Luminescence

VOLUME XXXV, Part I (January 1939) of the *Transactions of the Faraday Society* contains, for the most part, the proceedings of a general discussion on *Luminescence,* held under the auspices of the Society in September 1938. The subject includes all forms of emission of light by matter either on irradiation with ultra-violet or visible light, or on bombardment with X-rays or cathode rays or accompanying chemical or biochemical reactions. Altogether 28 papers bearing on different aspects of the problem and running over 238 pages are presented and discussed. The symposium has provided a forum for review and discussion of the theoretical and experimental advances made so far in this important branch of spectroscopy and the published proceedings furnish an authoritative and comprehensive reference number, especially as the list of contributors contains names of scientists who have made the subject what it is to-day. The discussion has been divided into three groups, namely, (1) luminescence of liquids and vapours; (2) luminescence of solids; and (3) chemiluminescence.

Luminescence of Liquids and Vapours

Absorption of light by matter leads, in general, to excitation of electrons associated with individual atoms or groups of atoms or radicals, to higher states of energy. This excess electronic energy may be converted to thermal or other forms of energy due to collisions of second kind, or be emitted in the form of energy of *luminescence.* When the emission of light takes place during the period of excitation the phenomenon is termed *fluorescence* and the emission after the exciting source is cut off is termed *phosphorescence.* Both fluorescence and phosphorescence co-exist and are difficult to separate spectroscopically except at very low temperatures. The simplest type of fluorescence which is easy of interpretation is the resonance radiation of mono-atomic gases and vapours. The *fluorescence-efficiency* expressed by the ratio of number of light quanta emitted to that absorbed is great in the case of these gases, provided the vapour pressure is small. The increase of pressure or the introduction of foreign gases results in mutual collisions between the excited atoms and their neighbours, which leads to *quenching* of fluorescence due to loss of energy as chemical or thermal effects. Two papers were presented on the photoluminescence of gases by R. G. W. Norrish, and by Terenin, Vartanian and Neporent, both of which are concerned with the low fluorescence efficiency of polyatomic molecules. In these cases, due to interaction between the vibrational and rotational degrees of freedom with electronic transition, the fluorescence has a banded structure. The diffuseness in certain parts of the spectra and the total disappearance in others have been generally attributed to predissociation; but Norrish points out that these effects may also be due to internal quenching of fluorescence by the internal vibrations of associated groups.

When we pass on to condensed systems, the fluorescence is no longer a rule as in gases but a rare exception. In these cases, most of the absorbed energy is converted to heat or other forms of energy. The general problems relating to the fluorescence of solutions to which E. J. Bowen refers in his introductory paper, are the efficiency of emission, spectral distribution of energy and the depolarisation. Connected with fluorescence-efficiency is the quenching of fluorescence of foreign substances and by surroundings. This problem of quenching has attracted a good deal of attention. Bowen and Norton discuss the quenching of fluorescence in solutions of anthracene dissolved in a number of solvents, at different concentrations and temperature and in the presence of various quenchers. Peter Pringsheim examines some of the explanations offered for the cause of the variation in fluorescence intensity in dye-stuffs and aromatic compounds and deals in particular with the quenching due to increase of concentration. This "concentration quenching" is explained as due to (1) collisions of second kind resulting in loss of absorbed energy as heat, and (2) the formation of non-fluorescing associated molecules. Due to its importance in sensitisation of photographic plates, the paper by Joseph Weiss on *Photosensitised Reactions and the Quenching of Fluorescence in Solution* is of great interest. The discussion following the papers leaves one the impression that the mechanism of quenching of fluorescence in liquids and solutions is far from being fully understood.

Polarisation measurements of fluorescent light in liquids and solids furnish important data leading to conclusions as to the orientation of oscillators responsible for the emission of light with respect to the length of the exciting molecule. The only paper dealing with this question is on the *Polarisation of Fluorescence of Dye-stuffs Dissolved in Meso-phases* by Zocher.

