

INFLUENCE OF SURFACE RESISTIVITY AND TEMPERATURE ON VARIATION WITH TIME OF CURRENT PULSES IN AIR AT OPTIMUM PRESSURES

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The variation of discharge current pulses with the surface nature of electrodes has been investigated by producing discharge in the intense ionizing zone of two ozonizers (A&B) containing pure, dry air at a pressure of 4 & 10mm of mercury respectively. The course of reaction in the tube A showed that the periodic rise and fall of discharge counts through a series of recurrences whose amplitude varied randomly. During this reaction, steady potential, temperature of the electrolytic bath, counting time and pulse height were kept fixed. The phenomenon obtained for both the tubes is produced within a critical range of conditions. The results have been interpreted on the basis of activated adsorption at a temperature of 90° and 100°C and discussed on the theoretical grounds of change of surface resistivity upon the glass walls. Use of different coatings on annular surface in the same system with appropriate levels of electrolytic solution for a definite value of height-pulses and temperature, etc. shows significant variations in the discharge counts.

In general, there are three processes which occur when a gas is brought in contact with a solid: absorption, diffusion and adsorption¹⁻³. These three phenomena are summarised by a single name sorption. Among these, adsorption is of marked importance and is the only process which is found to occur (at ordinary temperature) with substances like silver, glass, copper etc., which are in common use as electrode materials.

As the influence of adsorbed films received much attention while studying photo and thermo-electric currents, the variation of discharge current pulses with the surface nature of the electrodes especially with solid dielectric material, was not investigated. It has, however, been mentioned⁴ that the discharge current and the mechanism there of, are markedly dependent upon the electronic work function of the cathode chiefly the gases adsorbed on it. This and other factors have now been investigated in some details.

THEORY AND METHOD OF INVESTIGATION

When two different phases come into contact, the concentration of a solute dissolved in one phase is greater at the interface than in its bulk. The phenomenon, the tendency for accumulation to take place at the surface, is called adsorption. There are, in general, two types of adsorption. The surface of many substances is inert in the sense that the valency requirements of their atoms are satisfied by bonding with adjacent atoms. The adsorption on such a surface takes place simply through forces of physical attraction and is called physical or Van der Waal's adsorption. On the other hand, some surfaces are unsaturated, the valency requirements of their surface atoms not being fully satisfied by bonding with the nearby atoms. Such a surface will tend to form chemical bond with atoms in a nearby phase and this process is called Langmuir's adsorption or chemisorption. The chemisorption occurs at high temperatures, while the physical adsorption occurs at low temperatures. However, there can be intermediate cases where physical adsorption merges into chemisorption.

Adsorption is a consequence of the unbalanced forces of attraction on the atoms of the surface perpendicular to the surface plane which bestow a certain degree of unsaturation to the surface atoms. There are several types of forces, (a) Van der Waal's attractive forces; (b) forces between dipoles; (c) Coloumb's forces between ions or ions and electrons; (d) Valence forces and (e) repulsive forces. The first three of these forces are usually considered to vary with $1/r^7$; $1/r^4$ and $1/r^2$ respectively, where r is the distance between the molecules or dipoles or ions. Since all these factors can affect at the surface of glass wall as well as in the interiors of the solids and liquids they take part in adsorption phenomenon. There should thus be various types of adsorption, such as (i) ion-exchange adsorption; (ii) adsorption of ions by metal; (iii) adsorption isotherm with modification of the potential theory; (iv) adsorption of electrolytes by crystals⁶; (v) adsorption of non-polar molecules⁷; (vi) Langmuir's adsorption^{8,9}; corresponding to above cited several types of forces which hold the atoms or molecules on the surfaces of glass wall.

