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WALL INFLUENCE IN THE PRODUCTION OF THE JOSHI EFFECT IN CHLORINE UNDER SILENT ELECTRIC DISCHARGE

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INTRODUCTION

The essentially surface origin of the Joshi effect (5, 6, 7, 13, 15, 16), defined as a practically instantaneous and reversible photovariation $\mp\Delta i$ of the conductivity i under electrical discharge, was inferred by Joshi (12, 13) from the pronounced influence, on both the magnitude and sign of Δi, of the nature of the excited surface (1, 6, 9, 11) and of 'aging' (3, 4, 5, 9) under the discharge. Joshi observed that a positive effect ($+\Delta i$) in, for example, chlorine under a "normal" ozonizer discharge, is detectable only within restricted conditions and special means (*vide infra*); it is, however, larger and more easily produced when the annular space is filled with powdered glass, indicative of a "wall effect" (13). This has obvious significance for a general mechanism of Δi. It appeared desirable, therefore, to compare in some detail the Joshi effect under a "normal" discharge and that subject to wall influence.

DESCRIPTION OF APPARATUS AND METHOD

The apparatus and circuit employed are shown in figure 1. Single-phase alternating current of 50 cycles frequency was obtained from a rotary convertor from 220-v. D. C. mains. Its A.C. output was fed to the primary of a high-tension (H.T.) transformer. One of its secondaries was earthed; the other was connected to the inner electrode (formed with sodium chloride solution) of the discharge tube in either of its positions shown in figure 1. The discharge tube, filled with purified chlorine at an optimum pressure of 170 mm. in respect of the effect Δi, and the wall material in the divided form, was designed and kindly prepared by Professor Joshi. It could be used without disturbing the operative conditions, in two ways: When the powdered wall material was outside the discharge region (N);

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this is "normal" discharge. Then by mere inversion of the discharge tube, the whole wall material could be brought into the discharge region (*IV*, figure 1). The discharge now is "wall influenced." The ozonizer had a solenoid-like copper wire, wound tightly over the annular space; this formed the low-tension (L.T.) electrode. The capacity of the system between this low-tension electrode and the inner one in the "normal" position was about 6 $\mu\mu$ farads. On inverting it, so that the powdered glass collected in the annular space, the capacity increased to 16 $\mu\mu$ farads. The low-tension electrode was earthed through one of the various detectors, each connected to the galvanometer G. The detectors used were a vacuum junction, a double diode 6H6 (RCA), and a triode 30 (RCA). In almost

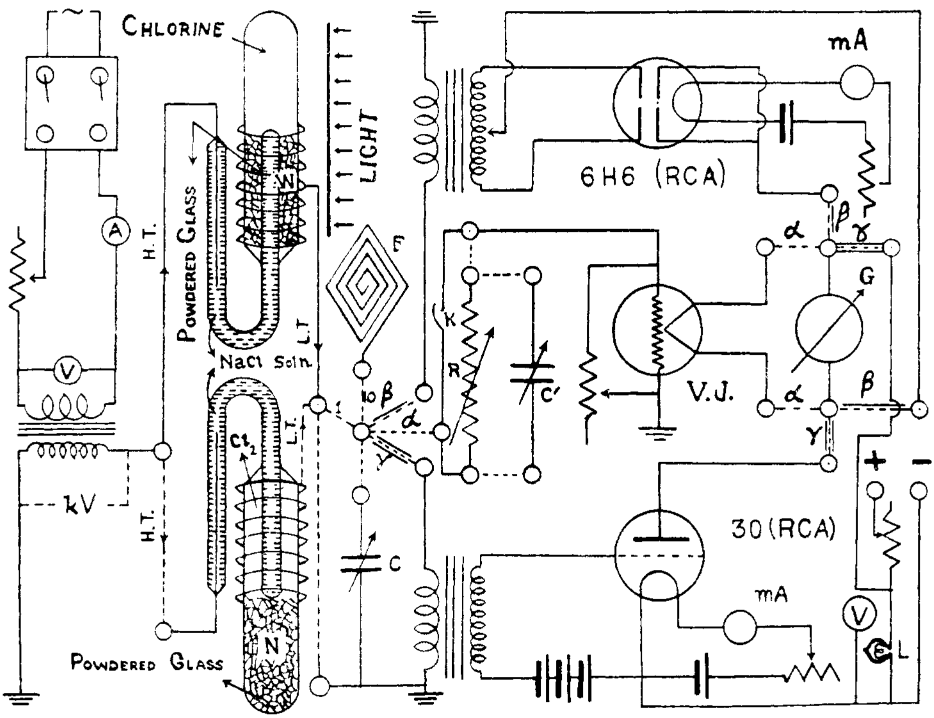

FIG. 1. Wall influence on the Joshi effect in chlorine; design of apparatus

all cases of the "normal" and the "wall-influenced" discharges, two series of current observations were made: (*1*) when the detector was introduced in the low-tension line and (*2*) when connected to a small-size frame aerial (F), about 3 ft. from the ozonizer. The system was excited in the range 8–14 kv. (kilovolts, r.m.s.). For irradiating the discharge tube, a 200-watt, 200-volt (glass) bulb was used, screened by a shutter. The galvanometer deflections in the case of valve detectors indicate the corresponding current i in arbitrary units; with vacuum junction, they are proportional to i^2, and shown within brackets below the corresponding i. The discharge currents in the dark (i_D) and in the light (i_L) were measured at different applied potentials, under various conditions of excitation

... produced "normally" and under "wall influence"

