INTERACTION OF NITROGEN AND SULPHUR UNDER SILENT ELECTRICAL DISCHARGE: PRODUCTION OF A REVERSE CHANGE

BY G. S. DESHMUKH, M.SC.
(Asstt. Professor of Chemistry)
AND S. SIRSIKAR, B.SC.
(Benares Hindu University)

Received October 27, 1947
(Communicated by Prof. S. S. Joshi, D.SC., F.A.SC., F.N.I.)

PREVIOUS results[1] for the behaviour under electric discharge of phosphorus films towards nitrous oxide, air and nitrogen showed very marked and sudden changes in the conductivity during the removal of nitrogen by phosphorus. It was of interest therefore, to investigate the corresponding reaction with sulphur. Anticipated by Joshi as possibly associated with the production under silent discharge, of a periodic effect in the interaction of nitrous oxide with hydrogen and decomposition of nitrogen dioxide,[2, 3] the present work has revealed a spontaneous *self-reversal* in the over-all direction of a discharge reaction. This *reversal* is not a transient or spurious effect; but a reproducible characteristic under well-defined conditions; and shown by markedly synchronous changes in the gas pressure (p), the discharge current (i) and nature of the corresponding glow, which do not appear to have been recorded in the literature.

EXPERIMENTAL

The general apparatus and the electrical circuit used were essentially the same as described elsewhere.[1] The discharge vessel consisted of two soft glass tubes fitted co-axially, as in a Siemens' type ozoniser, with a rubber greased ground joint. The inner tube and the one surrounding the outer tube were filled with a moderately concentrated salt solution and served as two terminals of the ozoniser. The temperature of the system was kept constant by circulating water at a slow but constant rate through a water jacket enclosing the ozoniser. A uniform and thin film of sulphur was deposited on the outer surface of the inner electrode by coating it with a concentrated solution of sulphur in carbon disulphide. The tube was fitted in the ozoniser system and the solvent was removed completely by evacuating it on the Töpler. The main experiment was commenced only when the system maintained a satisfactory vacuum at least for 24 hours.

Nitrogen was obtained from a commercial cylinder. The gas was bubbled slowly through a series of traps filled with a freshly prepared solution of alkaline pyrogallol and was led over heated copper turnings to remove traces of oxygen. It was dried carefully by streaming it slowly through a train of tubes containing phosphorus pentoxide and calcium chloride and admitted to the ozoniser at a desired pressure.

The A.C. output of 50 cycles frequency, obtained from a rotary converter worked off 220 volt D.C. mains, was fed to the primary of a step up transformer. Its secondaries were connected to the inner and outer electrodes, *i.e.*, the H.T. and L.T. terminals of the ozoniser. The potential applied to the ozoniser V, expressed in kilo-volts (r.m.s.) kV, was calculated from the primary potential and the step-up ratio of the transformer. The discharge current *i* was measured by a Weston's moving iron A.C. milliammeter or an oxide rectifier type Cambridge A.C. micro-ammeter connected between the earth and the low-tension terminal of the ozoniser.

