ADHESION OF ELECTRONS TO ATOMS IN TRIPLE COLLISIONS

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Submitted to JETP editor March 16, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 49, 852-856 (September, 1965)

The probabilities for adhesion of electrons in triple encounters e + A + B and e + e + A are expressed in terms of the corresponding cross sections for the disintegration of the atomic systems A⁻ and B⁻. The method employed is based on the statistical principle of detailed balancing. It is shown that at target-gas densities of $10^{13}-10^{15}$ cm⁻³ adhesion of electrons to neutral atoms in triple encounters is more probable than photo-adhesion. The pressure and temperature ranges in which the rate of the reaction $e + e + A = A^- + e$ is greater than that of the reaction $e + A + A = A^- + A$ in a gas in thermal equilibrium are obtained.

1. The formation and disintegration of negative ions play an important role in astrophysics and in the physics of the upper layer of the earth's atmosphere, in gas discharges, and in the acceleration of charged particles. Among the most intense processes of formation of negative atomic ions are collisions between electrons or heavy atomic particles and molecules [1-5]. In heated atomic gases (for example, vapors of alkaline metals), when the molecule concentration is negligible, these processes are negligible. The negative ions can then be produced by photo-adhesion of the electrons to the atoms, and also by triple-collision processes.

We express these reactions in the following manner:

$$e + A = A^- + hv, \tag{1}$$

$$e + \mathbf{A} + \mathbf{A} = \mathbf{A}^- + \mathbf{A},\tag{2}$$

$$e + e + \mathbf{A} = \mathbf{A}^- + e. \tag{3}$$

During the process of photo-adhesion (1), the excess of energy is transferred to the photon. The cross section of this process is $\sim 10^{-23}$ cm^{2 [4]}. In processes (2) and (3) the electron energy is transferred to a third body (atom or electron). Reaction (3) is analogous to triple recombination of positive ions:

$$e + e + A^+ = A + e,$$

which plays an important role in the decay of a dense plasma.

Massey ^[5] and Smith ^[6] estimated the probabilities of processes (2) and (3), considering the direct problem of the motion of a system of two electrons (or an electron and an atom) in the field of a neutral atom. They found as a result that processes (2) and (3) can prevail over photo-adhesion (1) at electron densities larger than $10^{17}-10^{18}$ cm⁻³. In this paper we express the probability of adhesion of an electron to an arbitrary monatomic system in triple-collision processes (2) and (3) in terms of the cross sections for the disintegration of the corresponding atomic systems by an atom and an electron, with the aid of the principle of detailed balancing, which is the consequence of the reversibility of the laws of mechanics with respect to time. The probabilities obtained in this manner for the adhesion of electrons to neutral atoms exceed by several orders of magnitude the results of Massey and Smith. The electron densities for which the intensities of processes (2) and (3) and of process (1) become equalized, are of the order of $10^{13}-10^{15}$ cm⁻³.

2. We characterize the processes (2) and (3) respectively by the quantities β_a and β_e , equal to the probability of the adhesion of the electron to an atom per unit time and referred to one electron and atom per unit volume (β_{ae} has here the dimension cm⁶/sec). The energy conservation laws can be written in the following manner. In process (2) we can neglect the electron momentum (if its energy does not exceed the relative energy of the heavy particles by a factor M/m), and therefore

$$T_a + W + E_0 = T_a',$$
 (2')

where T_a and T'_a are the energies of relative motion of the heavy particles before and after the collision, W is the kinetic energy of the adhering electron, and E_0 is the binding energy of A^- . In the process (3) we can assume that the energy of the heavy particle remains constant, and we obtain

$$T_e + W + E_0 = T_e', (3')$$

where T_e and T'_e are the kinetic energies of the

electron (which disintegrates A^- in a process that is the inverse of (3)) before and after the collision.

We see thus that in either case one of the energies is conserved: in process (2)—the energy of translational motion of the center of gravity of the heavy particles, and in process (3)—the energy of the heavy particle. This simplifies the situation, and we can write the principle of detailed balancing in the form

$$n_1 n_2 f_a(T_a') dT_a' d\sigma_a(W, T_a') v_a$$

= $n_2^2 n_3 f_a(T_a) dT_a f_e(W) dW \beta_a(W, T_a),$ (4)

$$n_1 n_3 f_e(T_e') dT_e' d\sigma_e(W, T_e') v_e$$

= $n_2 n_3^2 f_e(W) f_e(T_e) dT_e dW \beta_e(W, T_e),$ (5)

where v_a is the relative velocity of the heavy particles, and v_e the velocity of the electron which disintegrates A⁻; $f_a(T_a)$ and $f_e(T_e)$ are the distributions of the heavy particles and electrons relative to the energies T_a and T_e , with

$$\int_{0}^{\infty} f(x) \, dx = 1;$$

 n_1 , n_2 , and n_3 are the equilibrium concentrations of the negative ions, atoms, and electrons respectively; $d\sigma_a(W)$ and $d\sigma_e(W)$ are the cross sections for the disintegration of a negative ion by an atom and electron, under the condition that the knocked-out electron has an energy W.