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The treatment of adsorption as a unimolecular layer from the standpoint of equilibrium between gas molecules striking the surface and those which evaporate off after the lapse of a certain time is Langmuir's adsorption. The equation for this may be written in the form⁹

$$\frac{mp}{x} = \frac{1}{K_1 K_2} + \frac{p}{K_2} \quad (1)$$

Brunauer, Emmett and Teller¹⁰ extended Langmuir's approach to a multilayer adsorption and the equation can be written as

$$\frac{x}{v(1-x)} = \frac{1}{\alpha v_m} + \frac{(\alpha-1)x}{\alpha v_m} \quad (2)$$

and

$$\alpha = e^{(E_1 - E_L)/RT}, \quad (3)$$

where x is the mass of gas adsorbed by m grams of adsorbing material at the pressure p , K_1 and K_2 being constants for given system and temperature, v is the volume of the gas adsorbed at a given pressure p , $X = p/p_0$; p_0 is the vapour pressure at the experimental temperature, v_m is the volume of the gas adsorbed when the surface is completely covered by the single layer, E_1 is the heat of adsorption of the gas in the first layer, E_L is the heat of liquification of the gas and R is the universal gas constant. Because of various types of adsorption, a single gas may be adsorbed on a given surface in several different ways.

From the above fact, it can be pointed out that in thermionic and photo-electric emission, sorption of even minute quantity of solid substance on emitter lowers the electronic work function. The minimum value of this work function has been shown by Becker¹¹ to correspond to the state when the emitter (cathode) is just covered with monoatomic layer of the foreign metal. As the fraction of Na^+ ions on cathode surface (outer electrode) increases, the surface resistivity of glass walls increases. Because of this, a constant applied V decreases. The catalytic activity of certain spots on the surface may be simply due to the presence of adsorbed ions which lower the electronic work function.

The influence of Langmuir's adsorption on the surface resistivity and the electrical conductivity of a gas has now been investigated. For this purpose a known quantity of dry air was introduced in the annular space of the ozonizers and excited by a definite steady potential. The variation of its current pulses was studied at regular intervals of time during the progress of sorption under discharge.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental discharge was produced in the intense ionizing zone of the Siemen's type ozonizer formed by sealing together two cylindrical glass tubes coaxially. The two ozonizers called A and B containing well dried and purified air at a pressure of 4 and 10 mm of mercury respectively were used for this investigation.

Tightly wound equidistant external electrode sleeves, each made up of few turns of silver coil, and the salt solution in a glass beaker served as low tension electrode which was grounded through an electronic scaler (SS 361 A), the other being a probe, inserted in the innermost coaxial tube filled with mercury, was connected to the high tension terminal of the dc supply unit along with a series resistance, 4.7 meg-ohms. Fig. 1 shows the experimental circuit.

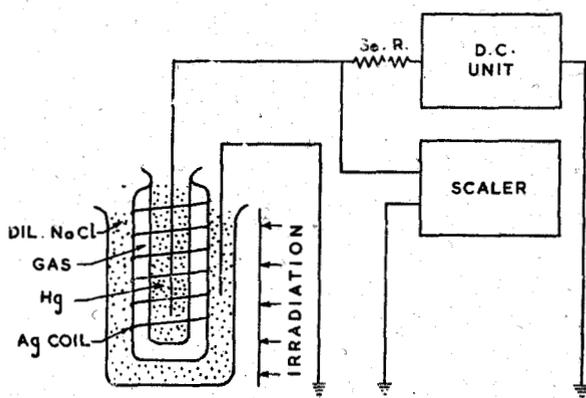


Fig. 1—Experimental arrangement.

If the dc supply unit is connected through a resistor R to a positive (inner) electrode and negative (outer) electrode, the discharge current can be made to flow through an annular space containing air at moderate pressure. For a certain range of value of R and of the potential across the electrodes, the discharge count rate may oscillate continually and it may show a well-defined period. If the resistor R is small, overshoot phenomena can occur for certain cases. Oscillations were found for air in this system (the potential across the electrodes was constant, 1500 V dc).

Whenever slow overshoot is present and the voltage is changed suddenly keeping R small, it can produce oscillations if R is increased and potential is kept at about the same value. The frequency at small amplitude is well-defined, and increases with increasing concentration and with increasing voltage (i.e. becoming more positive) across the electrodes.

