STUDIES OF THE JOSHI-EFFECT IN CHLORINE UNDER OZONIZER EXCITATION—INFLUENCE OF TEMPERATURE

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ABSTRACT The influence of temperature, varied in the range 8' 67°C on the magnitude of the Joshi Effect in Cl_2 taken in the pressure range 55 5 -30 o mm and excited in a Siemens ozonizer due to potentials of 50 cycles frequency has been studied The magnitude of both the net as well as the relative effect decreases with increase of temperature, the influence of applied potential is to increase the net effect and decrease the relative effect This inhibitive influence of temperature is more in evidence at lower than at higher applied potentials The intercorrespondence between light absorption by Cl_2 which increases, and the Joshi Effect, which decreases with increase of temperature, is in accord with Joshi's view that Al is not entirely a consequence of selective light absorption by the excited gas but rather a quantum or frequency effect

The Joshi Effect having been originally discovered in chlorine (Joshi, 1943, 1945), most of the workers in this field have naturally devoted their attention to a detailed investigation of the production of the effect in this gas and the influence of the various factors which affect the nature and magnitude of the effect It was only subsequently that other gases, e g., H_2, O_2, Br_2, I etc , and metallic vapours, e g., Hg, K, Na, etc., were taken up for similar exhaustive study. But a survey of the now considerable literature on the effect in chlorine revealed the absence of any information regarding the influence of temperature on the Joshi-Effect in chlorine, except for the preliminary note of a general nature by Joshi and Deshmukh (1941) and by Deo and Padmanabhalu (1944). The present investigation was hence undertaken in order to find the dependence of the Joshi-Effect in Cl_2 on temperature

EXPERIMENTAL

The general nature of the apparatus was the same as used in some of the previous investigations The discharge vessel was a Siemens' ozonizer which was excited by single phase alternating potentials of 50 cycles frequency, obtained from a rotary converter worked off the 220 volt D C. mains and stepped up by means of a transformer of ratio 227·1 The source of illumination was a 200-volt 200-watt incandescent bulb enclosed within a box provided with a movable shutter.

Chlorine was prepared electrolytically from strong HCl, using graphite electrodes. A current of 0.25 ampere was employed for electrolysis. The current was first passed in one direction and then in the other alternately for some time in order that the acid might be saturated with chlorine and any organic impurities in the acid destroyed. After this precaution was

taken, it was found that hydrogen and chlorine were evolved in equivalent quantities. The gas, Cl_2 was then passed through a water trap in order to remove vapours of HCl and allowed to stand over fused $CaCl_2$ and P_2O_5 for the removal of moisture. The gas was finally purified by freezing it out in a liquid air trap and pumping off any uncondensed impurities by means of a Topler pump. It was then stored in a reservoir kept in communication with the drying tubes in order that the gas might be thoroughly dried.

Since chlorine attacks mercury easily, the use of a mercury manometer was precluded. Hence a Bourdon gauge of glass-spoon type, used by one of the authors (K S.V.) in connection with his work on NO_2 and described earlier (Visvanathan, 1948), was employed

The influence of temperature on the magnitude of the Joshi-Effect in chlorine was studied by taking the gas in the pressure range 55.5—390 mm and observing the variation in the effect at three different temperatures, viz., 8°, 30° and 67°C, and for some pressures, also at 25°, 50° and 60°C the applied potential being kept constant. The temperature variation of the Joshi-Effect was determined at different applied potentials, viz., 6.68, 8.01, 9.35, 9.88, 10.68, 12.02 and 13.35 kV (r.m.s.), the frequency of the A.C. supply being the same in all cases, viz., 50 cycles per second

The discharge currents, i_0 and i_1 (i.e., when the ozonizer was in dark and under irradiation respectively), were measured by means of an oxide rectifier type micro-ammeter. The net Joshi-Effect, Δi (i.e., i_1 – i_0) as well as the relative effect, $\%\Delta i$ (i.e., $100 \cdot \Delta i / i_0$) has been calculated Results indicated in Tables I-VI are selected as being typical of a large mass of data obtained for a number of initial pressures of the gas and applied potentials and temperatures. The initial pressures of chlorine thus selected are 55.55, 137, 224, 238, 381 and 390 mm.

INFLUENCE OF TEMPERATURE ON THE JOSHI-EFFECT IN Cl₂ UNDER OZONIZER EXCITATION

TABLE I

Pressure of Cl_2 · 55 5 mm

Applied Potential →	6 68 kV				8.01 kV				9 35 kV			
Temperature	i_0	i_1	$-\Delta i$	$-\%\Delta$	i_0	i_1	$-\Delta i$	$-\%\Delta i$	i_0	i_1	$-\Delta i$	$-\%\Delta i$
8°	34.3	17.0	17.3	50.4	41.8	21.8	20.0	47.8	50.0	28.0	22.0	44.0
30°	35.8	24.0	11.8	33.0	44.0	31.8	12.2	27.7	55.0	37.0	18.0	34.7
67°	40.0	3.0	7.0	17.5	50.5	41.8	8.7	17.2	63.0	51.5	11.5	18.3

TABLE II

Pressure of Cl_2 : 137 mm

8"	34 8	21 8	13 0	37 3	49.0	34 0	15 0	30 6	62 8	43 8	19 0	30.3
30"	38 0	22 0	6.0	21 4	45 8	35 0	10 8	23 6	59.0	45 0	14.0	23 7
67"	42 8	32 0	10 8	25 2	56 0	13 0	13 0	23 2	69 0	55 0	14 0	20 3

TABLE III

Pressure of Cl_2 224 mm.