Let us consider thermal equilibrium, when f_a and f_e are Maxwellian. We have, obviously, with the aid of (2') and (3')

$$\frac{f_{ae}(T_{ae}')}{f_{ae}(T_{ae})} = \left(\frac{T_{ae} + W + E_0}{T_{ae}}\right)^{\frac{1}{2}} \exp\left[-\frac{W + E_0}{\Theta}\right], \quad (6)$$

where Θ is the temperature. Substituting this in (4) and (5), we get

$$\beta_{ae}(W, T_{ae}) = \frac{\sqrt[4]{\pi}}{2} \frac{n_1 \Theta^{\prime \prime *}}{n_2 n_3} e^{-E_0 / \Theta} \left(\frac{T_{ae} + W + E_0}{T_{ae} W} \right)^{1/2} v_{ae} \frac{d\sigma_{ae}}{dW}.$$
(7)

The ratio of the concentrations n_1/n_2 , n_3 at equilibrium is a function of the temperature only^[7]. In analogy with the case of positive ionization for thermal equilibrium we obtain

$$\frac{n_1}{n_2 n_3} = \frac{g_-}{2g_a} \left(\frac{2\pi}{m}\right)^{3/2} \frac{\hbar^3}{\Theta^{3/2}} e^{E_0/\Theta}, \qquad (8)$$

where g_{-} and g_{a} are the statistical weights of the negative ion and the atom, and m is the electron

mass. Substituting (8) in (7), we obtain

 $\beta_{ae}(W, T_{ae})$

$$=\frac{\pi^2}{\sqrt{2}} \frac{g_-}{g_a} \frac{\hbar^3 v_{ae} d\sigma_{ae}/dW}{m^{3/2} W^{1/2}} \left(\frac{T_{ae}+W+E_0}{T_{ae}}\right)^{1/2}.$$
 (9)

We see that in (9) the dependence on the equilibrium distribution function f(x) has disappeared completely. The intermediate results (7) depend on the form of the considered statistical equilibrium. The final result (9), as expected, does not contain f(x), since the β_{ae} are characteristics of the elementary process.

Formulas (8) and (9) do not change at all if A denotes in reactions (2) and (3) an arbitrary monatomic system: a neutral atom or an ion with arbitrary charge. Moreover, in reaction (2) the two heavy particles can be different, i.e., we can consider the reactions

$$e + A + B = A^- + B$$
, $e + A + B = A + B^-$.

In this general case, E_0 in (8) and (9) stands for the binding energy of the electron with that system to which it adheres, and g_- is the statistical weight of the system A^- or B^- (in the state in question), which has one more electron than A or B.

The adhesion frequency per unit target particle $(n_{ae}\beta_{ae}$ for triple collisions, and $\sigma_{ph}v_e$ for the photoadhesion process) has a different dependence on the gas density. There exists therefore a "critical" density

$$n_{\rm cr} = \sigma_{\rm ph} v_e \beta_{ae}^{-1},$$

above which adhesion in triple collisions prevails over photo-adhesion.

Inasmuch as the cross sections for the destruction of negative ions by an atom and an electron are approximately two orders of magnitude larger than the corresponding cross sections for the ionization of neutral atoms, the relative roles of processes (2) and (3), compared with process (1), become significant at lower gas densities than in the case of formation of neutral particles.

Let us estimate the order of magnitude of β_{ae} in (9). Obviously, $d\sigma/dW$ has the same order as $\sigma_{ae}E_0^{-1}$ and $v_{ae} \sim (T_{ae}/\mu)^{1/2}$, where μ is the reduced mass of the two atoms or of the atom and the electron. As follows from several papers^[8-10], the total cross section for the disintegration of a negative hydrogen ion by an atom is $\sigma_a \sim 10^{-15}$ cm². In the case of $T_{ae} \sim W \sim E_0$, we obtain for hydrogen $\beta_a \sim 3 \times 10^{-32}$ cm⁶/sec. The cross section for