Luminescence of Solids

The scientific and commercial application of the luminescence of solids has, in recent years, given a new impetus to theoretical and experimental studies in the subject. From the theoretical point of view, luminescence in solids has been discussed briefly in an introductory paper by F. H. Spedding and in greater detail by Gurney and Mott, Frederic Seitz, C. J. Milner and N. Riehl. Two distinct types of luminescence in solids exist, namely, of pure solids and of those activated by impurities. But essentially, the fluorescence and phosphorescence in solids are associated with non-ideal crystal lattice, resulting from imperfections or distortions in the lattice brought about by heating or pressure or by the introduction of foreign impurities. Experimental evidence seems to show that the impurity atoms are distributed throughout the bulk of the parent substance. The part played by the imperfections of the lattice on the one hand, and the impurity atoms on the other, in the re-emission of absorbed light is essentially the same. J. T. Randall has shown in his paper on *Some Recent Experiments in Luminescence* that many inorganic solids in the pure state yield fluorescence spectra at very low temperatures. It is possible that in these cases 'interstitial' metal atoms in the lattice like Zn in ZnS., act as luminescent centres just as foreign impurities in ordinary *phosphors*. The questions that present themselves in the case of solids are, (1) what is the mechanism of absorption of energy, and (2) what is the process which results in the emission of light. Riehl believes that the energy is absorbed by the atoms of the bulk material as well as of the impurity and the absorbed energy in units called '*exciton*' wanders over without radiation to the few impurity atoms or '*activators*' and is then re-emitted. The modern theory of semi-conductors and insulators formulated by Brillouin, Wigner and Seitz offers a quantum-mechanical explanation for the process of light-emission by solids and its relation to photo-conductivity. According to this theory, the valence electrons of the component atoms in a crystalline solid exist in energy states associated with the lattice as a whole. The periodic potential field due to these electrons causes the possible transitions of electron energy to be restricted to certain bands or '*zones*' with '*forbidden regions*' lying between them. The function of the impurity atoms or imperfections in the lattice is to introduce additional energy levels in the forbidden region. The absorption of energy by an electron of the lower level leads it to go to a higher level leaving a '*hole*' behind. The excited electron may lose its excess energy as heat radiations without exhibiting any luminiscence or fall back to any of the lower states (stable or meta-stable), but not necessarily to the hole which it left behind, with the emission of radiation (luminescence). By a combination of Pauli Exclusion Principle and Frank-Condon curves, Milner gives a theoretical interpretation of the observed facts about sulphide phosphors and Seitz explains the characteristics of the alkali-halide-thallium phosphors and zinc sulphide phosphors which exhibit photo-conductivity. But the theory is by no means able to explain all the observed facts satisfactorily. Experimental observations which would be helpful for formulating a theory of sulphide phosphors are given by Levy and West in their paper. Expressions for quantum-efficiency of luminescence in solids and the laws of decay of phosphorescence in mono-molecular and bi-molecular reactions are given by Gurney and Mott. Influence of crystallisation upon the intensity and duration of luminescence in certain glasses is dealt with by Maurice Curie and a useful review of the experimental results with luminescence of inorganic solids is given by J. Ewles.

As shown by Spedding in his introductory paper, luminescence of solids yields two classes of spectra, (1) the *continuous* spectra and (2) the discrete or *line* spectra. In the light of the theory given above, if the energy states of the valence electrons are broad, either due to the influence of the neighbouring atoms or due to the thermal agitation of atoms (Debye waves) or the lattice oscillations, the spectra are continuous. Discrete spectra are given when the upper and the lower states are sharp. This condition is secured, among others, in crystals containing the elements of the transition groups and divalent manganese and trivalent chromium ions and in organic compounds containing unsaturated resonating bonds. Lowering temperature simplifies the spectra in all cases and renders the continuous spectra generally sharp. From the papers presented and the discussions, it is clear that there is much scope for further experimental work by employing low temperatures and single crystals. The influence of lattice oscillations and molecular vibrations and rotations on the position and distribution of intensity in the spectra remains to be worked out.

In a very interesting paper on the *Application of Phosphorescence Spectra to the Investigation of the Structure of Solids and Solutions*, R. Tomaschek outlines a new method of investigation of (1) the structure of glasses, (2) the nature of phosphorescent centres, (3) the hyperstructure of crystals and (4) the constitution of liquid solutions. The method consists in embedding ions of Cr, Ni, or Co or the rare earths in solids which otherwise yield continuous spectra and in analysing the resulting line spectra in terms of the energy scheme for the activator. Further development of the method promises to yield valuable information regarding the nature of forces in the solid and the liquid media. The technical importance of investigations in luminescence in solids is shown by papers dealing with fluorescence efficiency of discharge tubes containing neon by Jenkins and Bowtell, with cando-luminescence by Minchin and with the practical application of luminiscent solids for the manufacture of high lumen-efficiency mercury discharge lamps and of decorative signs and for the preparation of luminescent screens for television by T. J. Davies. Developments of commercial value in illumination engineering may be expected to arise out of researches in this direction in the near future.

