8. J. J. THOMSON THEORY OF THREE-BODY RECOMBINATION

For many conditions of interest, the results of the rigorous classical theory of elastic scattering are in accord with quantum theory. Classical calculations have also been performed for nonelastic processes (see Secs. II 4 and II 8), but such calculations are of an *ad hoc* nature, and are not justifiable *a priori*. Rigorous calculations for nonelastic cross sections must be performed using quantum mechanics. Such calculations are usually involved and the accuracy of the results uncertain.

In this section we wish to discuss a rather simple classical theory for three-body recombination proposed by J. J. Thomson in 1924 (see Massey and Burhop, 1952, p. 623). This theory was originally developed to describe ion-ion recombination for reactions such as

\[ \text{Al}^+ + \text{Ai}^+ + \text{X} \rightarrow (\text{AlAi})^+ + \text{X}, \]  

(8.1)

and has since been extended to describe electron-ion recombination. Rather remarkably, this theory agrees well with both experiment and with more elaborate theories.

The basic ideas underlying Thomson’s theory are as follows: In the absence of collisions the total relative energy of an ion pair, defined in accordance with equation (2.13), is positive and constant, and the trajectories are therefore unbounded. When the two ions approach one another, the relative kinetic energy increases at the expense of the potential energy. If one of the ions experiences a “thermalizing” collision with a third body while in the vicinity of the other ion, then the relative kinetic energy is reduced. If such a thermalizing collision occurs within a certain minimum separation distance \( r_0 \) between the ions, the total relative energy of the ion pair can be reduced to a negative value. The ions will then move in bound trajectories about one another, and recombination will have resulted.

At some instant prior to recombination, when the separation between the ions is \( r \) and the relative speed is \( g \), the total relative energy will be

\[ E = \frac{m_{12} g^2}{2} - \frac{e^2/4\pi\epsilon_0}{r}. \]

The total relative energy for an average ion pair may be evaluated by going to the limit \( r \rightarrow \infty \), in which case we obtain \( E = m_{12} g^2/2 = 3kT/2 > 0 \). In the absence of collisions with other particles, this value of \( E \) remains unchanged during the encounter between \( \text{Al}^+ \) and \( \text{Al}^+ \). At some finite separation such as indicated in Fig. 11 the relative kinetic energy \( m_{12} g^2/2 \) will exceed \( 3kT/2 \). Let us suppose that at such a juncture, one of the ions
experiences a thermalizing collision with a third body $X$, i.e., a collision which results in changing the relative kinetic energy from $m_1 g^2/2$ to $3kT/2$. The new total relative energy of the ion pair after this collision is then

$$E' = \frac{3kT}{2} - \frac{e^2/4\pi\epsilon_0}{r}.$$  \hspace{1cm} (8.2)

The new trajectories of the ions will be bounded if

$$E' < 0,$$  \hspace{1cm} (8.3)

and the condition for this is that the collision with the particle $X$ take place at a value of $r$ satisfying the inequality

$$r < r_0 = \frac{2}{3} \frac{e^2/4\pi\epsilon_0}{kT}.$$  \hspace{1cm} (8.4)

There are thus two requirements to be met in order to have a recombination. First, the two ions must be within a distance $r_0$ of each other. Second, while they are within the distance $r_0$, one of the ions must experience a thermalizing collision with a third body. The frequency with which one $A_1^-$ ion passes within a distance $r_0$ of an $A_2^+$ ion is

$$\nu_{12} = n_2 \bar{g}_{12}(\pi r_0^2),$$

where $n_2$ denotes the number density of $A_2^+$ ions, and where

$$\bar{g}_{12} = \left(\frac{8kT}{\pi m_{12}}\right)^{1/2}.$$  

The total number of such encounters per unit volume and unit time which are potentially capable of leading to recombination is therefore

$$R_{12}^{(p)} = n_1 n_2 \bar{g}_{12} \pi r_0^2.$$  \hspace{1cm} (8.5)
Let us next define $s_1$ as the probability that an $A^-$ ion will make a thermalizing collision with an X particle while within a distance $r_0$ from an $A^+_2$ ion, and define $s_2$ similarly. The probability of recombination taking place in any one of the above reactions is therefore\(^4\) $(s_1 + s_2)$, and the total number of recombination reactions per unit volume and unit time is

$$R_{12}^{(\text{recomb})} = n_1 n_2 \tilde{g}_{12} \pi r_0^2 (s_1 + s_2). \quad (8.6)$$

