

As the mean life  $\tau$  of the state  $M$  is much longer than that of the level  $F$ , the phosphorescence is quenched appreciably more than fluorescence. This follows from the formula  $I = \frac{I_0}{1 + k\tau}$ , where  $k$  is the probability of a quenching act,  $I$  the observed intensity of photoluminescence.

The absorption band  $N-M$  (inverse transition) must also appear if the transition  $M-N$  takes place, notwithstanding its small probability. However, it will have a very small intensity as compared with band  $N-F$ .

Under the influence of disturbing fields, for example of the surrounding molecules of the solvent, the probability of transition  $N-M$  can become appreciably greater than that of the isolated molecule.

In solutions, practically all the molecules which have reached the level  $M$  in any possible way will be quenched. Therefore the absorption band  $N-M$  must be completely inactive.

Such inactive bands, overlapping on the longer wave-length side the active absorption bands ( $N-F$ ), can cause the falling off of efficiency as observed in fluoresceine solutions<sup>3,4,5</sup>. It is to be noted in this connexion, that in the region of abrupt falling off of yield, the values of absorption coefficients of fluoresceine solutions reach only from 0.2 to 2 per cent of the maximal value.

In the above considerations I have supposed for the sake of simplicity that the levels for absorption and emission acts are identical. I have dealt elsewhere with the relative displacements of emission and absorption bands.<sup>6</sup>

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<sup>1</sup> H. Kautsky, "Energieumwandlungen an Grenzflächen", *Ber. Deutsch. Chem. Ges.*, **64**, 2053 and 2677; 1931; and **65**, 401; 1932.

<sup>2</sup> O. Stern and M. Volmer, *Phys. Z.*, **20**, 183; 1919.

<sup>3</sup> S. Valentiner and M. Rössiger, *Z. Phys.*, **36**, 81; 1926.

<sup>4</sup> S. I. Wawilow, *Z. Phys.*, **42**, 311; 1927.

<sup>5</sup> A. Jabłoński, *Acta Phys. Pol.*, **2**, 97; 1933.

<sup>6</sup> A. Jabłoński, *Z. Phys.*, **73**, 460; 1931. See also P. Pringsheim, "Handb. d. Phys.", **23**, Part 1, second edition, 241.

### Interaction between Radio-Waves?

THE coming into operation of the Luxembourg high-power broadcasting-station on a wave-length of 1190 m. has caused the following remarkable phenomenon. For the first time on April 10 of this year it was observed at Eindhoven, Holland, that when a radio-receiver was tuned to Beromünster (460 m.), the modulation of the Luxembourg station could be heard on the background to such an intensity that during the weak passages of the programme of Beromünster the programme of Luxembourg was heard with an annoying strength. Since the field-strength of Luxembourg at Eindhoven has the quite normal value of about 10 mv./m. (the distance from Luxembourg to Eindhoven is somewhat more than 200 km.) and the same phenomenon was observed with different types of receivers, this cannot be due to cross-modulation in the receivers. It was also observed with a battery set away from the electric distribution system of the town, so that any disturbing influences from these sources were eliminated. Hence it seems that the phenomenon has its origin somewhere in the transmission between Beromünster and Eindhoven. It may be remarked that Luxembourg is situated nearly on the line joining Beromünster and Eindhoven.

Since the first observation the same phenomenon has been observed at Eindhoven with different intensities on Radio Paris (1725 m.), Budapest (550 m.), Munich (533 m.), Lyons la Doua (466 m.), Sottens (404 m.), Muhlacker (361 m.), Strasbourg (345 m.), Milan (332 m.), Poste Parisien (328 m.) and Frankfurt (259 m.), which all lie somewhat in the direction from Eindhoven to Luxembourg and at a greater distance from Eindhoven than Luxembourg. It has also been observed on Beromünster at Rotterdam, near Arnhem and at Dusseldorf. It was always the modulation of Luxembourg which could be heard on the background. This modulation has not been observed on Langenberg (472 m.) and Brussels (509 m., 338 m.), or on a British station.

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### Kinetics of the Iodine-Oxalate Reaction

SINCE 1916, when one of us<sup>1</sup> reported that this reaction is very sensitive to light and that the dark reaction has a high temperature coefficient, a large amount of work has been carried out on this chemical change by several chemists<sup>2</sup>.