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
	PHENOMENON IN LOW-TENSION LINE								PHENOMENON IN AERIAL LINE							
POTENTIAL	Detector, 10 ma. vacuum junction Gas only, in the discharge space				Detector, 10 ma. vacuum junction Gas + wall material in the discharge space				Detector, 10 ma. vacuum junction Gas only, in the discharge space				Detector, 2.5 ma. vacuum junction Gas + wall material in the discharge space			
	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi
kv.																
8	3.16 (10)	2.24 (5)	−0.92	−29.1	2.35 (5.5)	1.23 (1.5)	−1.12	−47.7	1.73 (3)	1.00 (1)	−0.73	−42.2				
8.5	4.80 (23)	4.12 (17)	−0.68	−14.2	3.16 (10)	1.73 (3)	−1.43	−45.3	2.55 (6.5)	1.73 (3)	−0.82	−32.2	2.45 (6)	1.41 (2)	−1.04	−42.4
9.1	7.35 (54)	6.25 (39)	−1.10	−15.0	4.36 (19)	3.32 (11)	−1.04	−23.9	3.87 (15)	2.45 (6)	−1.42	−36.6	3.74 (14)	3.46 (12)	−0.28	−7.5
9.6	8.60 (74)	7.48 (56)	−1.12	−13.0	7.14 (51)	7.62 (58)	+0.48	+6.7	5.20 (27)	3.00 (9)	−2.20	−42.3	8.25 (68)	9.22 (85)	+0.97	+10.5
10.2	9.64 (93)	8.66 (75)	−0.98	−10.2	12.17 (148)	12.49 (156)	+0.32	+2.6	6.00 (36)	3.46 (12)	−2.54	−42.3	13.41 (180)	14.00 (195)	+0.59	+4.4
10.7	10.91 (119)	9.64 (93)	−1.27	−11.6	17.89 (320)	18.08 (327)	+0.19	+1.1	6.40 (41)	3.61 (13)	−2.79	−43.6	17.89 (320)	18.30 (335)	+0.41	+2.2
11.2	11.87 (141)	10.53 (111)	−1.34	−11.3	21.21 (450)	20.79 (432)	−0.42	−1.9	6.93 (48)	3.74 (14)	−3.19	−46.0	21.68 (470)	21.93 (481)	+0.25	+1.2
11.8	12.41 (154)	11.09 (123)	−1.32	−10.6	23.37 (546)	22.93 (526)	−0.44	−1.9	7.75 (60)	4.00 (16)	−3.75	−48.4	24.17 (584)	24.39 (595)	+0.22	+0.9
12.3	13.00 (169)	11.36 (129)	−1.64	−12.6	25.61 (656)	25.12 (631)	−0.49	−1.9	8.19 (67)	4.12 (17)	−4.07	−49.7				
12.8	13.34 (178)	11.75 (138)	−1.59	−11.9					8.60 (74)	4.24 (18)	−4.36	−50.7				

TABLE 2

Comparative Joshi effect with diode and triode detection, produced under "wall influence"

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
	DETECTOR, DIODE 6H6 (RCA)								DETECTOR, TRIODE 30 (RCA)							
POTENTIAL	Phenomenon in low-tension line				Phenomenon in aerial line				Phenomenon in low-tension line				Phenomenon in aerial line			
	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi
kv.	*ma.*	*ma.*	*ma.*						*ma.*	*ma.*	*ma.*					
8	0.044	0.032	−0.012	−27.3	3.5	2.0	−1.5	−42.9	0.079	0.033	−0.067	−58.2				
8.5	0.066	0.046	−0.030	−30.3	5.0	3.5	−1.5	−30.0	0.129	0.069	−0.060	−46.5				
9.1	0.096	0.066	−0.030	−31.3	8.0	7.0	−1.0	−12.5	0.205	0.135	−0.070	−34.1				
9.6	0.130	0.104	−0.026	−20.0	15.0	18.0	+3.0	+20.0	0.309	0.229	−0.080	−25.9				
10.2	0.184	0.158	−0.026	−14.1	45.0	48.0	+3.0	+6.7	0.504	0.404	−0.120	−19.9				
10.7	0.248	0.208	−0.040	−16.1	77.0	81.0	+4.0	+5.2	0.659	0.529	−0.130	−19.7	57.0	54.0	−3.0	−5.3
11.2	0.300	0.252	−0.048	−16.0	99.0	102.0	+3.0	+3.0	0.779	0.639	−0.140	−18.0	65.0	60.0	−5.0	−7.7
11.8	0.337	0.282	−0.055	−16.3	138.0	141.0	+3.0	+2.2	0.859	0.709	−0.150	−17.5	78.0	73.0	−5.0	−6.4
12.3	0.372	0.312	−0.060	−16.1	167.0	171.0	+4.0	+2.4	0.939	0.769	−0.170	−18.1	91.0	85.0	−6.0	−6.5
12.8	0.402	0.337	−0.065	−16.2	205.0	210.0	+5.0	+2.4	1.019	0.839	−0.180	−17.7	113.0	107.0	−6.0	−5.3
13.4	0.437	0.367	−0.070	−16.0	235.0	240.0	+5.0	+2.1	1.099	0.899	−0.200	−18.2	140.0	132.0	−8.0	−5.7

and detection. The difference $i_D \sim i_L$ gives the net Joshi effect; its relative value $100\Delta i/i_D$ = per cent Δi is suitable for comparison.