Mechanism of DC Discharge

In the present study, the dc potential as obtained from the high tension supply associated with a 'utility scaler' fabricated by the Atomic Energy, Trombay, Bombay, has been used. The instrument has a total count capacity of 9999999 pulses, a resolution time of 250 microseconds and a wide range, highly stable, electrically regulated high voltage supply. In it, a Geiger-Muller tube has been used to make it a complete simple counting system.

Under dc excitation the discharge takes place due to surface charge field produced by applied V . The electrical stress in air, E_a , due to wall charge is given by the equation¹²

$$E_a \cdot \epsilon_a = E_w \cdot \epsilon_w \tag{4}$$

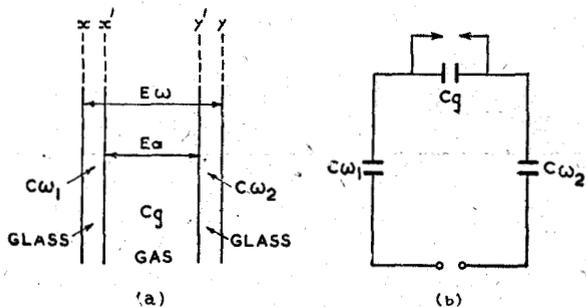


Fig. 2—Mechanism of continuous discharge.

where E_w is the stress across the glass walls as shown in Fig. 2(a) and ϵ_a and ϵ_w are the permittivities of air and the wall material respectively. Since the permittivity of glass is greater than that of air (≈ 1), the electrical stress in air-medium is greater than that in the surrounding wall insulation¹². The charges on the inner wall surfaces x' and y' are held under opposite forces (i) the electrical stress in medium of air and (ii) the electrical field across the glass walls. On account of these two forces, the charges are not held firmly and can be released easily when an applied V is greater than the threshold potential of air. In the discharge process, the electrons from the outer electrode wall, produce electron avalanches in air medium, which after reaching the

opposite glass wall reduce the positive charge on its surface. Thus, when the potential difference becomes smaller than the breakdown voltage, the discharge is terminated. The subsequent discharge takes place only when the voltage across the two small elementary areas or spaces on the opposite walls is restored. This restoration of the voltage occurs as a result of leakage of the charges through the glass walls or perhaps also in part, by surface conduction. The finite interval between the two successive pulses is the time constant which is $R_w \cdot C$, where C is the condenser and R_w is the linear resistance of the glass wall. Its theoretical value can be estimated from the following relation¹²

$$\tau \approx \epsilon_w \times \rho_w \times 10^{-13}, \tag{5}$$

where ρ_w and ϵ_w are the resistivity and the permittivity of the glass respectively. Taking the values of ρ_w and ϵ_w for quartz at a particular temperature, the value of τ can be found out. The value of τ for Pyrex

glass estimated by Kanitkar¹³ was about 43.8 seconds which is higher in magnitude. This difference can most probably be attributed to the reduction of the resistivity of glass during the experiment. Resistivity of glass is known to decrease with the increase in applied voltage¹⁴⁻¹⁷ and temperature^{18,19} sorbed gases in glass also cause a change in the resistivity^{15,20}.

The following experiments were conducted in order to see whether the count rate emission decay with time is given by an admixture of gases, such as air, at experimental operational conditions. Air at a definite pressure was introduced into the intense ionising zone of the ozonizer and subjected to a steady potential of 1500 V, the ozonizer being kept in the dark by enclosing it in a wooden box. The progress of the reaction was followed by noting the time-variations of the discharge current pulses (counts). The current in the dark was read initially at a certain time, it was referred as the starting time of the discharge and therefore its value considered as zero. The time-variations of current pulses were noted till the current reached near about a constant value, indicative of an equilibrium like steady state in the ozonizer. It is seen from the data that the count rate emission with time occurs definitely in air. It may also be stated that this constitutes the first instance of the observation of this phenomenon in an admixture of gases like air. Since most of the current pulses showed oscillations through the small value of a resistor R included serially in the circuit, the count rates emission are not brought out to the full extent. That the effect is produced to an appreciable extent is unmistakable.

