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TRANSITIONS BETWEEN ATOMIC AND MOLECULAR IONS

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We calculate the coefficient for transformation of an atomic ion into a molecular ion as a result of triple collisions between the atomic ion and gas atoms. We consider the case of a gas discharge in which the gas temperature is considerably lower than the molecular-ion dissociation energy. The transitions between the atomic and molecular ions are determined in this case by the polarization interaction between ions and atoms in triple collisions. An expression is derived for the ion conversion coefficient for the case when the atom corresponding to the atomic ion and the gas atoms are of the same or different type.

AT temperatures that are low compared with the dissociation energy of molecular and complex ions, the presence of molecular ions in the gas is statistically more favored than that of atomic ions, and the presence of complex ions is more favored than that of simple ones. The usual methods of ion production in a gas, by discharge, by radiation, by fast electrons, or by heavy particles, is connected with ionization of the gas particles and the appearance of atomic or simple ions. Thus, in an inert gas, the atomic ions are produced first, and are then transformed into molecular ions as a result of triple collisions with the gas atoms. A similar situation takes place also in molecular gases at normal pressures and at low temperatures. For example, under normal conditions the stable hydrogen ions are H^+, H_3^+, and H_5^+, whereas ionization of the molecular ion leads to the formation of the H_2^+ ion and of the proton. The transformation of these ions into complicated ones is the result of triple collisions between these ions and the hydrogen molecules.

We define the coefficient k_c of transformation of an atomic ion into a molecular ion (the conversion coefficient) by means of the relation

$$\left.\frac{dN_+^{\mathrm{mol}}}{dt}\right|_{t=0} = k_c N_+^{\mathrm{at}} N_a^2, \qquad (1)$$

assuming that there are no molecular ions at the initial instant of time. Here N_+^{mol} N_+^{at}, and N_a are the densities of the molecular ions, atomic ions, and atoms. We note that the transformation of the atomic ion into a molecular one in triple collisions is a process similar to impact recombination of an electron and a positive ion in triple collisions. Therefore, the conversion coefficient k_c which was introduced by us is similar to the coefficient of triple recombination. Knowledge of the conversion coefficient k_c is essential in the study of the kinetics of ions in a gas.

Let us calculate the coefficient of transformation of the atomic ion into a molecular one in triple collisions. We assume that the temperature of the gas is much lower than the dissociation energy of the molecular ion. Then for the excited states of the molecular ion, for which the binding energy of the atom and of the ion in it is of the order of the gas temperature, the potential of the interaction between the atom and the ion is determined essentially by their polarization interaction. Since the particles colliding in the gas exchange an energy on the order of the temperature, we have for the conversion coefficient

$$N_a^2 k_c \sim N_a \langle v\sigma \rangle w_{\mathrm{dec}}, \qquad (2)$$

where $N_a\langle v\sigma\rangle$ is the frequency of transition of the molecular ion from the state with a dissociation energy on the order of the temperature into more strongly bound states as a result of collision with the gas atoms, and $w_{\mathrm{dec}} \ll 1$ is the ratio of the probability of the transition of the excited molecular ion into more bound states to the probability of its dissociation upon collision with the gas atoms. From the detailed-balancing principle it follows that $w_{\mathrm{dec}} \sim \rho(-T)/\rho(T)$, where ρ is the density of the states of the molecular ion per unit energy interval. With this, for polarization interaction of the ion with the atom we have $w_{\mathrm{dec}} \sim (\beta e^2/T)^{3/4} N_a$, where β is the polarizability of the atom. Using in formula (2) the polarization-interaction cross section $\sigma \sim (\beta e^2/T)^{1/2}$ for the transition of the ion into weakly excited states, we obtain for the conversion coefficient

$$k_c = \mathrm{const}(\beta e^2/M)^{1/2}(\beta e^2/T)^{3/4}, \qquad (3)$$

where M is the mass of the gas atoms, and this coefficient characterizes the process

$$X^+ + 2X \to X_2^+ + X. \tag{4}$$

The result (3) can be obtained on the basis of the Thomson formula.[1] Indeed, according to Thomson's theory, the critical radius b, at distances below which capture of the ion by the atom is possible, is determined by the relation

$$U(b) = \beta e^2 / 2b^4 = {}^3/_2 T, \qquad b = (\beta e^2 / 3T)^{1/4}.$$

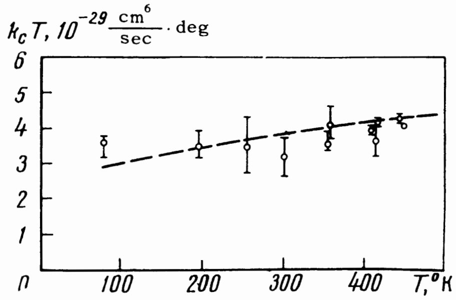
The frequency of formation of the bound state of the atom and of the ion is the product of the frequency of penetration of the atom into the critical region $N_a \bar{v} \pi b^2$ and the probability of the concurrent collision of the ion with another atom $bN_a\sigma$, as a result of which the ion loses energy and is left in a bound state with the first atom. Here N_a is the density of the atoms, $\bar{v} = 4(T/\pi M)^{1/2}$ is the average relative velocity of collision of the ion with the atom, and σ is the average cross section for the polarization capture of the ion by the atom. It follows from this that the conversion coefficient, which is equal to the molecular-ion formation frequency divided by the square of the density of the atoms, is given by formula (3). The constant in (3), calculated by Thomsen's formula, is ~ 16.