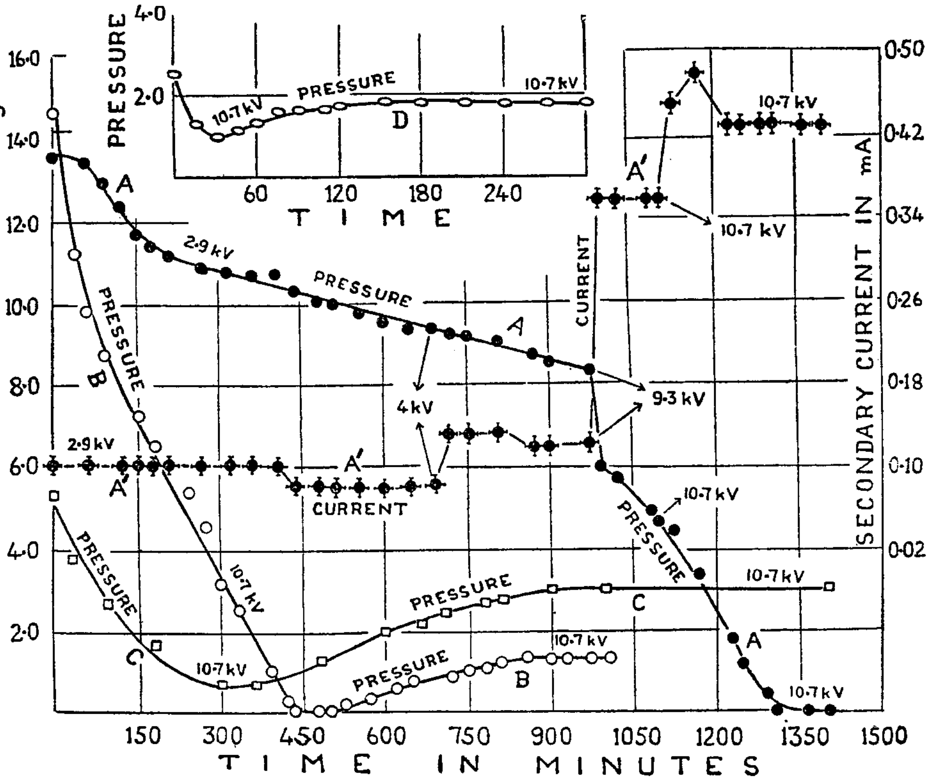

FIG. 1. Pressure, Current Variation during S—N_2 Reaction at 2·9, 4, 9·3, 10·7 kV. 50 Cycles Sec.$^{-1}$

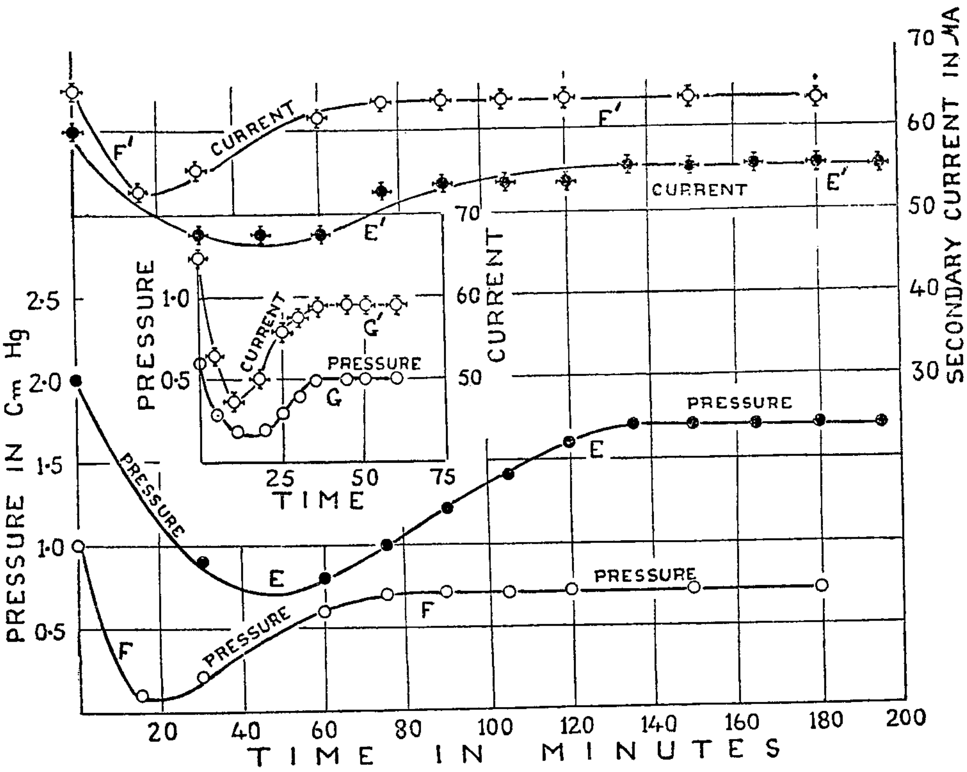

FIG. 2. Pressure, Current Variation during S—N_2 Reaction at 10·7 kV. 50 Cycles $Sec.^{-1}$

The ozoniser was filled with purified nitrogen at different initial pressures and subjected to discharge at V varied in the range 2 to 11 kV of 50 cycles frequency; a fresh film of sulphur was used in each experiment. The progress of the reaction was followed by a time to time determination of the pressure of the reaction mixture at constant volume and also the corresponding discharge current *i* flowing through the ozoniser at a given applied V.

