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Temperature as a Determinant in the Comparative Study of Budde Effect, Joshi Effect and Corona Pressure Effect in Chlorine

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A comparative study of the Budde effect, Joshi effect and corona pressure effect in chlorine admixed with a little air and water vapour enclosed in the annular space of Siemens type ozonizer has been made in the temperature range 37 to 98°C. Budde effect has been found to be independent in the above temperature range. This has been attributed to the fact that both the characteristic convergence frequency and light absorption in chlorine are practically unaffected by a 61°C temperature rise. And, water acts as a 'poison' by forming an adsorption layer on the wall surface. The Joshi effect and the corona pressure effect have been found to increase in the above temperature range. This is in accord with Joshi's theory for the phenomenon Δi.

INTRODUCTION

The corona pressure effect $(\Delta p)_V$—the instantaneous increase in gas pressure at an applied potential V due to the onset of electrical discharge has been ascribed[1] to a heat effect, where the heat due to discharge is dissipated fast owing to the high velocities of the ions—the 'electrical wind' moving in the direction of the applied field. Joshi effect Δi—a sharp reversible variation (usually, though not inveriably, a decrease —Δi) of the discharge current when exposed to external irradiation from infra to X-rays and even γ-rays, is widely producible in halogens and specially in chlorine gas. —Δi has been attributed to the space charge effect[2]. This recalls a partially similar observation of Budde effect[3]—an instantaneous increase of gas pressure in chlorine by exposure to an external light. Budde effect $(\Delta p)_{V=0}$ is a heat effect[3] due to recombination, in the homogeneous gas phase, of the primary products of photo-dissociation of chlorine. All the work on Budde effect has been carried out in spherical bulb-like vessels where the surface to volume ratio is minimum. On the other hand, most of the work on Joshi effect has been in Siemens type full-ozonizers distinctive of the large surface to volume ratio. It appeared, therefore, to be of interest to investigate into the above three phenomena $(\Delta p)_V$, Δi and $(\Delta p)_{V=0}$ and specially to examine the possibility of their co-occurrence, of likely significance to the mechanism of —Δi with the help of examining the influence of temperature on them.

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EXPERIMENTAL

The glass assembly of the apparatus and the electrical circuit employed were similar to those reported earlier[4]. The soda-glass full-ozonizer while under vacuum was filled with a predetermined mixture of chlorine (p_{Cl_2} = 385 mm Hg, 37°C), air (p_{Air} = 0.4 mm Hg) and water vapour (p_{H_2O} = 0.5 mm Hg) optimum for Budde effect[5]. The gas presssures were measured with a Bourdon type gauge. For the studies at elevated temperatures, the ozonizer was heated for about 1 h at a desired temperature in an asbestos-lined electric heater as reported earlier[6] and the temperature was recorded at three different regions of the ozonizer and kept constant.

RESULTS AND DISCUSSION

A study of the change in the intensity of the various progressions in chlorine spectrum with temperature[7] has revealed that the convergence progression became stronger; all the other progressions increased in intensity with increae of temperature. The convergence limit of chlorine is not affected sensibly by increasing the temperature in the range 37–98°C. Furthermore, for the above rise of temperature, *viz.*, 61°C the data for the influence of temperature on the light absorption show that it also would be unaffected by moderate heating. Absorption and emission are intimately interdependent and since Budde effect is a consequence of characteristic light absorption, it follows that the magnitude of Budde effect should not be affected by a temperature rise of 61°C as has been actually observed (cf. Curve 1 in Fig. 1).

Many phenomena[8] which like the operation of homogenous catalysis are found to be different under close examination. The characteristic reactions of atomic hydrogen appear only in the presence of water vapour[9], which might seem to show that the action of water is to poison the wells of the discharge tube which otherwise cause an immediate recombination of atoms. The union of hydrogen and chlorine under the influence of visible light is inhibited if the partial pressure of water is reduced below 10^{-7} mm, while at all higher partial pressures, it proceeds normally. These show that water vapour acts as a 'poison' by forming an adsorbed layer on the wall surface. It is reasonable to assume that the poisoning action will be proportional to the area covered by the vapour. Since the moderate temperature rise of the order employed in the present study will not change the amount of adsorption on the surface, it would appear that the poisoning action will be constant over the temperature range investigated; therefore no change in the magnitude of Budde effect will arise.

