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# Three-body ion – molecule processes

G V Karachevtsev (deceased), P S Vinogradov

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**Abstract. Theoretical models used in the studies of three-body ion – molecule reactions are considered and the experimental methods for the study of these processes are described. The results of experimental studies are presented, including those for gas phase reactions at ultra-low temperatures and for the kinetic isotope effect induced by the symmetry of the species. The bibliography includes 130 references.**

## I. Introduction

Three-body ion – molecule processes of the type

$$A^+ + B + M \longrightarrow \text{products}, \quad (1)$$

where $A^+$ is an atomic or polyatomic ion (in this case, positively charged) and B and M are neutral species, constitute an important class of reactions which can affect substantially the composition and electrophysical properties of the low-temperature plasma.

In gas-phase chemical kinetics, the term 'three-body reactions' denotes reactions the rates of which depend on the concentrations of the components $A^+$, B and M. The rate of a third-order reaction is represented as

$$W = k_t[A^+][B][M],$$

where $k_t$ is the rate constant independent of the component concentrations, these reactions may be regarded as a special case. Such a reaction order is characteristic, for example, of the association reaction at sufficiently low pressure.

The dependence of the reaction rate on the concentrations of the components over a wide pressure range is more complex. This dependence is determined by a combination of several processes: the formation of transition states (with a definite dispersion of lifetimes), decomposition of these states through different channels (into different quantum states with account of the conservation laws), as well as energy exchange between the species and its intramolecular conversion. It should be noted that the rates and branching ratios between the channels for some exothermic reactions which are formally represented as second-order reactions

$$A^+ + B \longrightarrow \text{products},$$

can depend on the buffer gas pressure. For some of the ion – molecule processes, this dependence can be noticeable even at a pressure of several Torr.

The majority of studies regarding three-body ion – molecule processes are devoted to the investigation of association reactions. The pressure range in which quantitative measurements of the rate constants have been carried out † usually does not exceed 10 Torr. The most reliable values of the rate constants are obtained by the mass spectrometric method where reactions occur in a flow or ion drift in an electrical field at a buffer gas pressure of $\sim$1 Torr. Under these conditions, a third order reaction is observed for the majority of systems studied involving a small number of atoms. As the number of atoms is increased (for some systems, starting from seven or eight), a transition mode is established, which corresponds to a change from a third to a second order reaction.

The importance of the association processes is due to the fact that it is the composition of the positive ions that largely determines the loss rate of free electrons, *i.e.*, one of the basic parameters characterising the properties of an ionised gas. The recombination coefficients of various types of positive ions with electrons can differ by several orders of magnitude. This can be seen from two examples.

In the inert gas plasma, three-body association results in the formation of molecular ions such as $He_2^+$, $Ne_2^+$, $Ar_2^+$, which recombine with electrons much more efficiently (in dissociative recombination processes) than the corresponding atomic ions that have different neutralisation mechanisms.

In the atmosphere of Earth, as the altitude decreases, three-body association affects essentially the kinetics of ionic processes starting from the *D*-layer (height range 75 – 90 km). Rocket-based *in situ* measurements detected complex ions in the *D*-layer.[1,2] The formation of complex (cluster) positive ions results in a decrease in the concentration of free electrons, as the dissociative recombination coefficients for these ions are about two orders greater than those for non-cluster primary ions. In the Earth stratosphere, where the high-energy intergalactic species are the major ionisa-

**G B Karachevtsev** Moscow Institute of Physics and Technology, Institutskii per. 9, Dolgoprudnyi, Moscow region, 141700 Russian Federation. Fax: (095) 408-6869
**P S Vinogradov** Institute of Energetic Problems of Chemical Physics, Russian Academy of Sciences, Leninsky pr. 38/2, Moscow, 117829 Russian Federation. Fax: (095) 137-8258

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† Or rather, effective rate constants, since such processes are not elementary in the strict sense.

tion source, the ion chemistry is completely determined by transformations of positive and negative cluster ions.[3,4]

Three-body processes play an important role in high-pressure analytical mass spectrometry,[5,6] for example, where chemical ionisation and ionisation at atmospheric pressure are used, as well as in plasma chromatography.[7,8] Termolecular reactions can compete with some slow bimolecular reactions of species exchange[9–17] and with energy exchange processes.[11,18–20]

In this review, we discuss the specific features of three-body ion–molecule reactions and the application of the developed theories to processes involving ions; the theories based on statistical approaches occupy a special place among them. The experimental methods for the study of termolecular reactions are described. A separate section deals with the analysis of results of studies of the processes occurring at very low temperatures.