Figs. 1 and 2 illustrate the results obtained for the variation of *p* and *i* during the interaction of sulphur and nitrogen under the experimental conditions mentioned above. The products of the reaction were analysed when *p* and *i* reached the minimum stage. The discharge was discontinued at this stage; the film on the outer surface of the inner electrode was removed and analysed for the presence of sulphur nitride. Fig. 3 shows the time required for (*a*) the initial diminution of *p* to a minimum; (*b*) its subsequent increase to a maximum stage due to *reversal*; and (*c*) that for the total change (*a*) + (*b*). This as also the relative pressure recovery $100 \times \frac{\text{Final } p}{\text{Initial } p}$, serve

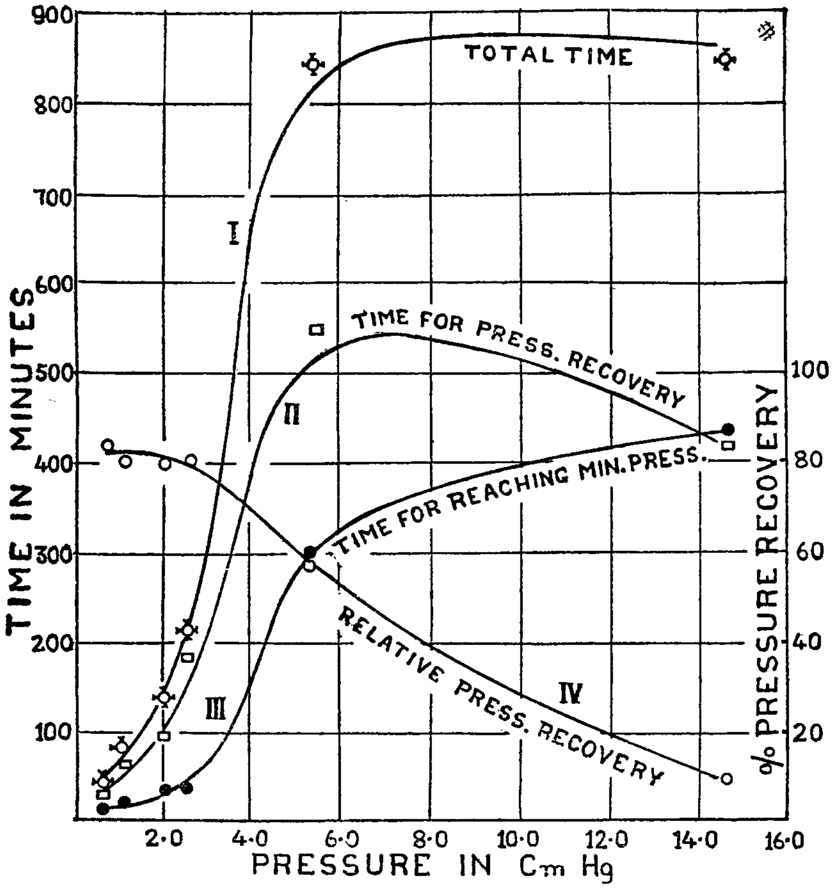

Fig. 3. Pressure, Time Variation during S—N_2 Reaction at 10·7 kV. 50 Cycles $Sec.^{-1}$

as a measure of the velocity of the reaction at different initial pressures of nitrogen and a constant applied V.