In experiments referred to in table 1, the currents i_D and i_L were measured with a vacuum junction (V.J., figure 1). In the first series, the low-tension line

TABLE 3

Potential variation with a constant resistive impedance of the "normal" and "wall-influenced" Joshi effect in the low-tension line

Resistance of 5,000 A introduced in series with the low-tension line

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
POTENTIAL	GAS ONLY, IN THE DISCHARGE SPACE DETECTOR, 10 MA. VACUUM JUNCTION				GAS + WALL MATERIAL IN THE DISCHARGE SPACE DETECTOR, 50 MA. VACUUM JUNCTION			
	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi
kv.								
8	2.00 (4)	1.73 (3)	−0.27	−13.5	1.00 (1)	0.71 (0.5)	−0.29	−29
8.5	2.92 (8.5)	2.65 (7.0)	−0.27	−9.2	1.41 (2)	0.71 (0.5)	−0.70	−49.6
9.1	4.36 (19)	3.87 (15)	−0.49	−11.2	1.87 (3.5)	1.00 (1.0)	−0.87	−46.5
9.6	5.29 (28)	4.80 (23)	−0.49	−9.3	2.45 (6)	2.00 (4)	−0.45	−18.4
10.2	5.83 (34)	5.39 (29)	−0.44	−7.5	3.54 (12.5)	3.00 (9)	−0.54	−15.2
10.7	6.04 (36.5)	5.52 (30.5)	−0.52	−8.6	3.74 (14)	3.08 (9.5)	−0.66	−17.6
11.2	6.48 (42)	5.92 (35)	−0.56	−8.6	5.75 (33)	5.15 (26.5)	−0.60	−10.4
11.8	6.71 (45)	6.16 (38)	−0.55	−8.2	6.48 (42)	5.83 (34)	−0.65	−10.0
12.3	6.96 (48.5)	6.40 (41)	−0.56	−8.0	7.07 (50)	6.33 (40)	−0.74	−10.4
12.8	7.18 (51.5)	6.63 (44)	−0.55	−7.6	7.62 (58)	6.86 (47)	−0.76	−10.0

was connected to 1, α, and the key K, for both "normal" and "wall" discharges. The results are shown in columns 2–9. The low-tension line was now earthed. The aerial (F), 2, α, and K were connected. The results are shown in columns 10–17 for both the discharges.

A comparative study of the Joshi effect in a "wall" discharge, with diode and triode detections, was made in both the low-tension and the aerial currents. For the former the low tension was connected with 1, β, and the primary of a Bell transformer. Its secondaries were connected separately to the anodes of the diode. The cathodes, heated indirectly through the filament, were connected together through a milliammeter to the center of the secondary of the Bell transformer (step-up ratio 1:2). In using triode 30, the low tension was connected with 1, γ, and the primary of another iron core transformer of step-up ratio 1:3. For observing the effect in the aerial current, the low-tension line was earthed as before, and the connections made through 2, β for the diode and 2, γ for the triode. The rest of the circuit for the two valves was exactly the same as when working

TABLE 4

Variation with resistive impedance of the "normal" Joshi effect in low-tension circuit at a constant potential

Resistances introduced in series with the low-tension line; detector, 10 ma. vacuum junction; applied potential, 9.6 kv.

(1) R	(2) i_D	(3) i_L	(4) Δi	(5) PER CENT Δi
ohms				
0	10.04 (101)	8.66 (75)	−1.38	−13.7
100	9.54 (91)	8.18 (67)	−1.36	−14.3
1,000	7.75 (60)	6.93 (48)	−0.82	−10.6
3,000	5.92 (35)	5.2 (27)	−0.72	−12.2
4,000	5.34 (28.5)	4.80 (23)	−0.54	−10.1
5,000	5.2 (27)	4.9 (24)	−0.30	−5.8

in the low-tension part of the discharge current. The values of i_D, i_L, Δi, and per cent Δi obtained at various exciting potentials are shown in table 2.

In experiments referred to in tables 3 to 8 the vacuum junction was used as a detector in either the low-tension or/and the aerial line. Table 3 records observations of the Joshi effect with both "normal" and "wall" discharge with a 5000 Ω dublier resistance in the low-tension line by connecting 1, α, and R. Experiments were next made at a constant exciting potential, *viz.*, 9.6 kv., the above resistance in the low-tension line being varied from 100 to 5,000 Ω. Table 4 gives a typical group of these results with a "normal" discharge.

A more detailed study of the influence of a resistance, varied over the range

TABLE 5

Comparative variation with resistive impedance, in the low-tension and aerial currents, of the Joshi effect under "wall influence"