8"	21 5	3 3	18 2	84 7	32 3	6 8	25 5	78.9	43 8	10 3	34.5	75 1
35°	23 8	7 8	16 0	67.2	36 0	13 3	22 7	63 1	48 3	18.8	29 5	61 1
60"	24 0	8 8	15 2	63 3	35 3	14 0	21 0	61 0	50 0	22 0	28 0	56 0
75'	25 8	10 8	15 0	58	38 0	18 0	20 0	52 6	54 0	26 3	27 7	51 3

TABLE IV

Pressure of Cl_2 . 238 mm

	9.88 kV				10 68 kV				12 02 kV			
8"	45 5	30.3	15 2	33 1	54.8	36 0	18 8	34 3	69 0	48 0	21 0	30 4
30"	40 0	29 3	10 7	20 8	59 0	39 5	19 5	33 1	68 0	48 8	19 2	28 2
67'	53 8	37.5	16.3	30 3	58 0	13 8	14 2	21 5	73 3	54 8	18 5	25 2

TABLE V

Pressure of Cl_2 · 381 mm.

	9 88 kV				12 02 kV				13 35 kV			
8"	10 0	0	10 0	100	26.0	6 3	19 7	75 8	38 3	11.3	27 0	70 5
30'	11 8	1	10 8	91 5	30 0	9 3	20 7	69 9	43 0	16 8	26 2	60.9
67°	15 3	4.3	11 0	71 0	33 8	13 8	20 0	59 2	48 8	22.8	26 0	53 3

TABLE VI

Pressure of Cl_2 · 390 mm.

8"	16 0	0	16 0	100	34.0	2.3	31 7	93 2	51 3	8.5	42.8	83 4
30°	15	0	15 3	100	35.0	3.3	31 7	90 6	48 0	7 8	40.2	83 7
50"	20 8	3 3	17·5	81 1	42.8	18 0	24.8	57 9	58 3	19 3	39.0	66 9
67"	20.3	3 3	17 0	83 7	43 8	16 0	27 8	63 5	60 3	25.0	35 3	58 5

DISCUSSION

The results for the net and relative Joshi-Effect in Cl_2 show the characteristic and distinctive behaviour of the gas in regard to the facility with which Joshi-Effect of large magnitude is produced. Thus the occurrence of 100% Joshi-Effect at the pressures 381 and 390 mm of Cl_2 bears out the above observation. The range of pressure, *viz.*, 55 5 – 390 mm over which chlorine continues to give the Joshi-Effect of such large magnitude is remarkable, when it is seen that most of the other systems studied, *e g.*, H_2, N_2, air, etc, show the Joshi-Effect only for a limited range of pressure, which abruptly falls off to almost zero on crossing either of the limiting pressures For example, in H_2 subjected to ozonizer excitation at 50 cycles frequency, the Joshi-Effect which is maximum at 70 mm, falls off sharply in value and vanishes outside the range 30-200 mm. In conformity with earlier findings for Cl_2 and other gases, the net effect $-\Delta i$ increases (numerically) while the relative effect, $-\%\Delta i$ decreases (numerically) with increase of applied potential. Thus, *e.g.*, at 55 5 mm (*cf* Table 1), the net Joshi-Effect at 6 68, 8 01 and 9 35 kV at 8°C is 17 3, 20 0 and 22 0 respectively, while the relative effect is 50.4, 47 8 and 44 0 respectively. Similar results are obtained at the other temperatures as well But a close examination of the results shows that, in general, the inhibitive influence of the applied potential on the production of the Joshi-Effect is greater at lower than at higher temperatures

It is also seen from the results that temperature exerts an appreciable inhibitive influence on the system in respect of its ability to show the effect It is significant that though i_b increases with temperature, i_i increases much faster than i_b with the result that both Δi and $\%\Delta i$ show a (numerical) diminution as the temperature is increased Thus, *e g.*, at 6.68 kV, the values of $-\Delta i$ at 8°, 30° and 67° are 17.3, 11 8 and 7.0 respectively, and those of $-\%\Delta i$, 50.4, 33.0 and 17.5 respectively. It may also be generalised from the data that the influence of temperature in lowering the magnitude of the Joshi-Effect is less at higher than at lower potentials.

The above observations would appear to emerge from a consideration of the general theory proposed by Joshi for the effect (Joshi, 1940, 1947, Visvanathan, 1949).