A tube marked A was subjected to a dc constant potential, i.e. above the threshold potential V_{ga} . The ozonizer was kept in the dark at a temperature of 100°C and a pulse height of 5 V and the discharge current read at the beginning $T_m=0$ in one series; in other series the value of discriminator bias was changed to 50 V and the current pulses read from the starting time $T_m=0$. Thus, one typical set of data obtained is given for a tube A. The results for a tube A in Table show that the total continuous duration of discharge

TABLE I
TIME-VARIATION OF COUNTS AT A DEFINITE POTENTIAL

		TUBE No. A		TUBE No. B	
Pressure of air		4.00 mm Hg		10.00 mm Hg	
Films used in the inner tube of the ozonizer		Mercury		Mercury	
Temperature of the system		100° C		90° C	
Applied potential		1500 V (dc)		1500 V (dc)	
Current indicator		Electronic scaler		Electronic scaler	
Counting time		5 minutes		3 minutes	

Time (min)	C_D in arbitrary units at 5V	Time (min)	C_D in arbitrary units at 50V	Time (min)	Counts in dark in arbitrary units at 5V	Counts in dark in arbitrary units at 50V
T_m		T_m		T_m		
0	670	0	24	0	3158	3187
30	1219	60	20	15	2834	2740
75	0902	105	18	30	1863	2000
115	2126	120	19	60	1466	1595
165	3215	155	10	180	12033	9332
195	4796	195	8	210	11239	9946
230	2250	225	6	300	22283	19612
460	782	270	5	335	23857	19652
495	1744	485	16	420	39629	31484
540	1250	505	15	635	53412	33691
565	1331	525	33	660	53452	34064
		565	48	685	53000	34879
		590	60			
		610	47			

and a given counting time was equal to 10½ hours and five minutes respectively for C_D . This C_D at a pulse height of 50 V and at a definite value of system-temperature, viz. 100°C, decreased from an initial maximum value of 24 to 5 in about 4½ hours; thereafter it increased with time to 40/60 in 5½ hours. It is surprising that the C_D at a discriminator bias of 5V and at 100°C instead of reduction showed enhancement in the discharge counts from 670 to 4800 in about 3¼ hours, and then decreased instantaneously to about 1300 in about 6½ hours. From the above fact, it is instructive to note that the initial and final rise of the discharge counts in air at a constant pressure of 4 mm and at a temperature of 100°C for 5 volts-bias is contrary to the results obtained in air at a pressure of 4 mm and 10 mm of mercury for 50 V discriminator bias or/and for both the values of discriminator bias respectively.

Again, the higher value of pressure of air (10 mm) was subjected to the same potential (1500 V), pulse height, surface-filming, and the above experiment was repeated. In this experiment, the exposure-time to the discharge system was less. The interval between the current pulses was varied from 5 to 3 minutes, the pressure of air and temperature of the system were varied from 4 mm to 10 mm of mercury and from 100°C to 90°C respectively and a second typical set of data obtained for tube B.

It is seen from the results obtained for tube B (Table 1) that the total continuous duration of discharge and counting time was equal to $11\frac{5}{12}$ hours and three minutes for C_D respectively. Compared with the data obtained at 100°C, C_D is much greater at 90°C for a high value of discriminator bias, 50 V. The C_D at 90°C decreased from an initial value of about 3187 to a minimum of about 1595 in one hour only. It then increased to over 34880 during the remaining $10\frac{5}{12}$ hours. Here also C_D at a discriminator bias of 5 V decreased from an initial of about 3150 to about 1450 in one hour; thereafter it increased in the remaining $10\frac{5}{12}$ hours.

Thus, the above four series of experiments grouped in two typical sets of data were carried out under exactly the same conditions of potential (1500 V), discriminator bias (5 and 50 V), coating on the glass surfaces, for both the tubes, A and B; the first one was used for 100°C. On account of the difference in pressure of air, intense ionizing zone, counting time, system-temperature and the significant field producing the ionization, however, were not the same for both the tubes.