The majority of workers believe that the velocity of this reaction in light is not directly proportional to the light intensity but varies as the square root of the intensity of the incident radiation, although Bhattacharya and Dhar<sup>3</sup> have observed that by using an aqueous solution of iodine in the absence of potassium iodide, the relation between velocity and light intensity for this reaction approaches unity in radiations of mean wave-lengths 5650 Å. and 7304 Å.

We have carried out further experiments on this reaction using normal potassium oxalate and  $N/850$  aqueous solution of iodine without the addition of potassium iodide, and some of the results are as follows:

Dark 8750 Å. 8500 Å. 3340 Å. 3512 Å. 3452 Å. 3125 Å. 3536 Å.  
 $k_{25^\circ}/k_{15^\circ}$  4.64 3.92 3.54 2.02 2.25 2.38 2.38 2.44

When potassium iodide ( $N/277$ ) was added to the reaction mixture, the velocity was greatly diminished and  $k_{32^\circ}/k_{22^\circ}$  assumed the high value 8.84 in the dark.

In the absence of potassium iodide and with normal oxalate and  $N/850$  iodine, the following results were obtained for the relation between light intensity and velocity:

Wave-length in Å.	Observed ratios of velocities	Ratio of light intensity
3500	1.32	4
3340	1.79	4
3536	3.25	6.25
8500	3.97	4.34
8750	2.71	2.44

It appears that the relation between the velocity and light intensity varies from 1/3 to 5/4 approximately. Several other photochemical reactions taking place in aqueous solutions behave in a similar manner. It is now well known that the photochemical reactions between chlorine and hydrogen and bromine and hydrogen in the gaseous state are proportional to the square root of the light intensity under certain conditions and are directly proportional to the light intensity under other conditions. We have shown experimentally and theoretically that the relation

between the velocity and the light intensity (or the amount of absorbed light) in a photochemical change is not constant but changes with the acceleration of the reaction by light absorption<sup>4</sup>.

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<sup>2</sup> Berthoud and Bellenot, *Helv. Chim. Acta*, **7**, 307; 1924. Briers, Chapman, and Walters, *J. Chem. Soc.*, 129, 562; 1926. Mukerji and Dhar, *J. Phys. Chem.*, **32**, 1308; 1928. Allmand and Young, *Faraday Soc. Discuss.*, 515, April 1931. Young and Style, *ibid.*, 493. Griffiths and McKeown, *Trans. Faraday Soc.*, **28**, 752; 1932.

<sup>3</sup> Bhattacharya and Dhar, *J. Indian Chem. Soc.*, **6**, 473; 1929.

<sup>4</sup> Dhar and Bhagwat, *Z. Anorg. Chem.*, **190**, 415; 1930. Malaviya, Dhar and Bhagwat, *ibid.*, **199**, 406; 1931. Dhar, "Chemical Action of Light", Blackie and Son, 1931.

### Ultra-Violet Bands of Oxide of Phosphorus

THE Phosphorus arc in air gives out a band spectrum in the ultra-violet, which is attributed to the PO molecule. The vibrational quantum analysis of these bands has been previously done by one of the authors<sup>1</sup>. The rotational structure analysis of the (0, 0) band at  $\lambda$  2477.80 shows that it consists of six main branches, namely,  $P_1$ ,  $Q_1$ ,  $R_1$  and  $P_2$ ,  $Q_2$ ,  $R_2$  and two other faint satellite branches. For low quantum numbers, the satellite branches  $R_{Q_{21}}$ ,  $Q_{P_{21}}$ ,  $P_{Q_{12}}$  and  $Q_{R_{12}}$  are superposed on the main branches. The intensity of the lines of the different branches satisfy the criterion of a  $^2\Sigma \rightarrow ^2\Pi$  transition. The band structure is analogous to the  $\nu$ -bands of NO<sub>1</sub> as is anticipated from theoretical considerations. The following molecular constants (cm.<sup>-1</sup> units) have been obtained.

$$\begin{aligned} v'_e &= 1.416 \times 10^{-8} & v''_e &= 1.458 \times 10^{-8} \\ B'_e &= 1.3060 & B''_e(\frac{\pi}{2}) &= 1.2332; B''_e(\frac{3\pi}{2}) &= 1.2256 \\ D'_e &= -4.60 \times 10^{-6} & D''_e(\frac{\pi}{2}) &= -4.96 \times 10^{-6}; \\ & & D''_e(\frac{3\pi}{2}) &= -4.86 \times 10^{-6} \\ \alpha' &= \alpha'' &= 0.0073 \end{aligned}$$

The detailed results will be published elsewhere.