## II. Theoretical models for three-body reactions

Three-body reactions involve several steps. The Lindemann scheme of three-body association is rather simplified, however, it gives a qualitative idea of the multistage character of the process. The first step implies the formation of an excited complex in a bimolecular collision; the complex can then undergo a spontaneous decay into the original species

$$A^+ + B \xrightarrow{k_f} AB^{+*},$$

where $k_f$ is the rate constant for the formation of the collisional complex,

$$AB^{+*} \xrightarrow{k_d} A^+ + B,$$

where $k_d$ is the rate constant for the spontaneous decay of the collisional complex.

In parallel with the decay, stabilisation of the excited complex can occur upon collision with the third species M

$$AB^{+*} + M \xrightarrow{k_s} AB^+ + M,$$

where $k_s$ is the rate constant for the collisional stabilisation of the excited complex. Assuming the concentration of $AB^{+*}$ to be quasi-steady, the rate of, *e.g.*, the association process can be presented as

$$W_a = \frac{d[AB^+]}{dt} = k_s[M][AB^{+*}] = k_f k_s \frac{[A][B][M]}{k_d + k_s[M]}.$$

The rate constant for a three-body reaction $k_t$ (which is of the third order and a dimensionality of $cm^6\ s^{-1}$) equals

$$k_t = \frac{k_f k_s}{k_d + k_s[M]}. \qquad (2)$$

At the low pressure limit, where

$$[M] \ll \frac{k_d}{k_s},$$

$k_t$ does not depend on [M]

$$k_t = \frac{k_f k_s}{k_d}.$$

If the equality (2) does not hold, the association rate constant is usually represented as an apparent rate constant of a quasi-bimolecular second-order reaction (dimensionality $cm^3\ s^{-1}$) which depends on [M]:

$$k_{ef} = \frac{k_f k_s[M]}{k_d + k_s[M]}.$$

The dependence on [M] disappears only at the high pressure limit; in this case, $k_{ef} = k_\infty = k_f$.

Some authors supplement the scheme with the formally possible decomposition of the $AB^{+*}$ complex upon collisions with M

$$AB^{+*} + M \xrightarrow{k_{-s}} A^+ + B + M.$$

Note that the scheme does not take radiative stabilisation into account

$$AB^{+*} \xrightarrow{k_r} AB^+ + h\nu.$$

This process does not require stabilisation by a third species and can compete with the stabilisation only at very small concentrations of M ($[M] \leqslant k_r/k_s$).

The Lindemann model is based on formal kinetics concepts. Nevertheless, the model shows the key role of the intermediate excited complex $AB^{+*}$. It is the formation of this complex with an energy sufficient for its decay that allows one to consider three-body association using various approaches developed in the studies on unimolecular decomposition.[21–25]

An important role in the transformations of the $AB^{+*}$ complex belongs to energy exchange, including both intramolecular energy conversion of the highly excited species $AB^{+*}$ ('reactive molecule' in terms of the unimolecular decomposition theory) and energy exchange with the buffer gas (collisional relaxation–activation). The contemporary theoretical approaches used for the description of the energy exchange and reactions of highly excited polyatomic molecules, as well as the results of optical experimental studies of these processes, are described in sufficient detail elsewhere.[26]

### 1. Association of atomic species

In the simplest case, where $A^+$ and B are atomic species, the rate constants can be calculated using the method of trajectories. It is also useful to consider other ways of estimating that give a qualitative idea of the magnitudes of the rate constants for this type of reactions.

For ion–atom processes at low energies, the ion–neutral species interactions are determined by the long-range potential and $k_f$ and $k_s$ have a typical value of $10^{-9}\ cm^3\ s^{-1}$. The minimum lifetime of a collisional complex $\tau_c = 1/k_d$ can approximately be estimated as the time during which one species is located near another one, *i.e.*, as the ratio of several characteristic sizes of the atoms to the velocity of their relative motion. Such an estimation yields a value of the order of $k_d \simeq 10^{13}\ s^{-1}$ and an association rate constant of atomic species of the order of $k_t \simeq 10^{-31}\ cm^6\ s^{-1}$ (see Refs 21 and 27).

