

tropopause and in the stratosphere to be only 1/50 that was expected from previous measurements. In a suggestive paper,³ he explained the low temperature of the tropical tropopause by considering that the amount of ozone to be less and the amount of water vapour to be more in the tropics than in the temperate latitudes. But he finds no reason why the amount of ozone should be less over the tropics than elsewhere. To import a fresh cause for this decrease may not be necessary. The agencies involved are sun's ultra-violet rays (photochemical action) water vapour and ozone. It is well known that ozone breaks up (slowly, but more rapidly than in the absence of water) in presence of water or water vapour. In many chemical reactions water vapour plays the role of a catalyst.

It is suggested, as a possible solution that the smaller amount of ozone in the tropical air may be due, as a condition of equilibrium, to the excess water vapour itself in presence of ultra-violet light. Similarly in summer in India, when water vapour increases the ozone content may diminish.

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S. L. MALURKAR.

1. Read before the Symposium of National Institute of Sciences, India, Bombay, August 30th, 1946. 2. *Memoirs Ind. Met. Dept.*, 1930, 25, 183. 3. *P.R.S.*, Feb. 1946.—*Bakerian Lecture for 1944.*

THRESHOLD POTENTIAL, CONDUCTIVITY AND COURSE OF A CHEMICAL CHANGE UNDER ELECTRICAL DISCHARGE

TOWNSEND'S theory of ionisation by collision contemplates sensibly the same change on reaching the 'dielectric strength', 'starting', 'break-down' or the spark (Paschen) potential. For elementary gases, this is identifiable with, or is a simple function of the corresponding 'threshold potential' V_m in especially ozoniser type discharges.^{1,2,3,4,5} Like Paschen potential, V_m is a sensibly linear function of the gas pressure. As found by the author for V_m ,^{1,2,5} it is extremely likely that 'electron affinity' of the excited gas, besides its ionisation potential is a chief determinant of the Paschen potential; comparatively, however, V_m would appear to be more sensitive to change of frequency of A.C. supply and of temperature especially in polyatomic gases and reactive mixtures.

The author's general finding^{1,2,3,4,5,6} that (i) a reaction occurs only above V_m and (ii) that at an applied potential V , velocity of the chemical change and the corresponding current i depend principally on $V - V_m$, has been confirmed by results of numerous discharge reactions studied in these Laboratories, including such quasi-chemical changes under discharge as the activation of nitrogen, its deactivation, 'latent image' formation, etc. (ii) led to the prediction and discovery by the author of a new *light-effect* Δi , an instantaneous and reversible photo-diminution of i observable from X-rays to extreme red in a number of gases and vapours under electrical discharge.^{2,5,6}

In part, V_m corresponds to the 'energy of activation' found chiefly from the temperature coefficient, which is a distinctive characteristic of a thermal reaction. It does not enable an experimental separation of a composite chemical change, e.g., into its consecutive reactions. This is possible, however, in a discharge reaction by excitation at V_m . It follows from (i) that near V_m the earliest of the (consecutive) reactions would set in with least velocity and minimum decomposition of its products. Excitation at V_m should, therefore, be, a valuable device for isolating (at any rate detecting) unstable, e.g., intermediate products in a discharge reaction. This has been substantiated by results for the decomposition under silent discharge of some oxides of sulphur and nitrogen *per se*, and also in contact with metallic and certain reactive films, studied in these Laboratories.

The marked utility of data for the time-variation of i as a means of elucidating the course of a discharge reaction has been emphasised by the author.^{1,2,5} It is about the only criterion of the progress of a reaction (e.g., hydrogen, chlorine combination) unaccompanied by pressure change, without disturbing the system as with a time-to-time analysis of the reaction mixture. This last, gas pressure p , i and such associated characteristics as wattage W dissipated in the system, the spectral nature of the discharge glow, etc., show a greater mutual synchronous variation during the reaction, the nearer to V_m is the corresponding applied V . This, in general, would also favour observation of discontinuities characteristic of the course of the reaction, corresponding to consecutive changes.

Under certain conditions, decomposition of nitrogen dioxide and especially the nitrous oxide + hydrogen reaction under silent discharge, reveal a remarkable periodic effect^{6,7} in respect of all variables mentioned above (p , i , W , etc.); from this and (ii), the corresponding V_m should vary periodically; this has been observed. Whilst in general, *Ceteris paribus* excitation near V_m favours the production of this periodic effect, the time-variation of some of the above quantities is affected markedly by but small changes in $V - V_m$ near V_m .

In a Siemens' type discharge tube, the total capacity is determined chiefly by that associated with the annular space which is the seat of both ionisation and the reaction. In a theory^{8,9} of the new *light-effect* Δi an assumption is made by the author of an 'electrode layer' derived from the ions and neutral molecules in the discharge space; and that under light *inter alia* a change of phase due to that of the capacity by the photoelectric emission leads to Δi . In the absence of light, an excited layer leading to such a capacitative change may well occur due to the surface activity of especially some of the reaction products. If this layer is deformed and in part restored intermittently, the periodic effect, as observed in i and the other associated quantities would follow. Such an electrode layer is anticipated to be stabler the lower the temperature of the system; this is shown by the marked reduction on cooling of the corresponding periodic effect.^{6,7}