Joshi assumes that an absorption-like boundary layer s' (Joshi, 1945 *b*), ionic plus molecular, is formed on the exited walls of the ozonizer, that this layer is characterised by a low work function so as to allow of photo-electric emission even under extreme red which is insufficient to cause a direct photo-ionisation of the excited gas; that these photo-electrons are captured by the atoms and molecules of the gas, on account of their electron affinity enhanced by electrical exitation, to form negative ions which, on account of their low mobility, bring about a diminution of the discharge current as a space charge effect

It is well known that the adsorption process is exothermic and hence, according to the Le Chatelier-Braun principle of mobile equilibrium, the amount adsorbed at equilibrium should decrease with increase in temperature. This has actually been found to be the case for numerous adsorption reactions. Now, since Joshi's theory also contemplates an 'adsorption-like boundary layer (s)' (Joshi, 1945 *b*) formed by the ions and neutral molecules and atoms of the gas on the walls of the ozonizer as the chief seat of the phenomenon of the Joshi-Effect, it is to be anticipated that the adsorbed layer would be deformed or destroyed by rise of temperature, resulting in a decrease in the number of photoelectrons with the consequent reduced fall in the discharge current.

Evidence has been adduced by one of the authors (K. S. V.) in his work on the Joshi-Effect in H_2 that selective absorption, by the gas, of the incident light cannot be the cause of the Joshi-Effect. Earlier, Joshi (1945 *a*) had shown that the Joshi-Effect in Cl_2 cannot be the consequence of selective absorption of light by chlorine He observed that while chlorine absorbs selectively chiefly in the region 6400 Å to 2500 Å with a pronounced maximum at 3340 Å, the production of the effect of as much as 15% occurred in the yellow region of the spectrum (*e.g.*, radiation from a sodium vapour lamp) where absorption by chlorine is minimum and only 3.5% in the relatively more absorbed and intense red band, *viz.*, 6100 to 7100 Å. Now the following considerations would appear to furnish additional evidence to establish the absence of any relation between selective absorption of the incident light by a medium and the production of the Joshi-Effect in it.

That photochemical reactions, in general, possess temperature coefficients of small magnitude, ranging between 1.04 to 1.4 is well known. It was thought that this temperature coefficient might be due to the increased light absorption by the reacting system at the higher temperature. This led to the investigation of the influence of temperature on the absorption of light by various systems. Thus Ribaud (1919) studied the absorption of light by bromine at various temperatures. Dobbie and Fox (1921) observed in the case of chlorine an extension of absorption towards longer wavelengths at higher temperatures Later Kuhn (1926) studied the influence of temperature on absorption in the region of the band absorption spectrum around 5000 Å. It is seen from his data that the temperature coefficient of light absorption in this spectral region is 1.12 at room temperature

Thus if selective absorption of the incident light were to play any significant part in the production of the Joshi-Effect, an enhancement of the effect should be expected at higher temperatures on acount of increased light absorption. The observed decrease in the magnitude of the effect with increase of temperature, therefore, points to the conclusion that the effect is independent of any selective absorption

There are strong reasons for not identifying the 'photoelectric layer' responsible for the Joshi-Effect with that due to mere physical or chemical

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adsorption. The fact that gases like NH_1 and SO_2 which show large physical adsorption do not show the Joshi-Effect as readily and as markedly as other gases, *e.g.*, H_2, air etc. which show poor physical adsorption, discounts the possibility of any physically adsorbed layer as the seat of the phenomenon. Similary the anti correspondence between temperature and Joshi-Effect rules out chemisorption as the sole cause of the phenomenon, since chemisorption is favoured by rise of temperature. The fact that electrical exitation for various periods, *i e*, ageing, is necessary before the system develops the Joshi-Effect and that the magnitude and even the nature, *i.e*, sign of the Effect depends upon any pre-treatment given to the walls of the discharge tube, such as coating the walls with various substances, points to a " variable adsorption-like layer " (Joshi. 1945). Further electrical excitation will give rise to particles of various life periods and activity and in the absence of light, these particles deposited on the walls of the containing vessel, due to their surface activity may give rise to an " excited layer " (Joshi, 1946*a*)

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REFERENCES

Deo and Padmanabhalu, 1944, *Proc. Ind Sci Cong . Chem. Sci* , Abst. 30
Dobbie and Fox, 1921, *Proc. Rov. Soc* , A **99**, 450
Joshi and Deshmukh, 1941, *Nature*, **147**, 800
Joshi, 1943, *B. H. U. Journal*, **3**, 99
   -- , 1945, *Proc Ind. Acad Sci* , **22**, 389
    , 1945*a*, *Curr Sci.*, **14**, 317.
   -- , 1945*b*, *ibid.*, **14**, 175
   -- , 1946, *Proc Ind Sci Cong* , *Chem. Sec* , Abstract 30
   — , 1946*a*, *Curr. Sci.*, **15**, 28.
   — , 1947, *Curr Sci* , **16**, 19.
Kuhn, 1926. *Z. Physik* , **38**, 77.
Riband, 1919, *Ann. Physique*, **12**, 107.
Visvanathan, 1948, *Proc. Ind Acad Sci* , **27** 300.
    --- , 1949, *J I C S.*, **26**, 205.