Since the recombination coefficient $\alpha_{12}$ is defined by the relation

$$\frac{dn_1}{dt} = -R_{12}^{(\text{recomb})} = -\alpha_{12} n_1 n_2,$$

it follows that

$$\alpha_{12} = \tilde{g}_{12} \pi r_0^2 (s_1 + s_2), \quad (8.7)$$

and that

$$Q_{12}^{(\text{recomb})} = \pi r_0^2 (s_1 + s_2). \quad (8.8)$$

To calculate the probability $s_1$, let us suppose that $A^-$ approaches $A^+_2$ with an impact parameter $b$, as illustrated in Fig. 12. Assuming that $A^-$ does not suffer an appreciable deflection, it will travel a distance $d = 2\sqrt{r_0^2 - b^2}$ while passing through the sphere of influence of radius $r_0$ surrounding $A^+_2$. If $l_1$ denotes the mean free path for a thermalizing collision between $A^-$ and an X particle, then the probability that there will not be a thermalizing collision while $A^-$ is within the sphere of influence about $A^+_2$ is $e^{-d/l_1}$. Since

\(^4\) More accurately, this probability is $(s_1 + s_2 - s_1 s_2)$, since the chance that both ions make effective collisions with X particles when within a distance $r_0$ of each other has been included in both $s_1$ and $s_2$. We have dropped the term $s_1 s_2$ because we shall be interested in conditions for which $s_1$ and $s_2$ are both small.
the probability that the impact parameter lies between \( b \) and \( b + db \) is \( 2\pi db \), it follows that
\[
s_1 = 1 - \left[ \frac{2}{\pi} \int_0^{r_0} b e^{-2\sqrt{b^2 - b^2_0}} db \right] = 1 + 2 \left[ \frac{e^{-\beta_1}}{\beta_1^2} + \frac{e^{-\beta_2}}{\beta_2} - \frac{1}{\beta_1^2} \right],
\]
(8.9)
where
\[
\beta_1 = \frac{2r_0}{l_1}.
\]
(8.10)
We shall be interested in the application of this theory at pressures sufficiently low\(^5\) that the condition
\[
\beta_1 = \frac{2r_0}{l_1} \ll 1
\]
(8.11)
is satisfied. In practical terms, this condition corresponds to pressures of the order of 1 atm or less. Under these circumstances equation (8.9) simplifies and yields the value
\[
s_1 \approx \frac{4r_0}{3l_1}.
\]
(8.12)
This result has the simple physical interpretation that the probability of a thermalizing collision occurring within a sphere of radius \( r_0 \) is proportional to the ratio of \( r_0 \) and the mean free path for thermalization. Substituting for \( s_1 \) and \( s_2 \) into equation (8.7) leads to Thomson's result
\[
\alpha_{12} = \phi_{12} - 4\pi r_0^2 \left( \frac{1}{l_1} + \frac{1}{l_2} \right).
\]
(8.13)
When the masses of the \( X \) particle and the ions are comparable [cf. equation (11.63)],
\[
l_1 \approx \frac{1}{n_x r_0^2},
\]
(8.14)
and similarly for \( l_2 \). Results of experiments on ion-ion recombination have been shown to be in good agreement with Thomson's theory (see Massey and Burhop, 1952, p. 623).

\(^5\) At high pressures \( s_1 = s_2 = 1 \) and \( s_{12} = \pi r_0^2 \). However, Thomson's theory breaks down at high pressures because there may be more than one collision within \( r_0 \) which could restore some of the initial kinetic energy to the ions (see McDaniel, 1964, p. 571).