The dependence on temperature T of equilibrium concentration of the atoms and the corresponding molecules is given by the van't Hoff equation[10] $d \ln k/dt = \Delta E/RT^2$, where k is the equilibrium constant and ΔE the heat of reaction. Budde effect has been accepted[5] as being due to the evolution of heat produced on recombination of chlorine atoms. If the temperature of the system is raised, then according to the principle of mobile equilibrium[11], a change would occur in the system which reduce the evolution of heat. Thus, the increase of

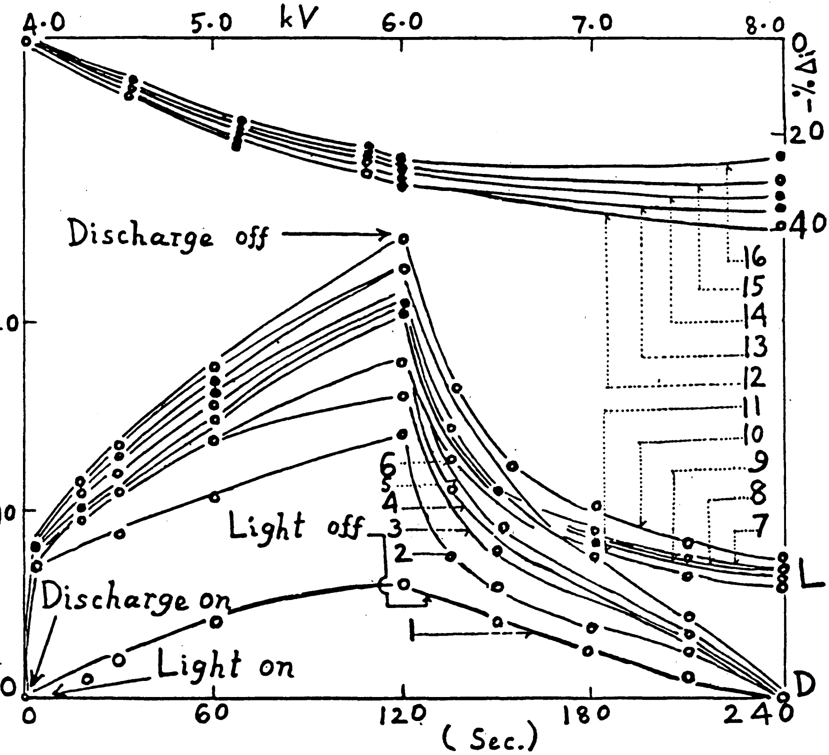

Fig. 1 Comparative study of the influence of temperatue on Budde effect $(\Delta p)_{V=0}$, Corona pressure effect $(\Delta p)_V$ and Joshi effect –% Δi in chlorine (p_{Cl_2} = 385 mm Hg 37°C) admixed with air (p_{Air} = mm Hg) and water vapour (p_{H_2O} vapour = 0.5 mm Hg). [Curve 1: Budde effect in scale divisions (1 scale division = 0.07 mm Hg) *vs.* time in seconds at 37–98°C; Curves 2–11: Corona pressure effect at 8.0 kV *vs.* time in seconds; D = in dark; L = in light form a 100 watt 220 volt glass bulb; Curves 2, 7: at 37°C; 3, 8: 63°C; 4, 9: at 79°C; 5, 10: at 89°C; 6, 11: at 98°C; Curves 12–16: relative Joshi effect –% Δi *vs.* applied potential in kV at 37, 63, 79, 89 and 98°C respectively.]

temperature would tend to cause a decrease in the recombination of chlorine atoms. The increased pressure on irradiation would also decrease the recombination. This would result in a decrease of Budde effect. If would appear, however, that any contribution on the basis of Le Chatelier and Braun's principle is small and beyond the sensitivity of the experimental technique as is evident from the fact that no Budde pressure change has been observed in the temperature range investigated.

The change in thermal conductivity K with the absolute temperature T of glass[12] is given by the equation $K = A + b \cdot \log_{10} T$, A and b are empirical constants, which for the particular type of glass used have the values of –0.003523 and +0.002454 respectively. The relative increase of conductivity is 19/259, *i.e.*, about 7%. The magnitude of Budde effect at 37°C is 6 scale-divisions. The change of Budde effect due to a change in the conductivity of glass for a 61°C rise of temperature would be 6/14 divisions, *i.e.*, $< \frac{1}{2}$ which is below the sensitivity of the indicator used.

The thermal conductivity of chlorine is given by[13, 14] $\lambda = C_V(1.9 \times kT^{3/2})/(C + T)$, where C is constant, C_V the molar heat at constant volume and $k = 168.2 \times 10^{-7}$. Since the thermal conductivity of chlorine is not appreciably affected by increasing the temperature from 37 to 98°C, the magnitude of Budde effect should also remain unchanged with temperature in the above range.