Discussion of Results

As with phosphorus films, oxidation under discharge of sulphur by air dried carefully, was found to set in only at a characteristic 'threshold potential' V_m, as located by an incipient current rise and pressure change. Much greater V_m than in the case of phosphorus was, however, required in the sulphur-nitrogen reaction due, in part, to the comparatively greater dielectric strength of sulphur. The pressure-time curves A–G in Figs. 1 and 2 show that during the initial stage of the reaction, p decreases continuously to a minimum and on continued exposure to discharge (at a constant applied V), increases slowly to a constant maximum; after this, no further pressure change occurs on continuing the discharge for an appreciably long time. The total time for the reaction, *i.e.*, when p reached its minimum on the time axis and then increased to a constant maximum during the *reversal* (see curve 1 in Fig. 3); and also the average time-rate of the pressure change increased with V and $1/p$. Thus *e.g.*, at 10·7 kV and an initial pressure corresponding to 14·6 and 5·6 cm. of nitrogen (curves B and C in Fig. 1) p reached the minimum in about 450 and 300 minutes respectively. This is in agreement with Joshi's deduction that the 'threshold potential' V_m increases with p and that the velocity of a discharge reaction depends on $V-V_m$.[4,5,6] Furthermore, curve A in Fig. 1 shows that with 13·6 cm. of nitrogen and V varied from 3 to 11 kV, the pressure decreased to a minimum in about 1,300 minutes. This slow pressure diminution, indicative of a reduction in the over-all velocity of the reaction, was more conspicuous when V was nearer to V_m. Thus at 2·9 kV, only 30 per cent. of the pressure change occurred in about 675 minutes and the rate of pressure diminution increased as V was raised progressively to 10·7 kV. Detailed experiments showed that the *reversal* of p was more pronounced at low initial pressures of nitrogen and was accompanied by a synchronous variation of the discharge current i (curves E–G and E′–G′ in Fig. 2). The percentage restoration of both the above quantities, at a given V, increased markedly as the initial pressure of the gas was reduced progressively (see curve IV in Fig. 3). Thus *e.g.*, at 10·7 kV and 14·6 cm. of nitrogen (curve B in Fig. 1), p became negligibly small in about 450 minutes and increased on continued exposure to discharge to a maximum corresponding to 1·3 cm., *i.e.*, to about 9% of its initial value (see curve IV in Fig. 3). Compared with this, the relative recovery of p (due to *reversal*) was much greater *viz.*, about 83% when the pressure of nitrogen was lower, *i.e.*, 2·0 cm. Hg (curve IV in Fig. 3 and curve E in Fig. 2).

Also, the current i showed a remarkably synchronous variation with p; it decreased from the initial 60 to 47 μA and increased again to 55 μA, *i.e.*, to about 90 per cent. of the original conductivity (curve E′ in Fig. 2). Results for the sulphur-nitrogen reaction at 10·7 kV, but lower initial pressures of nitrogen were found to be on the whole similar to those mentioned above (curves F–F′ and G–G′ in Fig. 2). The variation of i was less pronounced at high initial pressures of nitrogen. This was partly due to the use of a less sensitive indicator then available for these measurements. Curve A′ in Fig. 1, however, shows that at 13·6 cm. of nitrogen, i either remained sensibly constant or decreased at a given V when p decreased continuously. It, however, increased to a higher value on increasing V successively and was constant so long as the applied V was also constant. During this, it was observed that the intense violet appearance of the glow faded gradually with the decrease of p and i; it disappeared almost completely as both the above quantities reached the minimum and was not observed even during their *reversal* on continued exposure to discharge.