Let us note an interesting approach to the estimation of the rate constant for ion-atom association based on the data on the mobility of ions and polarisability of atoms. The rate constant for the process can be calculated using the formula [28]

$$k = 3.27 \times 10^{-27} \frac{Z^{5/2}(\alpha_M m/T m_A)^{3/4}}{\mu_0(m_A + m_B)}\ (cm^6\ s^{-1}), \qquad (3)$$

where $Z$ is the ion charge in elementary charge units; $m$ is the reduced mass

$$m = \frac{m_A m_M}{m_A + m_M},$$

$m_A$, $m_B$ and $m_M$ are the masses of species A, B and M in atomic mass units, respectively; $T$ is the temperature in K; $\mu_0$ is the reduced mobility of the ion in $cm^2\ (V\ s)^{-1}$ estimated using the Langevin formula (which is valid if the species A and M are different)

$$\mu_0 = 13.8 \frac{\alpha_B m_A m_B}{m_A + m_B},$$

$\alpha_B$ and $\alpha_M$ are the polarisabilities of B and M in $10^{-23}\ cm^3$. The experimentally measured mobilities $\mu_0$ are used in the calculations. This approach is based on the fact that the mobility is determined

by the cross-section and kinematics of collisions, *i.e.*, the averaged characteristics of energy transfer in collisions are used.

Formula (3) provides a fairly good description of the experimental data for the association of atomic species and can be used for reliable estimates of the association rate constants at temperatures from 70 K to 300 K. Similar calculated values of rate constants are obtained using an approach suggested elsewhere.[29]

A quantum-mechanical calculation with account of species tunnelling through a centrifugal barrier (*i.e.*, with account of resonance quasi-bound states) yields a correction (less than 20% at ambient temperature) to the data of a classical calculation even for the reaction of light species,[30] for example,

$$He^+ + He + M \longrightarrow He_2^+ + M.$$

Considerable discrepancies arise at very low temperatures. Experimental results for a flow cooled to 1 K after gas expansion through a nozzle[31–34] do not correlate with the temperature dependence which follows from formula (3). The reasons for this discrepancy are not known yet. Probably, one has to take the quantum effects in scattering processes into account in order to provide agreement between the experimental results and the calculation.[35] The importance of these effects has been noted, *e.g.*, in studies of the ion mobility in a gas at low temperatures.[36–38] In addition, the dynamics of the collisional complex at very low gas temperatures can be affected by thermal infrared radiation of the relatively 'hot' walls.[39] This radiation affects the energy redistribution in the system, which affects the lifetime of the intermediate complex.

The approach described above is of interest for the estimation of the association rate constants of electronically exited atomic ions. It is known that the mobility of such ions can differ from the mobility of ions in the ground state.[40] The difference is due to partial electron density transfer from the neutral species to the ion in collision. The transfer is possible over rather long distances (10 Å). This results in a decrease in the effective polarisability of the neutral species and should affect the collision cross-section and the association rate constant.

An analysis[41] showed that the available experimental results on the association rate constants involving polyatomic species are poorly described by the formula (3). Nevertheless, the following qualitative conclusions may be made from comparison of the experimental results and those of calculations presented in Fig. 1: the points above the straight line, which characterises the equality between the measured rate constants and those calculated using the formula (3), correspond to the formation of complexes with high bond energy (more than 1.5 eV); the points below the straight line correspond to the formation of weakly bound complexes. This correlation is related to the characteristic features of the energy exchange processes in polyatomic systems and may be explained based on more rigorous theoretical approaches with the use of the statistical theory.

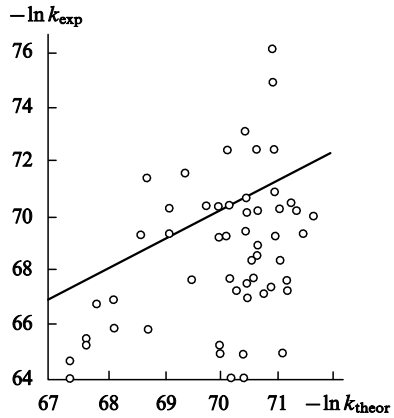



**Figure 1.** Correlation between the experimental rate constants for molecular ion association and those calculated using the formula (3).[41]

Qualitatively, the divergence between the calculations and experimental results can be explained by the fact that the characteristic lifetime of a complex is longer than that determined by the kinematics of collisions of 'point' species having no molecular structure. An increase in the lifetime of the complex in molecular systems virtually does not affect its mobility but results in an increase in the association rate constant.

