhat remarkable that few people have observed the beautiful chemiluminescence exhibited by the interaction of chlorine or chromyl chloride with ammonia, although I suppose the former reaction is demonstrated annually in at least one of the classes in every school where chemistry is taught.

Sir James Dewar noted a chemiluminescence when ozone is brought into contact with organic matter. Such chemiluminescence is particularly marked in the oxidation of certain dyestuffs both fluorescent and non-fluorescent; we may observe the phenomenon in a brilliant form in the case of alcoholic solution of both eosin and safranin. The chemiluminescent light is not identical with the fluorescent light of these dyes. This reaction may be modified so as to give a very vivid demonstration of the action of inhibitors. By addition of a small quantity of hydroquinone to the alcoholic solution of safranin we note that on exposure to ozone no chemiluminescence results, the dyestuff is not oxidised, but after a minute or two the hydroquinone is completely oxidised and the brilliant green glow of the dyestuff undergoing oxidation spreads over the bulb.

We have already indicated the possible connexion between chemiluminescence and reversed photochemical action, postulating in both cases the generation of an excited molecule formed in the former by chemical and in the latter by radiant processes. This analogy may be pursued somewhat further by a consideration of the mechanism of photochemical sensitisation and its reversal. In cases of photochemical sensitisation, a molecule excited by the absorption of radiation conveys by collision part or all of its energy to a molecule of another species which afterwards undergoes chemical reaction. The beautiful experiments of

Franck and Cario in forming chemically reactive hydrogen by sensitisation with mercury vapour excited by the line $\lambda 2537.4$ A. may be cited as a case of photochemical sensitisation. A similar complementary reaction in chemiluminescence has been observed by Kautsky, who showed that the energy liberated as chemiluminescence in the oxidation of the suboxide of silicon, siloxene, could be transferred to certain dyestuffs causing them to become excited and undergoing fluorescence. Only those dyestuffs such as fluorescein and eosine which are adsorbed by the crystals of the siloxene can be made to fluoresce, an indication that the energy necessary for excitation of the dyestuff molecule must be transmitted by collision from one of the surface molecules of the solid reacting siloxene, which in turn must pass through the stage of an excited molecule during oxidation.

The experiments initiated by Haber and Zisch on the interaction of the alkali metals with halogens and halides have more recently been re-examined by numerous investigators, notably Kondratjew, Ljalikoff, and Polanyi; these all exhibit beautiful chemiluminescent effects. The interaction of sodium and iodine vapour and of potassium and iodine demonstrate the various phenomena to be observed in these reactions, and analysis of the radiation, as well as of the distribution on the tube walls of the salt formed, gives us a clue to the mechanism of the reaction. In the interaction of sodium vapour and iodine we may compute the thermal changes accompanying all the possible reactions.

It is observed that the *D* line only is emitted, corresponding to a chemiluminescent emission of 48.3 cal. Of the four reactions listed above, only two are accompanied with sufficient energy for the liberation of the *D* line, namely, (2) and (3). A further observation that the chemiluminescence possesses in this case a negative temperature coefficient, suggests that only one of these reactions, namely, $\text{Na}_2 + \text{I} = \text{NaI} + \text{Na}$, is responsible for the chemiluminescence observed in the gas phase, and that neither (2) nor (4) takes place in the gas phase except in a reaction more involved than a bimolecular one. The tube walls catalyse both reactions (2) and (4) effectively. The surface catalysed reaction is clearly observed in the union of potassium and iodine, for the reaction (3) above does not occur to an appreciable extent when sodium is replaced by potassium on account of the low concentration of diatomic potassium molecules in the vapour of the element.