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
	RESISTANCES INTRODUCED IN SERIES WITH THE LOW TENSION LINE DETECTOR, 10 MA. VACUUM JUNCTION									RESISTANCES INTRODUCED IN SERIES WITH THE AERIAL LINE DETECTOR, 2.5 MA. VACUUM JUNCTION							
R	At 8.5 kv.				At 9.6 kv.				R	At 8.5 kv.				At 9.6 kv.			
	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi		i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi
ohms									*ohms*								
0	8.72 (76)	4.69 (22)	−4.03	−46.3	24.33 (592)	25.34 (642)	+1.01	+4.2	0	6.71 (45)	2.83 (8)	−3.88	−57.8	23.45 (550)	24.97 (623)	+1.52	+6.4
500	7.07 (50)	3.87 (15)	−3.20	−45.3	15.87 (252)	15.39 (237)	−0.48	−3.0	100	6.33 (40)	2.65 (7)	−3.68	−58.1	23.47 (551)	24.35 (593)	+0.88	+3.7
1,000	6.33 (40)	3.74 (14)	−2.59	−40.9	13.86 (192)	13.19 (174)	−0.67	−4.8	200	5.83 (34)	2.45 (6)	−3.38	−58.0	20.74 (430)	21.89 (479)	+1.15	+5.5
2,000	5.48 (30)	3.32 (11)	−2.16	−39.4	10.39 (108)	9.59 (92)	−0.80	−8.0	300	5.39 (29)	2.24 (5)	−3.15	−58.4	19.92 (397)	20.57 (423)	+0.65	+3.2
3,000	5.00 (25)	3.00 (9)	−2.00	−40.0	9.33 (87)	8.37 (70)	−0.96	−10.3	400	5.00 (25)	2.12 (4.5)	−2.88	−57.6	18.57 (345)	19.42 (377)	+0.85	+4.6
4,000	4.69 (22)	2.83 (8)	−1.86	−39.6	8.19 (67)	7.35 (54)	−0.84	−10.3	500	4.80 (23)	2.00 (4)	−2.80	−58.3	18.00 (324)	18.61 (346)	+0.61	+3.4
5,000	4.47 (20)	2.65 (7)	−1.82	−40.7	7.94 (63)	7.00 (49)	−0.94	−11.8	600	4.47 (20)	1.87 (3.5)	−2.60	−58.2	17.23 (297)	17.86 (319)	+0.63	+3.6
10,000	3.61 (13)	2.24 (5)	−1.37	−38.0	5.92 (35)	5.20 (27)	−0.72	−12.2	700	4.12 (17)	1.73 (3)	−2.39	−58.0	15.9 (253)	16.28 (265)	+0.37	+2.3
15,000	3.16 (10)	2.00 (4)	−1.16	−36.7	5.29 (28)	4.58 (21)	−0.71	−13.4	800	4.00 (16)	1.73 (3)	−2.27	−56.6	14.93 (223)	15.52 (241)	+0.59	+4.0
20,000	3.00 (9)	2.00 (4)	−1.00	−33.3	5.10 (26)	4.42 (19.5)	−0.68	−13.3	900	3.81 (11.5)	1.58 (2.5)	−2.23	−58.5	14.49 (210)	15.00 (225)	+0.51	+3.6
25,000	2.92 (8.5)	2.00 (4)	−0.92	−31.5	4.58 (21)	4.00 (16)	−0.58	−12.7	1,000	3.67 (13.5)	1.58 (2.5)	−2.09	−56.9	14.18 (201)	14.93 (223)	+0.75	+5.3

100–25,000 Ω introduced in the low-tension and also in the aerial line, was next made with "wall" discharge due to 8.5 and 9.6 kv. The reason for selecting these

TABLE 6

Influence of the high-frequency filtration on the potential variation of the "wall-influenced" Joshi effect in the low-tension and aerial currents

Capacity of the high-frequency filter = 0.1 μ farad

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
POTENTIAL	PHENOMENON IN THE LOW-TENSION CURRENT DETECTOR, 50 MA. VACUUM JUNCTION				PHENOMENON IN THE AERIAL CURRENT DETECTOR, 2.5 MA. VACUUM JUNCTION			
	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi
kv.								
8	1.23 (1.5)	0.71 (0.5)	−0.52	−42.3				
8.5	1.58 (2.5)	0.71 (0.5)	−0.87	−55.1				
9.1	2.00 (4)	1.23 (1.5)	−0.77	−38.5				
9.6	3.08 (9.5)	2.92 (8.5)	−0.16	−5.2	1.41 (2.0)	1.58 (2.5)	+0.17	+12.1
10.2	4.85 (23.5)	4.64 (21.5)	−0.21	−4.3	2.12 (4.5)	2.24 (5.0)	+0.12	+5.7
10.7	6.36 (40.5)	6.12 (37.5)	−0.24	−3.8	2.83 (8.0)	2.92 (8.5)	+0.09	+3.2
11.2	7.38 (54.5)	6.96 (48.5)	−0.42	−5.7	3.24 (10.5)	3.32 (11.0)	+0.08	+2.5
11.8	8.09 (65.5)	7.65 (58.5)	−0.44	−5.4	3.46 (12.0)	3.54 (12.5)	+0.08	+2.3
12.3	8.69 (75.5)	8.22 (67.5)	−0.47	−5.4	3.74 (14.0)	3.81 (14.5)	+0.07	+1.8
12.8	9.41 (88.5)	8.80 (77.5)	−0.61	−6.5	4.00 (16.0)	4.06 (16.5)	+0.06	+1.5
13.4	10.02 (100.5)	9.41 (88.5)	−0.61	−6.1	4.24 (18.0)	4.30 (18.5)	+0.06	+1.4

potentials is explained later. The connections were R$_{,}\alpha$ with 1 for the low-tension line, and with 2 for the aerial line.

Tables 6 and 7 refer chiefly to the influence of a by-pass capacity C (figure 1), in the low-tension and the aerial lines, on the corresponding Joshi effect in a "wall" discharge. The connections were 1, α, and K, which is by-passed by C, for the low-tension line; it was 2, α, K and the same by-pass C for the aerial line (table 6). The circuit was next altered to 1, α, R, and the above by-pass capacity

TABLE 7

Influence of the high-frequency filtration and resistive impedance in the low-tension line on the Joshi effect produced under "wall influence"

Value of the resistance.............................. 5,000 ohms
Capacity of the high-frequency filter................ 0.1 μ farad
Detector... 50 ma. vacuum junction

(1) POTENTIAL	(2) i_D	(3) i_L	(4) Δi	(5) PER CENT Δi
kv.				
8	1.00 (1)	0.71 (0.5)	−0.29	−29.0
8.5	1.23 (1.5)	0.71 (0.5)	−0.52	−42.2
9.1	1.41 (2)	1.00 (1)	−0.41	−29.1
9.6	1.87 (3.5)	1.41 (2)	−0.46	−24.6
10.2	2.65 (7)	2.00 (4)	−0.65	−24.5
10.7	3.32 (11)	2.83 (8)	−0.49	−14.7
11.2	3.87 (15)	3.32 (11)	−0.55	−14.2
11.8	4.36 (19)	3.67 (13.5)	−0.69	−15.8
12.3	4.74 (22.5)	4.00 (16)	−0.74	−15.6
12.8	5.10 (26)	4.36 (19)	−0.74	−14.5
13.4	5.48 (30)	4.69 (22)	−0.79	−14.4

C. The latter data show the combined influence of a serial resistance (R) and a by-pass capacitance (C) in the low-tension line (table 7).