The three-body collisions play an important role in the recombination of atoms, as in Budde effect. One of the problems associated with termolecular reactions is to account for the observation that the specific rate of the reaction between nitric oxide and oxygen actually decreases, to some extent, with increasing temperature[10]. A possible explanation would be that the number of ternary collisions as the temperature is raised, but this appears to be improbable. An alternative view is based on a mechanism involving the intermediate formation of the complex[15] $(NO)_2$ which subsequently reacts with oxygen in a bimolecular process. The specific reaction rate constant k will presumably increase with increasing temperature; but if the association reaction $2NO \longrightarrow (NO)_2$ is exothermic, as it probably is, the equilibrium constant K will decrease. If the activation energy for the reaction between $(NO)_2$ and oxygen is less than the heat change accompanying the formation of $(NO)_2$, k will increase less rapidly than K decreases, and consequently the observed specific reaction rate k′ will be diminished as the temperature is raised; k′ has been shown to be equal to kK.

The results have shown that, due to the rise of temperature in the range 37–98°C, the threshold potential V_m has decreased and the discharge current $i_{D,L}$ increased. It indicates a fall in the work function of the surface due to a decrease in the temperature of the system and/or the consequent increase, at constant applied potential V, in the effective potential V_g across the gas, as has been discussed in an earlier communication[16].

From the foregoing results, it is evident that the Budde effect is observed in neutral chlorine gas and caused by the recombination of chlorine atoms in the gas phase which are formed on dissociation of chlorine molecules exposed to light. It is also found that the Budde effect is unaffected by temperature in the range 37–98°C, whereas Joshi effect $-\Delta i$ $(= i_L - i_D)$ increases with increase of temperature initially and then decreases. The relative effect $-\%\ \Delta i$ $(= -100\Delta i/i_D)$ decreases progressively with the temperature. This is in accord with the Joshi's view that the net change in the discharge current between dark and illuminated excitation is not a consequence of selective light absorption by the excited gas. Thus, the Joshi effect does not appear to be an electrical analogue of the Budde effect. This is further suggested by the fact that the latter occurs appreciable under frequencies longer than 4900 Å where the Budde expansion is negligible. Moreover, it is found that well below V_m, the effect $-\Delta i$ is not detected in pure chlorine and also when admixed with air and water vapour despite the use in intense radiation[2, 17]. It confirms Joshi's view that unlike Budde effect, Joshi effect does not originate from a mere optical excitation of electrically unexcited gas or vapour.

The results of the influence of temperature on corona pressure effect have been discussed in earlier communications[18, 19]. Considering the ionic mobility in dark and under light at 8.0 kV at various temperatures, calculated from Tyndall and Searle's equation, it has been found that $-\Delta i$ is associated with a decrease in the ionic mobility. This is in accord with Joshi's views.

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REFERENCES

1. A.M. Tyndall and G.C. Searle, *Phil. Mag.*, **35,** 261 (1918).
2. S.S. Joshi, *Proc. Indian Sci. Cong.*, Presidential Address, Chem. Sec., (1943).
3. E. Budde, *Phil. Mag.*, **42,** 290 (1871).
4. J. Prashad, *Rev. Roumaine Chim.*, **18,** 1075 (1973).
5. ————, *Zhur. Fizi. Khim.*, **54,** 728 (1980).
6. ————, *Rev. Roumaine Chim.*, **20,** 1345 (1975).
7. H. Kuhn, *Zeit. Phys.*, **39,** 77 (1926).
8. C.N. Hinshelwood, Kinetics of the Chemical Change, The Clarendon Press, Oxford (1946).
9. H.O. Wood, *Proc. Roy. Soc. (London)*, **102A**, 1 (1922).
10. S. Glasston, Text Book of Physical Chemistry, McMillan & Co., London (1948).
11. ————, Elements of Physical Chemistry, D. Van Nostrand Co., New York (1955).
12. R.W.B. Stephens, *Phil. Mag.*, **14,** 897 (1932).
13. E. Rabinowwitch and H.L. Lehmann, *Trans. Faraday Soc.*, **31,** 689 (1935).
14. J.W. Mellor, Comprehensive Treatise on Inorganic and Physical Chemistry, Longman Green & Co., London (1956).
15. J. Prashed, *Rev. Roumaine Chim.*, **24,** 1321 (1979).
16. ————, *J. Hindi Sci. Acad.*, **15,** 79 (1972); **18,** 75 (1975).
17. S.S. Joshi, *Nature,* **147,** 806 (1941).
18. J. Prashad, *Acta Cienc. Indica*, **3,** 208 (1977).
19. ————, *Bol. Soc. Quim.*, **54,** 113 (1988); *Vijnana Parishad Anusandhan Patrika,* **4,** 109 (1998).

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