the disintegration of a negative hydrogen ion by an electron is of the order of $\sigma_e \sim 10^{-14} \text{ cm}^{2}$ [11], and therefore when $T_{ae} \sim W \sim E_0$ we obtain for hydrogen $\beta_e \sim 3 \times 10^{-30} \text{ cm}^6/\text{sec.}$ For alkaline-metal vapors, whose negative ions have a binding energy several times smaller than H⁻, the value of β_{ae} is approximately one order of magnitude larger than for hydrogen. The "critical" density for the adhesion of an electron to a neutral atom of hydrogen at $T_a \sim E_0$ is found to be: approximately 3×10^{15} atoms/cm³ for process (2) and approximately 3×10^{13} electrons/cm³ for process (3). The "critical" density for the process $e + e + H^{+}$ = H + e (H-hydrogen in the ground state) for T_e $\sim E_0$ is of the order of 10^{20} cm⁻³ (data on the cross section for the ionization of hydrogen by an electron, $\sigma_{\rm e}\sim 5\times 10^{-17}~{\rm cm}^2,$ and the cross section of photorecombination of a proton and electron, $\sigma_{\rm ph} \sim 10^{-21} {\rm ~cm^2}$, are taken from ^[4]). Since the cross sections for the ionization of an excited atom are considerably larger than for an unexcited atom, the corresponding "critical" densities for the reaction $e + e + H^+ = H^* + e$ should be smaller.

3. Of practical interest is the coefficient β_{ae} averaged over the distributions of the gas particles with respect to T and W. Let us calculate this coefficient for the reactions (2) and (3), assuming that the distributions with respect to T and W are Maxwellian. There are no definite published data on the spectrum $d\sigma/dW$ of electrons knocked out from negative ions. Starting from the results of Demkov ^[9] or Smirnov and the author ^[11], we can expect the spectrum to have a maximum at $W \sim E_0$ and to decrease rapidly when $W > E_0$. This fact allows us to average (9) over W in the limit when $\Theta \gg E_0$.

Since the principal role is played by $T_{ae} \sim \Theta$, the quantity $\beta f(W)$ can be expanded in powers of W/Θ and $(W + E_0)/T_{ae}$. Confining ourselves to the first term of the expansion, we get

$$\overline{\beta}_{ae}(T_{ae}) = \pi \sqrt[V]{2\pi} \frac{g_{-}}{g_{a}} \frac{\hbar^{3}}{(m\Theta)^{s/_{2}}} \sigma_{ae} v_{ae}, \qquad (10)$$

where σ_{ae} is the average cross section for the disintegration of the negative ion. If we taken (10) to be unity, then the next term of the expansion of $\beta f(W)$ in powers of W/Θ is

$$\left(\frac{W+E_{0}}{2T_{ae}}-\frac{W}{\Theta}\right)\frac{d\sigma}{dW}\sim\frac{E_{0}-W}{2\Theta}\frac{d\sigma}{dW}$$

and its averaging gives a relatively small contribution, since $d\sigma/dW$ has a maximum at $W \approx E_0$. This indicates that (10) is valid when $\Theta \gtrsim E_0$.

The next averaging over T_{ae} is easy to carry out, since the cross sections σ_{ae} are practically constants at energies T_{ae} not too close to the threshold E_0 [9-11]. We therefore obtain

$$\overline{eta}_{ae} = \pi \sqrt[V]{2\pi} rac{g_-}{g_a} rac{\hbar^3}{(m\Theta)^{s_2}} \sigma_{ae}(\Theta) \langle v_{ae}
angle, \qquad (11)$$

where $\langle v_{ae} \rangle$ is the average relative velocity of collision. For (2) we have $\langle v_a \rangle = 4\sqrt{\Theta/\pi}M$, where M is the mass of the atoms, and for (3) we have $\langle v_e \rangle = 2\sqrt{2\Theta/\pi}m$.

The total number of negative ions produced on the average per unit volume and per unit time is $n_a^2 n_e \overline{\beta}_a$ for (2) and $n_e^2 n_a \overline{\beta}_e$ for (3). The process (3) therefore prevails over (2) when $n_e \overline{\beta}_e / n_a \beta_a \ge 1$.

Since $\overline{\beta}_{e} \gg \overline{\beta}_{a}$, we obtain, by determining the degree of thermal ionization of the gas ^[7] when $n_{e}/n_{a} \ll 1$, the conditions under which the rates of the reactions (2) and (3) are equal:

$$\left(\frac{\sigma_e}{\sigma_a}\right)^2 \frac{M}{2m} = \frac{g_a}{2g_+} (2\pi)^{3/2} \frac{\hbar^3 N_0}{(\Theta m)^{3/2}} e^{E_1/\Theta}, \qquad (12)$$

where N_0 is the number of all the particles of the gas per unit volume, and E_1 is the ionization energy of the atom. For hydrogen we have $5\times 10^{26} \Theta^{3/2} \exp{(-E_1/\Theta)} = N_0$, where Θ is in eV and N_0 in cm⁻³. For example, when $\Theta = 0.5$ eV we have $N_0 \approx 2\times 10^{14}$ cm⁻³. Reaction (3) prevails, when $N \ge N_0$, and reaction (2) when $N \le N_0$.

In conclusion the author is deeply grateful to B. M. Smirnov and O. B. Firsov for numerous useful discussions.

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Translated by J. G. Adashko 112