INFLUENCE OF THE ELECTRODE-SURFACE ON THE JOSHI-EFFECT IN CHLORINE

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ABSTRACT. Joshi-effect was studied in 162 mm Hg pressure chlorine contained in five ozonizers of different lengths but of identical electrode diameters in the potential range 1-8 kV. Both the net and relative Joshi-effect increased by increasing the ozonizer length which is a measure of the excited electrode area. This increase shows saturation specially at low exciting potentials. The results are in accord with Joshi's theory that an adsorption-like electrode surface layer consisting of ions and electrons derived from the discharge space is a primary seat of this phenomenon.

The spectrum of chlorine under conditions productive of a large Joshi-effect Δi consisted (Joshi, 1943; Deo, 1948) almost entirely of faint bands due to Cl_2^+. The absence of any emission spectrum characteristic of atomic chlorine suggested that any reaction involving the latter was confined to the container surface. The surface sensitivity of Δi was also illustrated by the remarkable influence on its magnitude and even sign due to increase of surface to volume ratio by introducing powdered wall material in the discharge space (Shukla, 1949). This procedure, however, alters the field strength and the nature of the discharge and irradiation. It appeared, therefore, desirable to study the surface dependance of Δi under comparable conditions.

EXPERIMENTAL

Five ozonizers S_1, S_2, S_3, S_4 and S_5 (figure 1), of lengths 19.5, 15.8, 7.9, 3.1 and 1.9 cm respectively, were prepared from the same pair of glass tubes.

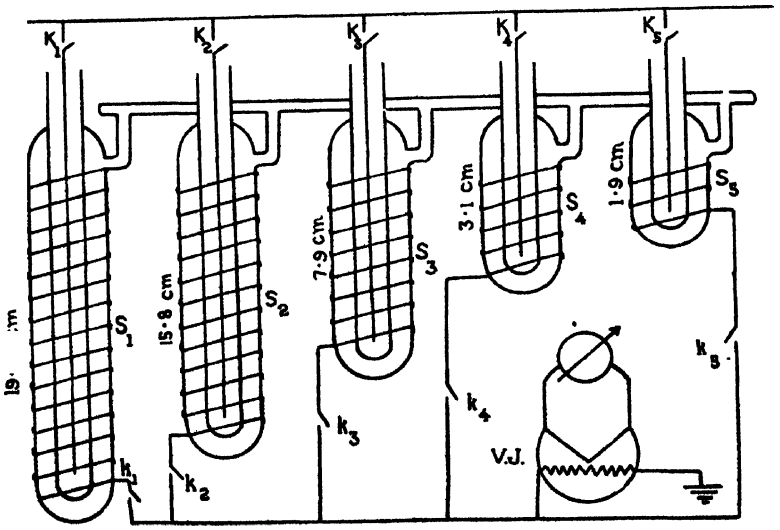

FIG. 1

They were filled carefully with purified chlorine from a given stock at the same pressure, *viz.* 162 mm Hg and excited by a transformer discharge. Each of the inner electrodes, formed with a saline solution, was connected to a common high tension line through a switch. The low tension electrodes formed with a solenoid-like winding of copper wire in well-spaced turns over the outer tubes were connected similarly to a common line which was earthed through a vacuo-junction feeding a mirror galvanometer. With a 180 volt, 200 watt bulb as the light source, the potential current characteristics V-i were observed in dark and under light, when (i) all the ozonizers S_1, S_2, S_3, S_4 and S_5 connected in parallel were excited; and when each of them (ii) S_2, (iii) S_1, (iv) S_3, (v) S_4, and (vi) S_5 was excited *separately*. The results of the observations are given in Table I (figure 2).

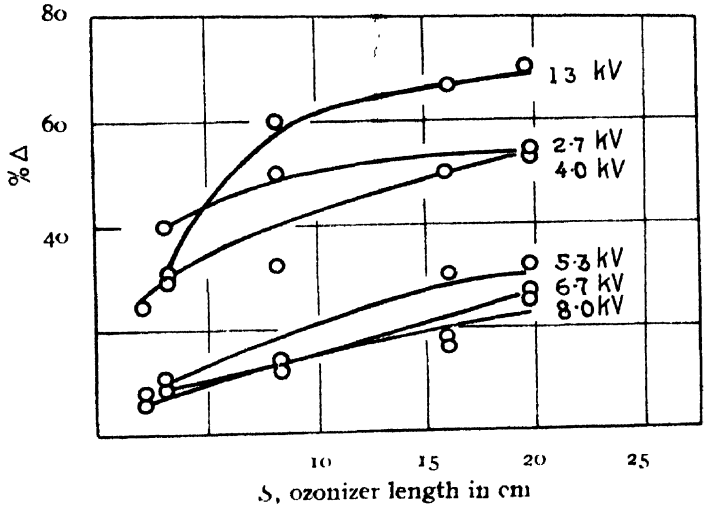

FIG. 2

TABLE I

	kV	i_{dark}	Δi	$\% \Delta i$		kV	i_{dark}	Δi	$\% \Delta i$
S_1	1.3	10	7	70	S_4	1.3			
	2.7	16	9	56		2.7	5	2	40
	4.0	20	11	55		4.0	6	2	33
	5.3	28	9	32		5.3	18	2	11
	6.7	33	9	27		6.7	21	2	9
	8.0	38	10	26		8.0	24	2	8
S_2	1.3	9	6	66	S_5	1.3			
	2.7	12	6	50		2.7			
	4.0	14	7	50		4.0	4	1	25
	5.3	24	6	25		5.3	17	1	6
	6.7	27	5	18		6.7	21	2	9
	8.0	31	4	16		8.0	23	2	8
S_3	1.3	8	5	62					
	2.7	10	5	50					
	4.0	12	4	33					
	5.3	21	3	14					
	6.7	25	3	12					
	8.0	30	4	13					