It is interesting to point out that if after the attainment of the constant maximum p (due to *reversal*) the residual gas was töplered out completely and the system re-excited at V applied previously, an increase of pressure ensued. Thus, *e.g.*, at 10·7 kV and 5·6 cm. of nitrogen (curve C in Fig. 1), p decreased to 0·7 cm. and increased again (on continued exposure to discharge) to 3·0 cm. in about 900 minutes. The experiment was discontinued at this stage. The ozoniser was evacuated on the Töpler and the discharge was switched on at the original applied 10·7 kV. It was now seen that p increased slowly and reached a constant stage corresponding to about 0·6 cm. in 130 minutes. On further evacuation on the Töpler and exposure to discharge under constant experimental conditions, the pressure increased once again but on the whole more slowly than before. Thus, after the second evacuation of the residual gas, 160 minutes were required for the same amount of pressure change, *i.e.*, 0·6 cm. rise of p. It is significant to observe that such a reversal of pressure after the attainment of minimum p, which (latter) in the case of phosphorus corresponded to practically zero pressure, was never observed in the phosphorus-nitrogen reaction under generally identical conditions even though the exciting potential was increased considerably.

Newman[7] found that certain elements deposited as thin films over the cathode, absorbed nitrogen rapidly under the discharge. With phosphorus, sulphur and iodine the absorption was most pronounced and the gas was not reliberated even on heating the discharge tube, which he attributed to the formation of a stable chemical compound. The general resemblance of the S–N_2 reaction under electric discharge as shown by the initial time-variation of p, with that when phosphorus was used instead, is suggestive. The removal of nitrogen by phosphorus was, however, attributed chiefly to the formation of a chemical compound since no *reversal* of pressure was observed and the termination of the reaction was characterised by a sudden and large drop of i to a stationary value when p became negligibly small. During the course of the reaction, the colour of the phosphorus film changed from yellowish white to dark brown and the reaction products revealed the presence of phosphorus nitride. In the present series of experiments the analysis of the products of the reaction indicated the formation of sulphur nitride. Judged by the time-rate of the variation of p, the 'clean up' of nitrogen by phosphorus was comparatively more rapid than that by sulphur.

Thus, at 4 kV and 11·3 cm. of nitrogen p became negligibly small in about 330 minutes in the P–N_2 reaction. Using almost similar pressure, *i.e.*, 14·6 cm. of N_2 and a much higher applied V, namely 10·7 kV, only 80% of the pressure change occurred in 330 minutes in the latter case (curve B, Fig. 1).

Kohlschütter and Frumkin[8] obtained phosphorous nitride by passing an electric discharge through a mixture of phosphorus vapour and nitrogen. No data are, however, available for the formation of sulphur nitride as a result of the interaction of sulphur and nitrogen under the discharge. The detection of sulphur nitride in the products of the reaction in the present series of experiments is therefore, interesting.

Three volatile modifications of sulphur nitride are known; of these, nitrogen tetrasulphide (N_4S_4) is comparatively more stable and obtained as a yellowish brown solid at ordinary temperature. The other two varieties, *viz.*, nitrogen persulphide (NS_2) and nitrogen pentasulphide (N_2S_5) were obtained by Usher[6] and Muthmann[10] by heating N_4S_4 with sulphur and carbon disulphide respectively. Both the above compounds are liquids with a characteristic deep red colour and are easily decomposed at ordinary temperature into N_4S_4 and sulphur. It is, therefore, suggested that the reaction products obtained under the discharge in the present experiments consisted chiefly of nitrogen tetrasulphide, as the formation of a liquid product was not detected at any stage during these experiments.

It is instructive to compare at this stage the relative stability of phosphorus nitride and sulphur nitride. Phosphorus nitride (P_3N_5) is fairly stable at ordinary temperature and decomposes only above 910°[11]; its heat of formation, using ordinary phosphorus was found by Stock and Wrede[12] to be + 81·5 K. Francis and Davis[13] observed that nitrogen tetrasulphide (N_4S_4) decomposes almost completely at 185°. Berthelot and Vieilli[14] found the compound to be *endothermic* having a heat of formation − 127 K. This shows that sulphur nitride is comparatively more unstable than phosphorus nitride.

The observed *reversal* of pressure accompanied by the synchronous time-variation of i (Figs. 1 and 2) may be attributed to the formation and subsequent decomposition of sulphur nitride and/or the adsorption and desorption of the gas on the sulphur film under the discharge.

