

Ionization Produced in Gaseous Reactions

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showing the same abnormal humps when  $A'$  and  $A''$  are assumed equal. If, from the value of  $(A' - A'')$  obtained from the (222) reflection, the ratio  $A'/A''$  is calculated, and the coefficients in the series adjusted accordingly, the humps are very nearly wiped out.

The data on intensity of reflection from diamond are not at all satisfactory. As Bragg indicated, there seems to be a strong effect of secondary extinction, which has been left out of consideration. This effect, or some unknown one, is illustrated clearly if Bragg's intensities are corrected by the factor  $\frac{\sin 2\theta}{1 + \cos^2 2\theta}$ , and plotted against  $\theta$ . The curve, instead of rising rapidly at small values of  $\theta$ , reaches a maximum and then decreases as  $\theta$  decreases. This anomalous behavior could be explained as a secondary extinction effect, which becomes more effective in decreasing the reflected intensity at small angles or large intensities. Some powder method data of Debye and Scherrer,<sup>5</sup> which is presumably free from the effect of secondary extinction, shows a normal decline of the corrected intensity for the first few reflections from diamond.

It is quite evident that no conclusions can safely be drawn from the curves concerning the electron density distribution in diamond. However, they serve to indicate that the more complex structure of diamond can be treated by this method, provided that accurate intensity data can be obtained.

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<sup>2</sup> Havighurst, Mack and Blake, *J. Amer. Chem. Soc.*, **46**, 2368 (1924).

<sup>3</sup> W. H. Bragg, *Proc. Phys. Soc., London*, **33**, 304 (1921).

<sup>4</sup> Hull, *Physic. Rev.*, **10**, 661 (1917).

<sup>5</sup> Debye and Scherrer, *Phys. Zeit.*, **19**, 474 (1918).

## IONIZATION PRODUCED IN GASEOUS REACTIONS

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The presence of ionization in chemical reactions has been detected by a large number of investigators. The nature of the ionization has remained obscure due largely to the fact that most of the reactions studied were accompanied by physical phenomena which might in themselves produce the observed ionization. The author has shown in previous papers<sup>2,3</sup> that reacting gases become conductors of the current; and that the conductance is proportional to the number of molecules reacting, and to the potential drop between the electrodes.

It is the purpose of the present paper to present evidence regarding the formation of ions in reacting gases, and to suggest an hypothesis to explain the mechanism of ion formation.

When ethy-alcohol and oxygen were allowed to react between gold electrodes, at temperatures below that of ignition, the following facts were observed: (1) The current flowing between the electrodes was proportional to the applied voltage over the range investigated (the mean potential gradient was varied between 0 and  $\pm 2400$  volts per centimeter). (2) The change of sign of the charge applied to the reaction chamber changed only the direction of the current, and did not change the order of magnitude. (3) The current increased exponentially with the temperature (a  $10^\circ$  rise in temperature resulted in a 40% increase in conductance).

When aluminum electrodes were substituted for the gold the current flowing through the reacting gas became barely detectable. (The apparatus was sensible to a current of  $10^{-15}$  Amperes.) Copper electrodes gave a current slightly larger than that observed with the gold when a negative charge was placed on the hot outer electrode; almost no current was observed when the electrode was charged positively. Glass electrodes gave a current for both positive and negative applied potentials, but the current for the negative was slightly larger than for the positive.

From these data it was concluded that the ions are formed in the layer of gas in immediate contact with a conducting surface, and not in the gas space between the electrodes; and that both positive and negative ions are formed in equal amounts on the same surface, showing the phenomenon to be ionic and not electronic.

The fact that no approach to a saturation current was observed, and that the ions were formed only in immediate contact with a conducting surface, lead to an interesting conjecture regarding the mechanism of ion formation and surface catalysis. An ion or polar molecule when coming within a certain distance (about  $10^{-4}$  centimeters) of a conductor, charged or uncharged, is drawn towards the surface by the attraction of its electrostatic image in the conductor. In immediate contact with the surface this force is comparable with the force holding ions together in the molecule. Although the exact conditions existing on the surface are not known, it is possible that it is this force that breaks the molecules up into ions, and thus produces the activation necessary for reaction.

On this hypothesis ions are formed at or near the surface, and are ejected by kinetic agitation. The rate of recombination of the ions in moving away from the surface is, of necessity, very rapid; this results in a like rapid increase in effective ion concentration upon approaching the surface.

The currents observed are constituted by those ions which the field is able to draw away against the image attraction. Neglecting kinetic considerations, any ordinary potential field will be able to remove only those

ions from the reacting film which have moved out to about  $10^{-4}$  centimeters from the surface. A voltage capable of giving saturation would be far above that sufficient to cause a spark. Consequently, this rapid increase in the concentration of the ions towards the surface must give rise to an apparent straight line relation between voltage and current, with no appearance of saturation.

If it is assumed that a certain critical velocity of the ions from the surface is necessary for their detection, the variation of the current with temperature follows directly from Maxwell's distribution law. This predicts that where there is a wide difference in mass between the positive and negative ions, the ionic current, for positive and negative applied voltages, will differ slightly in magnitude. The limited experiments that have been carried out to test this point tend to substantiate the hypothesis.

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<sup>2</sup> A. K. Brewer and Farrington Daniels, *Trans. A. Electrochem. Soc.*, **44**, 257 (1923).

<sup>3</sup> A. Keith Brewer, *J. Amer. Chem. Soc.*, **46**, 1403 (1924).

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## IONIZATION OF MERCURY VAPOR BY ULTRA-VIOLET LIGHT

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In 1909 Steubing<sup>1</sup> obtained experimental results which indicated that mercury vapor can be ionized by light from a quartz mercury arc. Later investigators have been inclined to doubt that he obtained true vapor ionization. One reason for this is that according to the quantum relation  $Ve = h\nu$  only light of wave length  $1188\text{\AA}$  or less should be able in a single process to ionize mercury vapor. Steubing used no wave lengths below  $1850\text{\AA}$ . Also Steubing's experimental conditions seem to have been such that a careful distinction could not be made between a true ionization of the vapor and a photo-electric effect from the electrodes. In view of these uncertainties a repetition of Steubing's work has been carried out under better experimental conditions.

Light from a quartz mercury arc is passed through mercury vapor between two plane parallel electrodes symmetrically placed with respect to