LETTER TO THE EDITOR

A correction of the Thomson-formula for the coefficient of three-body-recombination between electrons and ions

J. J. T h o m s o n (1924), and recently H. S. W. M a s s e y (1952), have derived a formula for the coefficient of three-body-recombination between electrons and ions from the corresponding formula for the ion-ion recombination by neglecting the mass of the electron as compared to the mass of the ion, and by adopting a certain expression for the effective mean free path of the electron. It will be shown below that their expression for the effective free path is open to two objections.

In addition to the usual mean kinetic free path of the electron, l_k , T h o m s o n defined an effective free path l_e as the mean distance(!) over which the electron has to travel for losing an additional amount of energy $\approx kT$ (which it may have acquired owing to the attractive force of the positive ion). If η is the mean fractional loss in the additional kinetic energy occurring when the electron collides with one foreign gas molecule, T h o m s o n assumed the ratio of l_e to l_k to be determined by $l_e/l_k = \eta^{-1}$. Any doubt considering this assumption may have far reaching consequences, since η^{-1} may be as large as 10^3 (cf. H u x l e y and Z a a z o u, 1949). It should be noted that η^{-1} is the (minimum) number of collisions between the electron and the gas molecules, which on the average is required before recombination occurs. The chance of more collisions may usually be disregarded.

The objections to be suggested concern the fluctuating direction of motion of the electron, and the calculation of the chance that a sufficient number of collisions occur within a given interval of space.

Evidently, the change in the direction of motion of the electron after each collision ought to be taken into account. With fair approximation one may say that under elastic collisions with molecules of relatively very large mass the direction of motion of the electron after each collision is determined by a stochastic function of chance. Therefore the results of the theory of the brownian motion (cf. D e H a a s - L o r e n t z, 1913) should be applied to the irregular motion of the colliding electron, leading to $l_e = \eta^{-\frac{1}{2}} l_k$; since $\eta \simeq 10^{-3}$, this makes a difference of a factor thirty, as compared to T h o m s o n's assumption.

In the second place, his formula can be shown to involve implicitly another assumption, viz. that the chance of η^{-1} collisions during the electron covering a path of total length x , equals η times the chance of one collision within x . Obviously, this does not hold. A less questionable expression for this chance can be found as follows.

For convenience sake, the gas molecules are assumed to be at rest; this is allowed since their mass is relatively large. Evidently, the chance of η^{-1} collisions within x is now equal to the chance that the electron meets η^{-1} times a molecule within an interval of path of length x , which again is equal to the chance that η^{-1} molecules are found within this interval at a given moment. If it is assumed that the chance of collision no. j is not influenced by the occurrence of $(j - 1)$ previous collisions at

the required, rather short distance from the ion, the chance in question $K(\eta^{-1}; x)$ is given by Poisson's formula:

$$K(\eta^{-1}; x) = (x/l_k)^{\eta^{-1}} e^{-x/l_k} / (\eta^{-1})!$$

Following up Thomson's argument, but allowing for the suggested corrections, a formula for the recombination coefficient can be derived from the chance that an electron suffers η^{-1} collisions within a sphere with radius r_0 . Here r_0 represents the critical distance with respect to the recombining ion, which occurs in recombination theory. From the foregoing it follows, that if the electron has moved away over a distance r_0 when having made η^{-1} collisions, it is expected to have travelled on the average a path with length $r_0 \eta^{-\frac{1}{2}}$. It follows then that the above mentioned chance equals:

$$K(\eta^{-1}; r_0 \eta^{-\frac{1}{2}}) = (r_0 / \eta^{\frac{1}{2}} l_k)^{\eta^{-1}} / (\eta^{-1})!$$

since under usual circumstances $r_0 \eta^{-\frac{1}{2}} \ll l_k$.

Accordingly the recombination coefficient α will be found by further applying the usual theoretical argument:

$$\alpha \simeq (8kT/\pi m)^{\frac{1}{2}} 2\pi r_0^2 (\eta^{\frac{1}{2}} l_k)^{\eta^{-1}} / (\eta^{-1})!$$

with m = mass of electron.

When putting $l_k = 4 \cdot 10^{-4}$ cm, $\eta = 10^{-3}$ and $r_0 = 4.8 \cdot 10^{-7}$ cm (which values refer to the actual circumstances in an acetylene-air flame we are dealing with), it appears that α becomes insignificant.

The use of Thomson's formula, as it stands, however, would erroneously yield in this case a value of α of magnitude comparable to the value computed for other recombination processes.

The applicability of the derived formula is doubtful, however, since no allowance has been made, either for the occurrence of electrons with initial kinetic energy smaller than the thermal energy (which require a smaller number of collisions before they recombine), or for the occurrence of collisions at which an amount of energy is transferred which differs from the average amount assumed in our calculations.

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