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<sup>1</sup> P. N. Ghosh and G. N. Ball, *Z. Physik*, **71**, 362; 1931.

### Conductivity of Mixtures of Gases

It is well known that the electrical conductivity of certain gases may be greatly increased by the addition of very small quantities of other gases. For example, the electrical conductivity of pure helium is greatly improved by the addition of 0.01 per cent of pure argon. In gases, the electrical conductivity in uniform fields between parallel plates depends upon the ratio  $X/p$ , where  $X$  is the electrical intensity in volts per centimetre, and  $p$  is the pressure in millimetres of mercury, and is a maximum for a certain value of  $X/p$  depending upon the nature of the gas. The photo-electric currents obtained with a constant force between parallel plates at different distances apart are represented by the ordinates of the curves, Fig. 1, and the potential differences between the plates by the abscissæ. The three curves give the currents in pure helium, in pure argon and in helium containing 0.025 per cent of argon. The

values of the ratio  $X/p$  were, 50 in pure helium, 200 in pure argon and 15 in the mixture. Under these conditions the rate of increase of the current with the distance between the plates was a maximum.

Two theories have been advanced to account for the increase in conductivity of the mixture, namely, the action of direct collisions of electrons with the atoms of argon, and the action of metastable atoms of helium which are formed by electron collisions

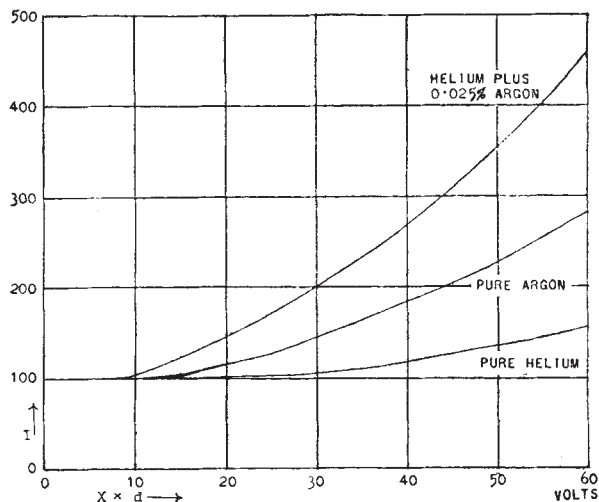


FIG. 1.—Conductivity between parallel plates.  $I$ , current between plates in arbitrary units;  $X$ , forces between plates in volts per centimetre;  $d$ , distance between plates in centimetres.

with helium atoms. These metastable atoms of helium may be formed when the electrons attain an energy corresponding to approximately 20 volts. It is then supposed that the metastable atoms of helium ionise the atoms of argon, which require an energy corresponding to approximately 16 volts. There is much controversy concerning the relative importance of these two processes. For example, Penning<sup>1</sup> states that the increase in conductivity may be attributed entirely to metastable atoms, whereas Townsend and McCallum<sup>2</sup> have pointed out that the effect of direct collisions of electrons may be considerable in these circumstances.

The results given in Fig. 1 are of importance in showing that a large number of new ions are formed in the mixture of 0.025 per cent of argon in helium when the potential between the plates is increased from 9 volts to 18 volts, the distance between them being adjusted so as to maintain a constant force. As no metastable atoms of helium could be formed until the electrons attained an energy of 20 volts, the increase in conductivity in these circumstances must be attributed to the direct collisions of electrons with argon atoms. It would not appear from the curve that any important new process occurs when the potential between the plates exceeds 20 volts, such as might be attributed to the action of metastable atoms.

More complete results will shortly be published elsewhere.

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<sup>1</sup> F. M. Penning, *Physica*, **12**, 66; 1932.

<sup>2</sup> J. S. Townsend and S. P. McCallum, *Phil. Mag.*, **5**, 695; 1928.