The bulk chemiluminescent processes can accordingly be represented as

Chemiluminescent methods may be employed not only to identify as noted above the nature of

the molecular processes involved in a chemical reaction, but also to fix, within certain limits at least, the energy of dissociation of certain gases. Thus, the simple dissociation process,

in reality must be much more complicated in operation than the unimolecular bimolecular dynamic equilibrium postulated by this equation given in the text-books. Whilst the efficiency of collision in causing reaction of complex molecules such as $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ is usually high, that of atomic recombination is very low, and if we regard a pair of normal atoms in close proximity to one another as the extreme case of dissociation, the absence of an electric moment in the system forbids the quantised emission of radiation. Thus reactions such as $2\text{H} \rightarrow \text{H}_2$, $2\text{Br} \rightarrow \text{Br}_2$, only occur in the presence of a third body or a surface, and the energy of combination transmitted to the third body is frequently emitted as chemiluminescence, a phenomenon readily observed with atomic hydrogen. The energy of combination of atomic hydrogen is found to be sufficiently great to excite the OH molecule to emission, but not the mercury line $\lambda 2537 \text{ \AA}$. in mercury atoms; this places the energy of dissociation of hydrogen between 94,000 and 112,000 cal per gram molecule.

Atomic hydrogen, readily prepared by Wood's method, is a convenient source of many chemi-

luminescent experiments. The afterglow of a number of gases, notably oxygen, nitrogen dioxide and nitrogen, when excited by the electric discharge, may all be regarded as chemiluminescent reactions in that the gases possess enhanced chemical reactivity in the glowing state. The glow of nitrogen dioxide and nitric oxide and the afterglow of Lord Rayleigh's active nitrogen are particularly brilliant, but the chemical processes involved are at present obscure. It seems at least definitely established that active nitrogen contains at least two chemically reactive species, both atoms and excited molecules. The cohesion of solid surfaces may be regarded as a species of chemical reaction in the solid state, and several of these reactions are found to be chemiluminescent; although frequently classified as tribo- or crystallo-luminescent reactions, the crystallisation of arsenious oxide and sugar exemplify this class of reaction.

Other quasi-chemical reactions which are luminescent include the fluorescence and phosphorescence excited in various substances, especially in solid solutions, by electron bombardment, some of the effects produced by the bombardment of minerals such as kunzite by high speed electrons being particularly brilliant. Finally, we may observe the chemiluminescence obtained with certain bacteria such as *B. fluorescens* and the reaction between luciferin and luciferase, the basis of biological light.

Obituary.

MR. S. S. BUCKMAN.

THE son of Prof. James Buckman, a well-known botanist and geologist of his day, Sydney Savory Buckman, born in 1860, early followed in his father's footsteps. His attention was particularly directed to the Brachiopoda and Ammonites of the Inferior Oolite, and so early as 1883 he contributed a paper on the former to the *Proceedings of the Dorsetshire Natural History Field Club*. Buckman will, however, be chiefly remembered for his work in connexion with the Ammonites, which he showed could be used as zone fossils for subdividing the Jurassic strata. His study of these was extensive, and a monograph of those from the "Inferior Oolite Series" (never really completed) formed one of the Monographs of the Palaeontographical Society (1887-1907), while he further traced their evolution through the successive strata, and in so doing was led to create a multitude of genera and species far beyond what had hitherto been deemed necessary.

In connexion with all this work and subsidiary to it, Buckman published very many papers and memoirs on the classification of Ammonites and Brachiopods. When his connexion with the Palaeontographical Society was severed, Buckman began in 1909 a work on "Yorkshire Type Ammonites," consisting of photographic figures of the types accompanied by the original descriptions. This was carried on until his eyesight failed six months ago. The geological structure of the Inferior

Oolite also received his attention, and he traced foldings in the beds that in some cases corresponded with those known to exist in the underlying Palaeozoic rocks, thus bearing out Godwin-Austen's principle of the continuity of folding with its economic consequences.

The physical geography of south-western England was the subject of a paper (*Natural Science*, 1899) far too little consulted by later writers, in which Buckman treated of the "Development of Rivers; and particularly the Genesis of the Severn." The capture of the headwaters of the Thames by the Severn has, perhaps, never been better set forth. Buckman's extensive and original work became absorbed to such an extent into contemporary geological thought that few of the younger generation of geologists realise how much they owe to him.

The value of Buckman's labours was recognised by the Geological Society, of which he was elected a fellow in 1882, by the award of the Murchison Fund in 1897, of the Lyell Fund in 1903, and the bestowal of the Lyell Medal in 1913. His researches stimulated many a geologist, and not in England alone, to a more detailed study of the rocks and their fossil contents, and all such he was ever ready to help in the most unselfish way. His death on Feb. 26 last was greatly regretted by all privileged to know him, and his memory will be cherished as one of the kindest of men.