In a theory of the newly discovered *Joshi-effect*, *viz.*, an instantaneous and reversible photo-diminution $-\Delta i$ of the discharge current i in chlorine and other gases and vapours, Joshi[15] has postulated the formation of a 'variable adsorption layer' derived in part, from the wall adsorption of the ions and excited molecules under the discharge. The formation of this layer would alter the electrical capacity of the annular space in the ozoniser and therefore, of the corresponding discharge current *i* at the given applied potential V. Furthermore, Joshi[16] has argued that a decrease of *i* in the ozoniser discharge can originate from (1) a decrease of C_w, the combined capacity of the walls and C_g, the capacity associated with the gas phase. This last may be regarded as shunted by an ohmic resistance R_g under discharge due to a given exciting potential V. $1/R_g$ is the conduction current determined by the average velocity and number of ions per c.c. *Ceteris paribus* the conduction current should ordinarily increase by decreasing the gas pressure. The decrease of the current with *p* and its increase during the latter stage characterised by pressure *reversal* cannot, therefore, be attributed to the variation in ohmic or the conduction part of the current, $1/R_g$. The observed variation of *i* may, therefore, be due to a change in C_w and/or C_g. Since $C_w = \dfrac{0 \cdot 2416\, lK}{\log 10 \frac{r_1}{r_2}}$, where *l* is the length of the ozoniser, r_1 and r_2 the radii of the outer and inner tube (constituting the ozoniser) and K the dielectric constant of the wall material; reduction in K should produce a corresponding decrease of C_w. Applying the Maxwell relation $\mu^2 = K$, data for the refractive index of sulphur and nitrogen tetrasulphide[17] (μ being 1·998 and 1·908 respectively), show that the dielectric constant of sulphur is greater than that of N_4S_4. Assuming that r_2 does not change appreciably during the course of the reaction, the synchronous diminution and *reversal* of *p* and *i*, characteristic of the formation and subsequent decomposition of nitrogen tetrasulphide may, therefore, be due to the corresponding variation of C_w. The above suggestion can only be a partial explanation since the observed current changes are far larger than the corresponding difference in the dielectric constants. Furthermore, C_g the capacity associated with the gas phase, should vary synchronously with the gas pressure *p*. The diminution of *i* with *p* and its subsequent increase during the *reversal* of pressure may, therefore, be anticipated.

The disappearance of the glow when *p* and *i* reach the minimum stage and its subsequent non-observation during their *reversal* in the latter part of the S–N_2 reaction is explicable on the assumption that during the initial stage of the reaction, the appearance of the intense violet glow may be due to the excitation of sulphur. With the replacement of sulphur by another emitter, *viz.*, N_4S_4, *p* decreases and the glow fades and disappears almost completely at the minimum *p* stage. The non-observation of the glow at this stage and also during the *reversal* of *p* suggests that the excitation potential of N_4S_4 may be greater than that of sulphur. Alternatively, the glow may be due to the excitation of sulphur by active or atomic nitrogen produced under the discharge. Production of active nitrogen under ' silent discharge ' has been observed, it would appear, for the first time by Joshi and Purushottam.[18] As p decreases the net concentration of atomic + active nitrogen falls and at minimum p it may not be sufficient to excite sulphur; the glow, therefore, fades and disappears almost completely. If during the *reversal* of p, indicative of the desorption of nitrogen and/or the decomposition of N_4S_4, the liberated gas is in the atomic state or/and ' active ', a reappearance of the glow should follow. Its non-observation during the *reversal* does not, therefore, support the latter assumption. It may, however, be assumed that during the initial stage of pressure reduction, a protective film due to the formation of N_4S_4 and/or adsorption complex of sulphur and nitrogen (having properties similar to N_4S_4) is formed on the surface of the sulphur deposit; the formation of this film may inhibit the excitation of sulphur and consequently the appearance of the glow even during the *reversal* of p.