The most complete information on the coefficient of conversion of the atomic ions into molecular ones was obtained for helium. The conversion coefficient, in units of 10^{-31} cm^6 sec^{-1}, for helium ions at 300°K is, in accordance with measurements by different authors, 0.62,[2] 0.35,[3] 1.08,[4] 1.05,[5] 1.15,[6] 1.09,[7] 1.12.[8] On the other hand, calculations by Bates[9] lead to a value 1.6. If, on the basis of these results, the conversion coefficient in helium is taken to be 1.1 × 10^{-31} cm^6 sec^{-1}, we obtain from formula (3) (const ≈ 42):

$$k_c = 42(\beta e^2 / M)^{1/2}(\beta e^2 / T)^{3/4}. \tag{5}$$

The coefficient of conversion of neon ions calculated in accordance with (5), namely 1.15 × 10^{-31} cm^6 sec^{-1}, is double the experimentally measured value obtained by Beaty and Patterson.[8] The conversion coefficient obtained by Kretschmer and Peterson[3] for argon ions (1.46 × 10^{-31}), as well as the conversion coefficient for helium ions (0.35 × 10^{-31}) do not agree with formula (5), which leads to a value 4.25. The conversion coefficient of mercury ions estimated by Biondi[10] (10^{-31} cm^6 sec^{-1}) at 400° C deviates noticeably from the results of formula (5) (4.7 × 10^{-31}).

The figure shows the dependence of the helium-ion conversion coefficient on the temperature, as measured by Niles and Robertson,[7] and which agrees satisfactorily with formula (3) $k_c \sim T^{-3/4}$. Niles and Robertson[7, 11] obtained a relation $k_c \sim T^{-1}$, using the hard-sphere model for the colliding particles in an analysis of a process that is the inverse of (4), and reconstructing the conversion coefficient from the rate of this inverse process. It should be noted that the result of Niles and Robertson is connected with model assumptions, whereas formulas (3) and (5) are valid if the potential of the interaction of the ion with the atom coincides with the polarization potential wherever the magnitude of this potential is of the order of the temperature.



Conversion coefficient k_c of atomic ions He$^+$ into molecular ones vs. gas temperature.

In conclusion let us consider the conversion of atomic ions into molecular ones, occurring with the participation of ions and atoms of different types. Let us investigate the following processes:

$$X^+ + 2Y \to XY^+ + Y, \tag{6a}$$
$$X^+ + X + Y \to X_2^+ + Y, \tag{6b}$$
$$X^+ + X + Y \to XY^+ + X. \tag{6c}$$

Let m be the mass of particle Y and let M be the mass of particle X, with m < M. To determine the conversion coefficient for each of the reactions (6), we use Thomson's theory. The critical radius b for the ion and the atom, which combine to form the molecular ion, is determined from the relation

$$U(b) = \beta e^2 / 2b^4 = {}^3/_2 T.$$

The cross section σ from the collision of the ion with the atom that carries away the excess energy, is determined by the impact parameters of the collision, at which the energy transfer is of the order of the temperature. In the case when the ion and atom have different masses, we get

$$\sigma \sim \rho^2, \qquad U(\rho)\,(m / M)^{1/2} \sim T.$$

Stipulating that in the case of identical particles the results coincide with formula (5), we obtain for the conversion coefficient of each of the reactions (6), respectively,

$$k_c = 42(m / M)^{1/4}(\beta_Y e^2 / T)^{3/4}(\beta_Y e^2 / m)^{1/2}, \tag{7a}$$
$$k_c = 42(m / M)^{1/4}(\beta_X e^2 / T)^{3/4}(\beta_Y e^2 / m)^{1/2}, \tag{7b}$$
$$k_c = 42(\beta_Y e^2 / T)^{3/4}(\beta_X e^2 / M)^{1/2}. \tag{7c}$$

In particular, for the process $Hg^+ + Hg + He \rightarrow Hg_2^+ + He$, at a temperature ~400 °C, formula (7b) gives for the conversion coefficient a value $\sim 1.5 \times 10^{-31}$ cm^6 sec^{-1}, which agrees with the measurements of Biondi[10] (1.7×10^{-31}).

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