Effect of Height-Pulses on Count Rate Emission Phenomenon

It is seen that in the dark, the number of current pulses decreases as the pulse height (discriminator bias) increases. Both the tubes, A and B, show that the discharge counts in the dark are greater, the lower the value of bias-potential. Thus, for example, at 1500 V, C_D for pulses of 5 V (as adjusted by the discriminator bias in volts) varies instantaneously from a minimum value of 670 to a maximum value of 4796 in tube A and from 1466 to 53452 in tube B, in the total discharge duration of 565 and 685 minutes respectively and those for pulses of 50 V, it varies from a minimum 5 to a maximum value of 60 and from 1595 to 34879. These results are markedly similar to those observed by different investigators for the pulse height spectrum of hydrogen discharge in an ozonizer excitation¹³, and for the pulse height spectrum of a gas discharge under dc excitation in photo-electric cell²¹ (RCA 868) which showed the simultaneity or co-occurrence of $\mp \Delta i$, the net negative light effect being linked preferentially with large height of pulses.

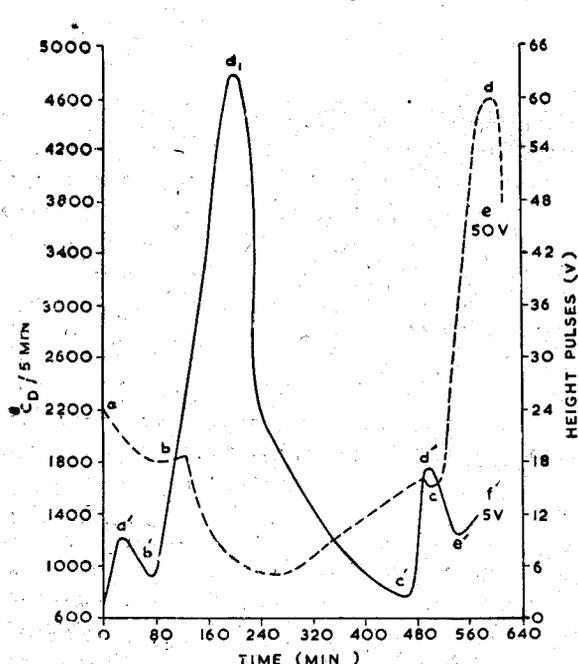


Fig. 3—Variation of discharge counts in dark with time of exposure to the discharge at constant steady potential of 1500 V and temperature of 100°C.

The comparative study of the plots of current pulses versus time in Fig. 3 shows that as the value of pulse height is lowered from 50 to 5 V, the minimum in the curves shifts to the lower values of the time and conversely as the height of pulses are raised, it moves to higher values. At each value of discriminator bias, the discharge current pulses in the dark flow at the corresponding critical, time serves as an excellent basis for the determination of the ozonizer discharge.

Influence of Temperature on Adsorption and on Counts

At low temperatures, the Van der Waal's forces alone would be sufficient to cause adsorption (Van der Waal's adsorption). According to Boer and Zwicker⁷, the adsorption-potential decreases exponentially with thickness, by a constant fraction from one layer to the next. A decrease in potential difference between the electrodes in contact with the gas may be due to Van der Waal's forces, which cause a reduction in number of pulses with time at a constant applied potential.

At higher temperatures, molecules on the surface may undergo chemical change and thus be

held by valence forces. The heat of adsorption at high temperatures is probably far greater than that at low temperatures. The reaction velocity of the chemical change may be too low at low temperatures, since there is an activation energy associated with every such reaction. Taylor²² has postulated the term activated adsorption for the adsorption which involves such chemical changes. Soderbanm²³ has pointed out the distinction between Van der Wall's adsorption and activated adsorption of CO and oxygen on platinum.