The above observations were continued, of which table 8 represents but one typical group. The discharge used was "wall influenced" and due to 8.5 and 9.6 kv.; the effect Δi was studied in both the low-tension and the aerial currents. Connections were 1, α, R with a parallel C′ for the low-tension line and 2, α, R with parallel C′ for the aerial line (see figure 1).

TABLE 8

Variation, with a resistance and capacitance in the low-tension and aerial circuits, of the Joshi effect produced under "wall influence"

Resistance = 500 Λ, introduced in series with the low-tension or the aerial circuit; capacitance = 3 μ farads, put in parallel to the above resistance

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	AT 8.5 KV.				AT 9.6 KV.			
CONDITION OF THE CIRCUIT	i_D	i_L	Δi	Per cent Δi	i_D	i_L	Δi	Per cent Δi
Phenomenon in low-tension circuit; detector, 10 ma. vacuum junction								
(a) No resistance or capacitance	9.64	5.10	−4.54	−47.1	22.63	23.47	+0.84	+3.7
	(93)	(26)			(512)	(551)		
(b) Only 500 Λ resistance........	7.62	4.24	−3.38	−44.3	14.39	13.82	−0.57	−4.0
	(58)	(18)			(207)	(191)		
(c) 500 Λ resistance + 3 μ farads capacitance................	9.38	5.00	−4.38	−46.7	22.20	23.09	+0.89	+4.0
	(88)	(25)			(493)	(533)		
Phenomenon in aerial circuit; detector, 2.5 ma. vacuum junction								
(a) No resistance or capacitance..	7.35	3.16	−4.19	−57.0	24.64	25.84	+1.20	+4.9
	(54)	(10)			(607)	(668)		
(b) Only 500 Λ resistance........	4.80	2.24	−2.56	−53.3	14.76	15.49	+0.73	+4.9
	(23)	(5)			(218)	(240)		
(c) 500 Λ resistance + 3 μ farads capacitance................	7.42	3.32	−4.10	−55.3	25.73	27.00	+1.27	+4.9
	(55)	(11)			(662)	(729)		

DISCUSSION

Results in table 1 show that in a "normal" discharge in chlorine a negative Joshi effect of 10–30 per cent is produced in the conductivity in the low-tension (L.T.) line over the potential range 8–12 kv. The corresponding effect Δi observed in currents picked up by a low-capacity aerial is much larger, *viz.*, 42–51 per cent. This agrees with a general result due to Joshi (8, 11) that $-\Delta i$ is associated preferentially with the high-frequency part of the discharge current, which has been substantiated by results (2, 18) in a number of systems studied in these laboratories. The data in table 4 show that at 9.6 kv. the Joshi effect diminishes (numerically) from 14 to 6 per cent as the value of a non-inductive and non-capacitative resistance (R) in the low-tension line is increased progressively from 100 to 5000 Ω. The same inhibitive influence due to a constant R = 5000 Ω is noticeable over the potential range 8–12.8 kv., as shown by data in columns 1–5 of table 3.

Joshi (11, 17) considers that the high frequencies are suppressed preferentially by an ohmic resistance. The inhibition, therefore, of the negative Joshi effect by R, as observed, follows.

The rest of the data in tables 1 to 8 refer to the "wall" discharge, obtained by filling up the ionization space with powdered glass. It is instructive to compare the characteristic curves in figures 2 and 2a for part of the data in table 1. Under the "normal" discharge, the general shape of V–i curves (aerial) differs sensibly from that in the low-tension line. This relative difference is much less marked between the corresponding pairs under the "wall" discharge. This is further

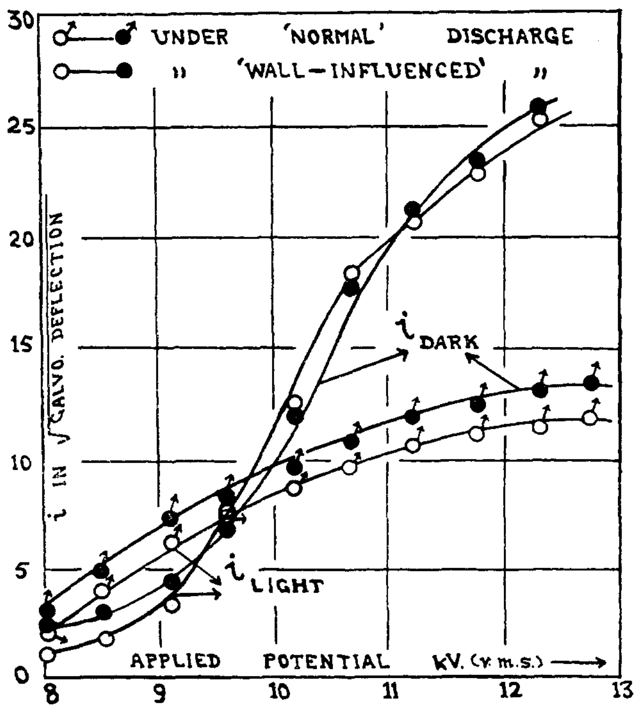

FIG. 2. Potential variation of i_D and i_L in the low-tension line under "normal" and "wall-influenced" discharges.