DISCUSSION

In a discharge tube of ozonizer type the entire surface is due to the electrodes. At a given applied potential, the nature of the field at the electrodes and in the gas phase, and especially the electrode asymmetry (Deb and Ghosh, 1946) determined by the ratio of the radius of the outer to that of the inner electrode is sensibly the same, *viz.* 5.5/3.3 in all the systems S_1.....S_5; the area of the electrode surface given by the ozonizer length is the only variable so far as the study of Δi is concerned. It is interesting to observe (Table I) that at a given potential, kV, applied to the ozonizer, the magnitudes of Δi and $\%\Delta i$ are in the order $S_1 > S_2 > S_3 > S_4 > S_5$. Thus, *e.g.* at 5.34 kV, the magnitudes of $\%\Delta i$ in S_1, S_2, S_3, S_4 and S_5 are respectively 32, 25, 14, 11 and 6, *i.e. ceteris paribus* the Joshi-effect increases by increasing the *net* excited surface. In each case the magnitude of Δi increases with kV, whereas, that of $\%\Delta i$ decreases, which is in accord with the generality of the results about this phenomenon (Deo, 1944; Prasad 1948).

Curves in figure 2 relate with the ozonizer length (which is a measure of the excited electrode area) the relative Joshi-effect $\%\Delta i = 100\Delta i/i$ dark. Essentially similar curves (not shown) are obtained by plotting Δi. Both Δi and $\%\Delta i$ increase by increasing the electrode surface. This increase is practically linear at large kV and slows off at smaller ones, indicative of a saturation effect. This is also brought out by considering the values of Δi and $\%\Delta i$ when all the ozonizers were connected in parallel. This is equivalent to a first approximation to a single ozonizer of area corresponding to $19.5 + 15.8 + 7.9 + 3.1 + 1.9 = 48.2$ cm. The observed Δi and $\%\Delta i$ at each of the series of applied kV for the combined system, are less than those to be anticipated by an extrapolation of the Δi and $\%\Delta i$ versus electrode length curves in figure 2, due to a saturation.

It is known (McBain, 1932) that the glass surfaces take up variable quantities of gases, and that this process may be favoured by the application of an electric field. This is illustrated by the well known clean up phenomenon, *e.g.* the hardening of the X-ray tubes. Its simplest view is that the charged ions penetrate into the wall. According to Campbell (1920, 1921, 1922, 1924) neutral atoms or excited molecules produced under the discharge also take part in the process. Since rare gases also 'clean up,' it is suggested that the reaction may be of the physical type. With reactive substances, chemo-sorption is, however, possible. Langmuir (1912, 1913, 1915, 1916, 1919) regards the 'clean up' of practically all except the inert gases as purely chemical in nature. Rodebush and Klingelhoefer (1933), working with chlorine subjected to an electrodeless high frequency discharge in a glass bulb, observed a white wall deposit attributed by them to chemosorption.

It is important to note that in all the above type of reactions the gas pressures are much lower than those now employed. An adsorption like

electrode layer would appear to be a determinant in the production of Δi. Rao (1945, 1948) observed that Δi in chlorine-air mixtures (ratio 1 : 1) decreased but little, when the system was evacuated completely with a topler (but not degassed), and the mixture was replaced by air alone at the original pressure. That the completion of this layer is a time reaction was suggested (Deo, 1945), since no sensible 'aging effect' obtained in the ozonizer after use for about one and a half years; and that when freshly prepared, Δi was found to vary appreciably with the time of exposure to the discharge. This was attributed to an interaction between the 'electrode' wall material and activated gas under the discharge. Ramanamurti (1948) observed that in a freshly prepared chlorine-filled ozonizer, the time-development of Δi follows equation for 'first order' reaction. It is suggested that the boundary layer formed during discharge is due to chemo-sorption involving electron transference (Ramanamurti, 1948).

According to Rebbeck and Furguson (1924) the electrical conductivity of glass is not affected sensibly by sorbed gases. They, in some cases, however, influence remarkably the conductivity of solids for high frequency currents, due to a change in the electrical capacity by sorption. This last might affect the accommodation coefficient, *i.e.* the degree to which reflected (Gregg, 1933) particle adjusts its energy to the reflecting surface. It is difficult to envisage how these processes would cause a large change in the *relative* Joshi-effect by variation of the electrode area $S_1 \ldots S_n$. Formation of an adsorption layer under discharge appears to be fairly certain as the first stage in the production of Δi. The subsequent stages according to Joshi (1946, 1947), are the emission of electrons under irradiation from this layer; and their subsequent capture by chlorine atoms resulting in the slow negative ions, causing Δi as a space charge effect.

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