In the present investigation, the chemical change in the initial stage of this experiment may be too low as seen at low temperatures. There occurs, therefore, a decrease in potential difference between the cylindrical glass electrodes in contact with the gas, which can cause a reduction in number of pulses. Table 1 shows a decay of discharge rate from about 3158, 3187 and 24 to 1466, 1595; and 5 in the time range of 0-60, 0-60; and 0-270 minutes respectively (Fig. 3 & 4). As the time increases, the chemical changes in activated adsorption can take place vigorously. This activated adsorption may result in the increase in number of sites or small elementary areas¹³, at a constant dc field strength, as the total area on the surface of electrode wall is constant. Because of this, an increase in total number of counts in the dark in the dc discharge process can be expected. Table 1 shows a growth of counts from 1467, 1595; and 5 to 53000, 34879; 47 in the time range of 61-685, 61-685; and 271-610 minutes respectively (Fig. 3 & 4).

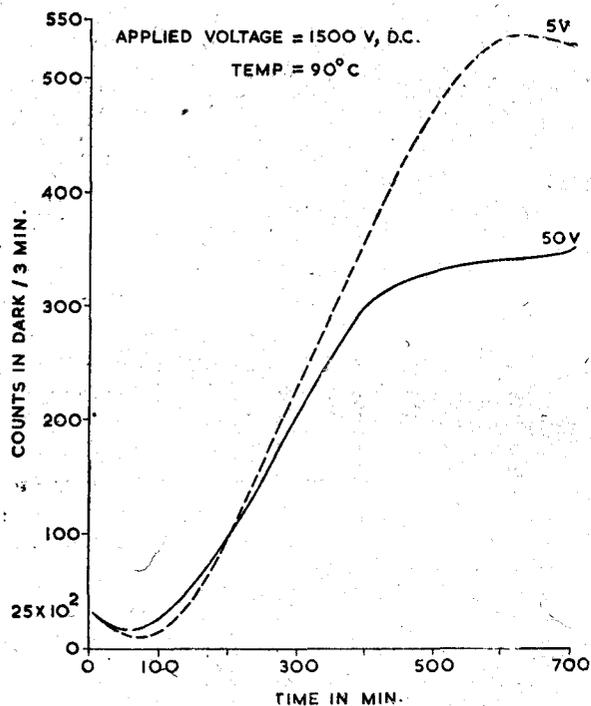


Fig. 4—Variation of discharge current with time at constant potential.

as the time increases, the discharge pulses in the dark decrease. The feature of additional interest and importance is the small sharp minima, notably *b* and *c*, at about 100 and 504 minutes. The region *c-d* of this curve shows that count rate per five minutes in dark for an amplitude of 50 V rises from 15 to 60 in the time range of 504-590 minutes. A marked selective peak is observed at 590 minutes, after this the count rate falls. The (I, T_m) curve for pulses of 5 V shows the three selective maxima near about 30, 196 and 496 minutes. The plot of discharge current against time for 5-volts-bias (Fig. 3) shows that the maxima obtained in are less sharper for longer time than in the Curve (dotted) for 50-volts-bias. The two curves of $I = f(T_m)$ (dotted) and the curve for 5-volt-bias (Fig. 3) demonstrate a pronounced change in height of the selective maxima. The solid curve for a pulse height of 5 V indicates that the maximum at 496 minutes is shifted to the right and the height of the maximum of a dotted curve for a bias of 50 V at 590 minutes is considerably reduced.

At sufficient low temperatures, films adsorbed on the glass are often condensed at higher vapour pressures, but because gaseous at very low pressures. At higher temperatures, either solution expanded or liquid intermediate phases may occur. Phase changes which are first order in the three dimensions usually become second order in two dimensions, though in the latter the condensation of vapour may be either first or second order.

Almost all theoretical approaches to the problem of the physical adsorption of the gases on the surfaces of glass have assumed a negligible interaction between the glass and film. But from the above results, this recent careful experimental work shows that this is incorrect.

Interpretation of Current Versus Time Curves

The plots of current pulses versus time in Fig. 3 and 4 show that the discharge rate is a function of time for both the heights of pulses at a constant potential and temperature. The measurements of discharge rate is in arbitrary units. The curve in Fig. 3 for α bias at 5 V shows the three prominent minima, viz. *b'*, *c'* and *d'* at about 76, 460 and 540 minutes, and three marked maxima. The [I, T_m] curve for a pulse height of 50 V shows that

The data presented in Fig. 4 for both the pulse heights show an initial marked fall of counts reaching a minimum (value of $C_D/3$ min falls to a minimum), followed by a rise again and then an equilibrium like steady state.