brought out by curves in figure 3. It is seen that in contrast with per cent Δi *versus* potential curves for $i_{L.T.}$ and i_{aerial} for the "normal" discharge, the per cent Δi for the "wall" discharge starts with large negative values and decreases rapidly to a positive maximum, for both $i_{L.T.}$ and i_{aerial}. From an examination of curves (not shown) similar to those mentioned above, for data in tables 2 to 8, it is found that under "wall effect" the behavior of $i_{L.T.}$ with respect to per cent Δi becomes closely similar to i_{aerial}. An outstanding feature of these data for the "wall" discharge is the widespread occurrence of the positive Joshi effect, *viz.*, a photoincrease ($+\Delta i$) of the discharge current i in both $i_{L.T.}$ and i_{aerial} at large exciting potentials. This deviates from Joshi's general result (16), deduced for "normal" discharges while working on an audio-representation of Δi, that the positive effect sets in at low V and over a small range of the exciting potential. It may also be emphasized that a large positive effect under "normal" discharge in iodine vapor in the presence of an annular film of KI_3 + KI was observed early during work in this field by Joshi (6). This positive effect, however, was found to be affected by "aging" under the discharge; "aging" produced irreversibly the more familiar negative Joshi effect. Under present conditions, however—and this may be emphasized to be a characteristic of the amplified "wall" effect—the transition $+\Delta i$ to $-\Delta i$, and conversely, is reversible and reproducible *ad libitum*.

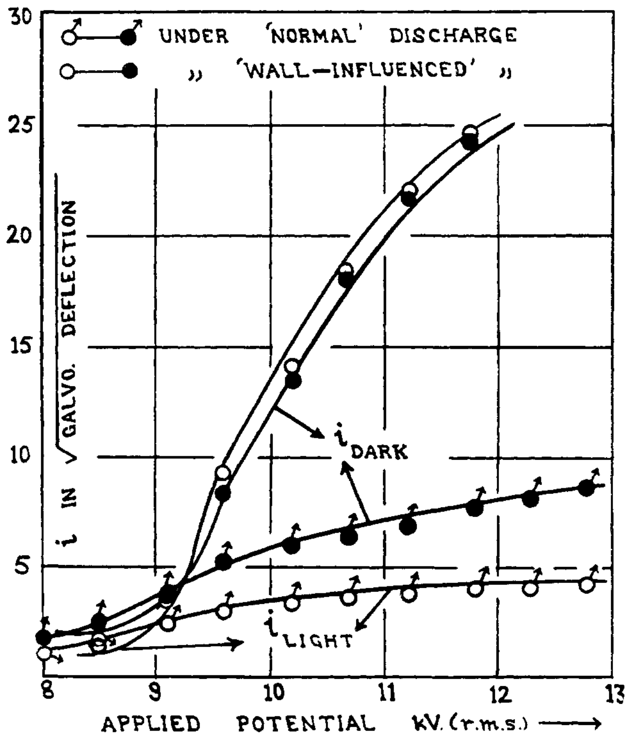

FIG. 2a. Potential variation of i_D and L_L in the aerial line under "normal" and "wall-influenced" discharges.

This remark applies also to potential inversion $-\Delta i \rightleftharpoons +\Delta i$ at both the positions, *viz.*, 9.2 kv. and 11 kv. on the $i_{L.T.}$ curve (*cf.* figure 3, curve III) and 9.2 kv. only on the i_{aerial} curve. It is also significant that these inversion potentials remain constant under a variety of conditions corresponding to tables 2 to 8.

The circumstance that the above results were obtained under vacuum junction detection has interest, since Joshi (6) observed the positive effect in iodine with a selective detector like an oxide rectifier and failed to do so with a vacuum junction, using "normal" discharge. Joshi (6, 10) has also emphasized the importance of the nature of the detector as a determinant of Δi. This factor has now been investigated, using a diode and a triode (worked for anode-bend rectification) introduced in both the low-tension and the aerial circuits for the "wall" discharge. The results with the diode show that whilst the negative Joshi effect diminishes (numerically) from -27 to -16 as the potential increases progressively from 8 to 13.4 kv., that in i_{aerial} is sensibly larger, about 43 per cent at the lowest $V = 8$ kv. This is to be anticipated, since i_{aerial} is richer in high frequencies than that in the low-tension line. As the potential is increased, however, per cent Δi decreases (numerically) rapidly and inverts to the *positive* Joshi effect. The triode records much larger (numerically) $-$per cent Δi, *viz.*, 58 per cent which decreases with the potential. The dependence of Δi on the nature of

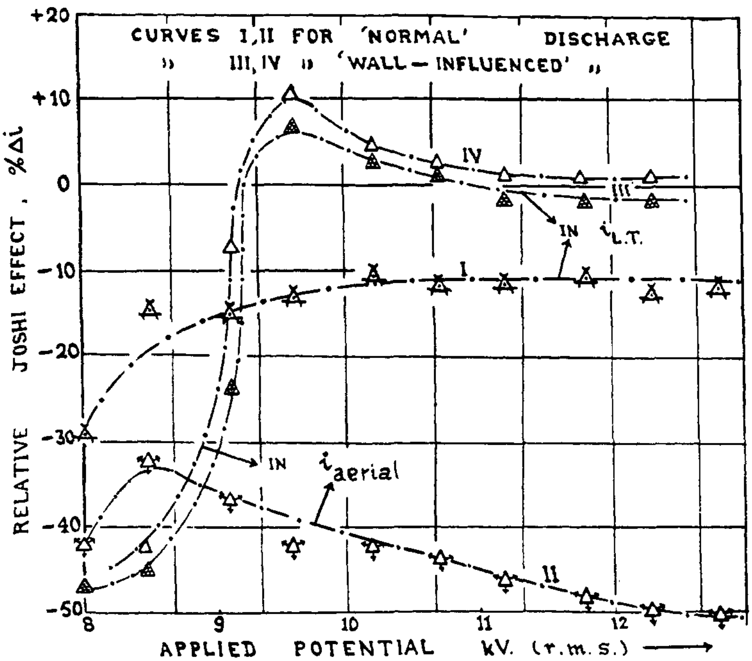

FIG. 3. Relative Joshi effect (per cent Δi) in $i_{\text{L.T.}}$ and i_{aerial} under "normal" and "wall-influenced" discharges.