Chemi-Luminescence

As in the luminescence of solids and liquids, the emission of light accompanying certain chemical reactions is explained as due to the production of excited ions, ionic complexes, or radicals during intermediate reactions, and consequent emission of photons. The explanation of different stages of chemical reactions involved varies from system to system and in fact, the spectral study of the emitted light yields important information regarding the kinetics of those reactions. The papers, dealing as they do with individual systems, are necessarily incoherent and cannot be brought under one common principle. The paper by R. Audubert contains interesting new observations on the *Emission of Ultraviolet Rays by Chemical Reactions*, which would be of help in future investigations of molecular transformations during chemical changes. The paper on Bio-luminescence by Harvey gives a brief review of the theories advanced in explaining the mechanism of production of light of high quantum efficiency by living matter.

In conclusion it may be stated that the contributions made in the Symposium and the lively discussions accompanying them show that while luminescence is a fundamental phenomenon and much has been done in the way of exploration, there is much more which awaits further investigation, both theoretically and experimentally, before a general theory of luminescence explaining all facts connected therewith could be formulated. By bringing together prominent workers in the field and publishing the proceedings in full, the Faraday Society has done a great service for the future workers in the subject.

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Einstein's Generalisation of Kaluza's Unitary Theory

THE Kaluza-Klein theory introduces a fifth dimension in attempting to derive a unitary theory connecting gravitation and electricity. Einstein has recently attempted to generalise this theory[1] by putting in physical concepts into the purely mathematical structure of Kaluza's theory.

The aim of this theory of Kaluza was to obtain some new physical aspect for gravitation and electricity by introducing a unitary field structure with the aid of a fifth dimension, the essential result being that such a five-dimensional structure could be built up so as to be equivalent to a four-dimensional structure *plus* a vector field which is the potential vector for the electro-magnetic field. This result, though elegant mathematically, was not productive of new physical ideas, and consequently many attempts were made to retain the essential formal results obtained by Kaluza without sacrificing the four-dimensional character of the physical space. But all such attempts have proved unproductive, and it appears impossible to formulate Kaluza's idea in a simple way without introducing the fifth dimension.

On the basis of these considerations, Einstein and Bergmann have now attempted to introduce the fifth dimension in a very effective manner without its being merely a sort of "catalytic agent" as in the Kaluza theory. To bring out clearly the generalisation proposed by Einstein, let us consider how Kaluza's five-dimensional structure is made equivalent to a four-dimensional one and a vector field. It can be shown that by a suitable characterisation of the 5-space with the metric

$$d\sigma^2 = \gamma_{\mu\nu}\, dx^\mu\, dx^\nu \; (\mu, \nu = 0, 1, 2, 3, 4) \;.. \quad (1)$$

the components of the fundamental metric tensor can, by the choice of a special co-ordinate system, be reduced to ten functions g_{mn} and the four functions A_m $(m, n = 1, 2, 3, 4)$ *which do not depend on* x^0. This reduction gives a four-dimensional description of the space, and the independence of the functions on x^0 shows the purely formal nature of the fifth dimension x^0 which is just put in only to be taken out later. On Einstein's new theory it is shown that, with a suitable modification of the postulates of the 5-space, it is possible to make an exactly analogous reduction to g_{mn} and A_m with this difference that the *components of* g_{mn} *are in general periodic functions of* x^0. The A_m, however, is independent of x^0 as in the old theory. Remembering that g_{mn} is a four-dimensional metric tensor, this amounts to an intimate physical connection of the space-time with the new dimension. The x^0 which is put in at first is not taken out after the reduction but left behind so as to modify the 4-metric. The periodicity of the components of this 4-tensor in the new co-ordinate enables one to interpret physically the fifth dimension. In a very rough way, one could describe this as a sort of a *phase*, and the *4-dimensional space-time* might be thought of as having been replaced by a *5-dimensional space-time-phase*. Since, however, this new co-ordinate is "dimensionless" there arises no contradiction with the empirical four-dimensional character of physical space.

From its very nature, the new theory is essentially complex in its physical aspects, and Einstein and Bergmann have given the derivation of the fourteen field equations starting from a variational principle, and also the identities satisfied by the field equations. The theory involves four universal constants of which one corresponds to the gravitational constant involving a connection between the units of length and mass, another depending on the unit of length, while the remaining two are "genuine" universal constants which cannot be eliminated from the theory.

When looked at from the purely geometrical point of view the new theory introduces some very interesting features. The five-dimensional space defined by the metric (1) is here closed with respect to one dimension, and this closed space will be represented by a space which is open and periodic with respect to this dimension. A point P of the physical space will be represented by an infinite number of points P, P′, P″ of the 5-space. This type of non-homeomorphic correspondence between general metric spaces is itself a rich mathematical concept capable of a large number of developments.

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[1] Vide *Annals of Mathematics*, July 1938, **39**, No. 3, 683.