It is well known that the reaction leading to the liberation of gases and the formation of certain compounds under discharge are essentially due to the electrolytic nature of conduction of electricity through glass²⁴. Professor Joshi^{25,27} had shown that in general, the rate of a reaction under discharge is determined by the potential difference $V - V_{ga}$, where V is the applied potential employed for studying the reaction. It follows from this that the smaller the difference ($V - V_{ga}$), i.e. the near the potential to V_{ga} the less marked is the rate of the discharge reaction. The voltage employed for the present studies was maintained above the breakdown potential of air (V_{ga}) such that the above changes would be maximum.

Furthermore, this would facilitate the studies of discharge current pulses mostly concerned with the surface of electrodes since it was shown in the earlier communications^{28,29} that at a potential above V_{ga} , the adsorption related to the outer electrode (low tension or cathode). Similarly at $V > V_{ga}$, the processes unconnected with the surface and concerned with the gas phase played an important role in the maintenance of the discharge³⁰.

The various stages of the plots of discharge rate versus time of exposure to a gas discharge in the present studies can be explained on the basis of non-distorted and distorted field^{30,31,32}.

The distortion and non-distortion phenomenon can possibly be related with the following relation

$$V_r = \frac{\Delta V}{V_{ga}} = \frac{V - V_{ga}}{V_{ga}}, \quad (6)$$

where V_r is the corresponding or reduced potential and ΔV is the over-voltage or potential difference between V and V_{ga} . The mechanism of ionization growth in a non-distorted field cannot produce collapse of the potential between the positive and negative electrodes. In such a circumstance, the field can remain non-distorted until the current pulses increase sufficiently. But when a large avalanches can grow in the annular space (intense ionizing zone) of the ozonizer within a transit time and the movement of charges can lower the potential of the inner electrode (high tension electrode or anode) before any charge from the electrode gap reaches it, There is thus a fall in constant potential employed to the tube. This reduction in corresponding potential can probably be due to the movement of charges.

DISCUSSION

It has been reported in the earlier communications^{29,33} that the [instantaneous] current pulses in the dark under ozonizer discharge are given by

$$\begin{aligned} I &= \left(\frac{2k}{P} \frac{R_i}{R_0^2} \right) (V^2 \cdot V_r) \\ &= D \cdot V^2 \cdot V_r \end{aligned} \quad (7)$$

Here D is a constant and is equal to $2k/P, R_i/R_0^2$ in one system. This value differs for other system and it depends on geometries and pressures of a gas enclosed in an annular space of the ozonizer. It can be obtained from the value of various factors, such as a pressure of dry air (P); radii of the outer (R_0) and inner cylinder (R_i) of the ozonizer and reduced mobilities of the ions (k) at a definite pressure. The discharge current pulses measured in the system are referred to by I in equation (7), rather than C_D .

Ives³⁴ showed that when the platinum was exposed to sodium vapour, the electronic work function decreased initially and increased after some time. This was attributed to the slow formation of adsorption layer, which when sufficiently thick showed the same electronic work function as sodium metal in bulk. It was further emphasised¹¹ that the associated adsorbed ions lower the work function of the composite surface and therefore the maximum current was obtained when single alkali metal-atoms were distributed over the surface. Hughes and Du Bridge³⁵ in his early experiments found that 30 atomic diameters' film-thickness may produce the maximum current. No such effect occurred when the film was entirely of unchanged atoms and when the ionization potential of the deposited metal was greater than electronic work function of the supporting surface¹¹. Keyes and Marshall³⁶ found a close parallelism between heat of sorption and dielectric constant of various gases. From the above fact, it is quite possible to correlate dielectric constant with the adsorption and it can be shown that small changes in composition of solids entail marked changes of dielectric adsorption in solids. White head³⁷ observed that impurities and moisture in small quantities caused a large change in adsorption. All these factors change the electrical capacitance of the ozonizer in the present system. This can be one of the probable causes for variations in a constant steady potential employed to the tube and hence a corresponding variations in the current pulses can follow from Equation (7).