the detector is brought out in the last vertical column in table 2, which shows only a negative Joshi effect in i_{aerial} even at large potential, where $+\Delta i$ was noted with a vacuum junction and a diode; the discharge was "wall influenced" in all these cases. It may be noted here that the inversion potential observed in i_{aerial} with the diode is the same, *viz.*, 9.2 kv. obtained under vacuum junction detection.

The influence of a serial resistance or of a by-pass capacitance is simplest for current in the aerial line, even in a "wall" discharge. The above factors but diminish the i_D and i_L; the corresponding relative Joshi effect per cent Δi, both positive and negative (*cf.* tables 5, 6 in part), is not affected sensibly. However, in $i_{L.T.}$, compared with the "normal" discharge, the influence of the resistive and reactive impedances is more complex under the "wall" discharge. This is chiefly due to the circumstance that at large potential a reversal occurs from a negative to a positive Joshi effect. In the lower potential range, where only the negative effect ($-\Delta i$) occurs, the influence of R is to decrease $-$per cent Δi numerically, as observed in "normal" discharge. A comparison of data in tables 3 and 4 with those in table 1 shows, however, that this inhibitive effect of the serial R at low potential is less pronounced than that observed in "normal" discharge. It is found that the "wall" discharge differs from the "normal" one chiefly in the general result that the former yields the positive Joshi effect at large enough potential. Studies were therefore made of the influence of both the resistive and the capacitative impedances, especially in this region of large potential, characteristic of $+\Delta i$. Tables 3 and 5, in part, record results for the influence of a serial R on current in the low-tension line. It is seen that the positive Joshi effect observed at large potential under "wall" discharge is eliminated by introducing R. It is suggested tentatively that in a "wall" discharge, at large applied potentials, there are produced besides the high frequencies, which are the chief seat of the negative effect, $-\Delta i$ (8, 11), a group of greater high frequencies in which latter the positive Joshi effect occurs and that both the negative and positive Δi occur simultaneously in these moderate high frequencies and the super high frequencies, respectively. The introduction in the path of the discharge current of the resistance R suppresses preferentially the super high frequencies and therefore eliminates the corresponding associated positive effect. It follows, therefore, that at any rate in a "wall" discharge, owing to the coproduction of the moderate and the super high frequencies and therefore of the associated $-\Delta i$ and $+\Delta i$, one observes the resultant; this last is smaller (numerically) than the larger of the $+\Delta i$ and $-\Delta i$ produced together. If the super high frequencies (and therefore the associated $+\Delta i$) are eliminated, say by suppression with the resistance R, the negative effect ($-\Delta i$) now left over is anticipated to be larger than that observed in the absence of R. This has been actually noticed. Thus, e.g., in the absence of R, over 11.2–13.4 kv., the effect $-$per cent Δi is about 2 (*cf.* column 9, table 1), as against 10 per cent with 5000 Ω (column 9, table 3). The above deduction is further supported by data in columns 6–9 of table 5, which show that excitation at 9.6 kv. gives a positive Joshi effect of $+4.2$ per cent in the absence of R. By increasing R from 500 to 25,000 Ω at the constant 9.6 kv., the effect observed increases (numerically) from -3 per cent to -12 per cent. It may also be mentioned that the simultaneous occurrence of $\pm\Delta i$ at different phase positions in the discharge current has been observed by Joshi in chlorine under semi-ozonizer excitation (13).

Introduction of a by-pass capacity (0.1 μ farad, C in figure 1) which should filter off the super high frequencies and therefore, on the above suggestion, the $+\Delta i$, should give a numerically enhanced $-$per cent Δi. The results in columns 1–5 of table 6 show that this is so in $i_{L.T.}$. The combined effect of a serial resistance R and a by-pass capacity C should be to eliminate more completely the super high frequencies and so $+\Delta i$, thereby yielding greater $-\Delta i$. The data in table 7, showing the comparatively largest $-$per cent Δi, are in full accord with the above deductions.

Results of experiments returned in table 8 give further support to the hypothesis that super high frequencies may be a seat of the positive Joshi effect. From general results illustrated by table 1, two potentials 8.5 and 9.6 kv., which produced respectively a negative and a positive Joshi effect, were chosen. At the former potential, in the absence of R, $-$per cent Δi is 47.1 owing to moderate high frequencies. Suppression of these last by $R = 500\ \Omega$ reduces the above $-$per cent Δi to 44.3; a condenser C′ (0.1 μ farad) across R by-passes the moderate high frequencies, with the result that $-$per cent Δi is 46.7, which is almost restoration to the initial value in the absence of R. Similarly, conversion of a positive Joshi effect at 9.6 kv. to the negative Joshi effect by the serial resistance R, and its reproduction due to the above condenser (C′ in figure 1), substantiates the proposed mechanism for the production of the positive effect. It may be emphasized that, as observed in both the low-tension and the aerial lines, the two inversion potentials in the former and only one in the latter remain unaltered despite the introduction of R and C′ (see figure 1).