It is suggested that like its formation, the decomposition of sulphur nitride may depend on $V-V_m$. This is illustrated by the general result that at a constant applied V and high initial pressure of nitrogen, the rate of change in p indicative of the formation and decomposition of sulphur nitride is comparatively slow, as V_m increases with p and $V-V_m$ is not large. p reaches the minimum rapidly and its relative recovery due to *reversal* is more pronounced as the initial pressure of N_2 is reduced progressively (Figs. 1 and 2). The constant maximum stage reached during the *reversal* may be attributed to the attainment of a steady state between the liberated gas and the undecomposed film. This is supported by the observation that on evacuating the ozoniser after p has reached the constant maximum due to *reversal* and re-exposing the film to discharge at a constant V in vacuum, an increase of p results. Relatively, however, the rate of increase of p falls on evacuating the system successively and re-subjecting the film to discharge, the exciting potential being kept constant throughout the series.

Grateful thanks of the authors are due to Professor S. S. Joshi, D.Sc. (London), F.A.Sc., F.N.I., for suggesting the problem and for valuable guidance during the work.

SUMMARY

Results are given for the interaction of sulphur films with nitrogen at various initial pressures p (2–15 cm. Hg) and excited in the range 3 to 11 kV (50 cycles). The occurrence of the reaction only above a minimum

'threshold potential' V_m and the dependence of its velocity, at a given V, on $V-V_m$ are in accord with Joshi's concept of the fundamental importance of V_m in discharge reactions.[4, 5, 6] With a fresh film of sulphur, p and i decrease progressively, reach a minimum and increase again to a constant maximum stage almost synchronously on continued exposure to discharge. The *reversal* of p and i is more pronounced as V and $1/p$ are increased. The formation of sulphur nitride is observed. The time variation of p and i suggest that the 'clean-up' of nitrogen is due to the formation of nitrogen tetrasulphide and/or adsorption complex of sulphur and nitrogen. The disappearance of the glow at the minimum p stage and its non-observation during the *reversal* is attributed to the formation of a protective film of N_4S_4 or/and adsorption complex on the sulphur film under the discharge.

REFERENCES

1. Deshmukh and Kane .. *Proc. Ind. Acad. Sci.*, 1947, **A 25**, 247–55.
2. Joshi and Deshmukh .. *Nature*, 1945, **155**, 483.
3. Joshi .. *Presi. Address. Chem. Sec., Indian Sci. Cong.*, 1943.
4. ——— .. *Trans. Faraday Soc.*, 1929, **25**, 118–28; 137–43.
5. ——— .. *Curr. Sci.*, 1946, **15**, 281; 1939, **8**, 548.
6. ——— .. *Trans. Faraday Soc.*, 1927, **23**, 227.
7. Newman .. *Proc. Phys. Soc.*, 1921, **33**, 73; *Trans. Amer. Electrochem. Soc.*, 1924, **44**, 77–86.
8. Kohlschütter and Frumkin .. *Zeit. Elektrochem.*, 1914, **20**, 110.
9. Usher .. *Journ. Chem. Soc.*, 1925, **127**, 730.
10. Muthmann and Clever .. *Zeit. anorg. Chem.*, 1897, **13**, 200; *Ber.*, 1896, **29**, 340.
11. *Cf.* Mellor .. *Comprehensive Treatise of Theoretical and Inorganic Chemistry*, Longmans, 1928, **8**, 123.
12. Stock and Wrede .. *Ber.*, 1907, **40**, 2925.
13. Francis and Davis .. *Journ. Chem. Soc.*, 1904, **85**, 259.
14. Berthelot and Vieilli .. *Compt. Rend.*, 1881, **92**, 1307; *ibid.*, 1883, **96**, 214, *Bull. Soc. Chim.*, 1882, (2), **37**, 388.
15. Joshi .. *Proc. Ind. Acad. Sci.*, 1945, **A 22**, 225; *Proc. Indian Sci. Cong., Phys. Sec.*, 1946, Abst., 26.
16. ——— .. *Curr. Sci.*, 1947, **16**, 19–21.
17. *Cf.* Hodgman .. *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., 28th edition, 1944, 2138, 2142.
18. Joshi and Purushottam .. *Nature*, 1942, **149**, 250.