The adsorption, system-temperature and electro-deposition cause a significant change in the surface resistance and capacitance of the glass [compound capacitance are formed by C_g , C_{w1} and C_{w2} , where C_{w1} and C_{w2} are formed by the inner and outer glass walls, which are practically equal and C_g is formed by the enclosed gas] on which count rate depends (cf. Fig. 2b). Consequently the only interaction which can possibly explain the increase in counts at a definite value of counting time under perfect darkness seems to be reduction in the surface resistivity on the charged glass wall of the ozonizer. This reduction in resistivity on the surface of glass walls increases the reduced potential (V_r) and this causes an increase in the potential difference ($V - V_{ga}$) in addition to that already produced by the impact of the current pulses. Since this additional process of increase in corresponding potential by reduction in surface resistivity on the surface of glass walls is gradually balanced by the adsorption on the glass walls, the time required to create the potential difference [ΔV] necessary to strike the discharge increases. Because the corresponding potential (V_r) itself depends upon the surface resistivity; adsorption and temperature of the system—current pulses also depend on these three factors. It may be mentioned here that in the case of light effect, phenomenon of over-voltage on counts would play a role similar to the variation in surface resistivity.

As explained above, as adsorption decreases, the surface resistivity on the surface of glass walls decreases which causes an increase in corresponding potential affecting the current pulses. The variation in reduced potential depends upon surface resistivity and formation of multilayers on the surface of glass walls, the discharge count rate with time also depends on these two parameters. Thus, the above interpretation of the effect of thickness of adsorption on surfaces of glass walls is helpful in understanding the phenomenon of pulsed emission in admixture of gases under continuous dc ageing. Similar phenomenon has recently been reported in air at a pressure of 1 mm of mercury by the author²⁹.

The emission of counts in the dark with continuous exposure of time to steady (dc) discharge increases as a result of the decrease in surface resistivity, rather than an increase in the reduced potential. Since the surface resistivity depends on the corresponding potential and adsorption, the observed decrease in current pulses in the dark with time leads to an increase in the surface resistivity, and the increase in current pulses in the dark leads to a decrease in the surface resistivity. Thus, in effect, the discharge rate in the curves of Figs. 3 and 4 rises and falls when the surface resistivity decreases due to decrease in adsorption and rises due to increase in adsorption on the surface of the ozonizer.

CONCLUSION

The count rate emission phenomenon consists in a periodic variation, usually a rise and fall, in the discharge current pulses when the admixture of gases at a definite value of pressure are subjected to electrical excitation in ozonizers and exposed by but time. The experimental results have been interpreted on the basis of Langmuir's adsorption. The chemisorption at a definite high temperatures, viz. 90° and 100°C, might

have caused the decrease of surface resistivity by the removal of residue by positive ions at a definite V , as the total resistance of the circuit was constant. The general conclusions, arrived at by equation (7), on the theoretical grounds, have been based on the variation of surface resistivity on surface of the glasswalls. The discharge current pulses in the dark, I , in a given counting time with continuous ageing decrease as a result of the decrease in the reduced potential, rather than an increase in the adsorption. Since the corresponding potential depends on the adsorption, the observed decrease in the count rate with time of exposure to discharge leads to a net decrease in the V_r and increase in the count rate leads to a net increase in the V_r . The count rate in the plots of discharge rate versus time is maximum and minimum when the V_r (or a constant steady V) rises due to decrease in surface resistivity at least up to the point where the space charge distortion starts and falls beyond a certain point which brings the condition right back to the problem of field distortion due to an increase in the surface resistivity. By means of count rate variation with time, the experiments also clearly demonstrate the great dependence of (1) exposure-time, system-temperature, pulse heights, purity of pressure of a gas and its value; and (2) the applied potential to the system, over-voltage and corresponding potential in (7) on the nature of the surface of glass walls.

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