The following equation for the instantaneous ozonizer current, i, is due to Joshi (13):

$$i = \frac{V}{jL\Sigma f + \dfrac{1}{jC_w\Sigma f} + \dfrac{1}{\dfrac{1}{R_g} + jC_g\Sigma f}} \tag{1}$$

where Σf represents the equivalent of the components of the discharge frequency including that of the A.C. supply and its harmonics, R_g is the inverse of the conductivity produced in the gas as a result of ionization at an applied potential V, C_g is the capacity of the annular space occupied by the gas, and C_W is the combined capacity due to the inner and outer electrodes of the ozonizer, shown by C_1 and C_2, respectively ($C_W = C_1 \cdot C_2/C_1 + C_2$).

V in the dark and in light is the same. The negative Joshi effect originates therefore from a decrease of the conduction current $1/R_g$ or/and of C_W and C_g. The positive effect may be associated with an increase of the above quantities under light. Joshi (12, 13) has postulated that a boundary layer, derived in part from an adsorption of the ions and molecules from the discharge space, is the seat of the effect $\mp\Delta i$. Irradiation releases electrons from this boundary layer. These electrons are captured by chlorine (atoms especially, whose electron affinity is enhanced due to excitation) to form the slow moving negative ions (12). This should reduce the conduction current $1/R_g$ in equation 1 and lead to the negative effect $-\Delta i$. Joshi (12, 13) considers that $-\Delta i$ might also originate as a space charge effect, due to the accumulation of negative ions near the (momentary) cathode. The increase in the relative surface by introducing the powdered wall material should enhance the photoelectric emission from the boundary layer and therefore the effect $-\Delta i$, as observed. The other characteristic of the "wall" discharge—namely, the production of the positive effect

($+\Delta i$) at large potential—may possibly be due to the emission under light of the positive ions, or/and to the circumstance that larger potential reduces the probability of electron capture (k/V) (14), so that a certain proportion of the photoelectrons released from the boundary layer and of those produced by them by collision with neutral particles by motion during free paths reach the electrode. The general result of a preferential association of $\pm\Delta i$ with the high-frequency components of the discharge current requires further investigation.

SUMMARY

The Joshi effect ($\mp\Delta i$) in 170 mm. chlorine has been studied in a modified Siemens tube in which the ionization space could be filled with and emptied of powdered glass, the discharge being "wall influenced" and "normal," respectively. With both of these, due to 8–14 kv. of 50 cycles frequency, in the dark and in light, current i was observed in the aerial and the low-tension lines. A vacuum junction, a diode, and a triode were used as current indicators. In "normal" discharge ohmic resistance R reduces $-$per cent $\Delta i = 100\Delta i/i_D$, owing to suppression of high frequencies, in which $-\Delta i$ predominates. $-$per cent Δi in $i_{\text{aerial}} >$ in $i_{\text{L.T.}}$.

Under "wall" discharge an inversion $-\Delta i \rightleftarrows +\Delta i$ occurs at 9.2 kv. and 11 kv. in $i_{\text{L.T.}}$, and only at 9.2 kv. in i_{aerial}. The inversion is entirely potential-reversible. Serial R and by-pass capacity C reduce (numerically) $-$per cent Δi at low potential. At large potential, where $+\Delta i$ occurs, both these parameters produce a marked $-$per cent Δi. It is suggested that the positive effect occurs in super high frequencies, simultaneously with *negative* effect (the latter being associated with moderate high frequencies). With $-$per cent Δi produced at large potential with a serial R, a capacity parallel to R, providing an alternative path to the super high frequencies suppressed by R, should restore the positive effect. This has been observed. The generality of these results is in accord with Joshi's theory of the surface origin of this phenomenon.

In conclusion, the author wishes to record his grateful thanks to Prof. S. S. Joshi, D.Sc. (London), F.R.I.C., F.N.I., Head of the Department of Chemistry, Benares Hindu University, for suggesting the problem and for his kind interest and instructive advice during the investigation.

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COÖRDINATION COMPOUNDS OF BORON TRICHLORIDE. VI

THE SYSTEMS PHOSGENE–BORON TRICHLORIDE AND PHOSGENE–BORON TRIFLUORIDE

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Over forty years ago Baud (1) reported the existence of molecular compounds between phosgene and aluminum chloride. Germann and Jersey (8) later reported that boron trifluoride and phosgene formed some compounds but gave neither empirical formulas nor names for these compounds. They postulated that boron trichloride also might be soluble in phosgene and form compounds with it.

Owing to the similar electronic structures of aluminum chloride and the boron halides, it is logical to expect the latter to form molecular compounds similar to those formed by aluminum chloride. The boron halides are known to be good acceptor molecules and to form many coördination compounds (2, 10, 13). With phosgene, it may be possible for either the oxygen or the chlorine atom to act as a donor. Inasmuch as other molecules containing each of these atoms have been found to be donors to boron halides, it seemed likely that phosgene would form such compounds with both boron trichloride and boron trifluoride.

It was of interest to investigate the phosgene–boron trifluoride system also because Brown, Schlesinger, and Burg (5) reported that phosgene and boron trifluoride did not coördinate at temperatures as low as $-120°C$.

The apparatus and procedure employed in these investigations have been described in earlier publications (3, 4, 7, 11, 14) except for two changes. Owing to the large amount of current required to operate the necessary relays for the controls of the automatic fractionating column, the wire contact in the control manometer becomes fouled and the mercury smuts the walls of the manometer, with the result that the contact sometimes fails. Therefore, a vacuum-tube circuit with thyratron tubes[1] is used now to operate the relays which in turn

[1] General Electric Thyratron Tube No. G-57.