For weakly bound complexes, the overestimated calculated rate constants for the processes involving molecular species may be explained by a decrease in the efficiency of the complex stabilisation. Upon a collision with the third body, the latter takes away a rather small fraction of the excess internal energy of the complex ($\sim kT$). Therefore, even after collision, the energy in the internal degrees of freedom of the complex is sufficient for its decomposition.

## 2. Characteristic features of ion – molecule interactions

Close similarities exist between the termolecular reactions involving only neutral species[42,43] and ion – molecule reactions. On the other hand, there are also differences caused by the specific character of interaction between ions and neutral species. They are characterised by longer-range interactions than colliding neutral species. In addition, there are also certain specific features in the interactions at short distances.

The peculiarity of long-range interactions results in the cross-sections of ion – molecule collisions, and hence the rate constants for collisions, being much greater than the corresponding values for neutral species. The formation of a collisional complex occurs in the first step of three-body processes, and this is one of the reasons why the overall rate for ion – molecule interaction is greater than that for neutral – neutral species.

The typical rate constants for collisions between ions and molecules at room temperature are of the order of $10^{-9}$ cm$^3$ s$^{-1}$. Therefore, the rate constants for three-body reactions of ions may be expected to be $\sim 2-3$ orders greater than similar reactions of neutral species at the low pressure limit due to the greater values of $k_f k_s$.

The dependence of the collision rate constant on the translational energy of species is determined mainly by the polarisation interaction (*i.e.*, the interaction of an ion with an induced dipole) and the ion – permanent dipole interaction if the neutral species has a permanent dipole moment $\mu_d$. If one assumes that the dipole is always directed along the radius-vector $\mathbf{r}$ connecting the colliding species regarded as point masses, the corresponding effective potential has the form

$$U_{ef} = \frac{L^2}{2\mu \mathbf{r}^2} - \frac{\alpha q^2}{2\mathbf{r}^4} - \frac{\mu_d q}{\mathbf{r}^2}, \tag{4}$$

where $L$ is the orbital angular momentum, $\mu$ is the reduced mass, $\alpha$ is the polarisability of the neutral species, and $q$ is the ion charge. The first term, *i.e.*, the centrifugal potential, considers the fact that the relative motion occurs in the central ion. If the molecule is non-polar ($\mu_d = 0$, the Langevin model), the collision rate constant is determined by the expression[44]

$$k_L = 2\pi q \sqrt{\frac{\alpha}{\mu}}. \tag{5}$$

If the neutral species has a permanent dipole moment, the dynamics of the collision process becomes much more complex. Formula (4) describes the so-called locked dipole model, while the dipole rotation, which is the closer to the free rotation the greater is $\mathbf{r}$, is not taken into account. One of the coordinates of the potential energy surface of species interacting over long distances, $U(\mathbf{r},0)$, is the angle $\theta$ between the direction of the dipole axis and the radius-vector

$$U(\mathbf{r},0) = -\frac{\alpha q^2}{2r^4} - \mu_d \frac{q}{\mathbf{r}^2}\cos\theta.$$

The effect of the ion–dipole interaction on the collision rate constants has been studied in sufficient detail[45–47] and procedures have been developed for the calculation of these constants.[45,48]

In spite of the fact that the ion–dipole interaction is long-ranged ($\sim -1/r^2$), its contribution to the overall collision cross-section is not great as compared to the contribution in the case of a locked dipole model. Because of the dipole rotation, the time phases of attraction ($\cos\theta > 0$) and repulsion ($\cos\theta < 0$) are averaged to some extent, and the total effect is comparable with the contribution from the polarisation interaction; however, dependence of the collision rate constant on temperature appears in this case.

For some molecules, the polarisability $\alpha$ can be anisotropic, *i.e.*, it can depend on the molecular orientation in an electrical field. However, taking into account the relationship (5) and the averaging effect described above, it may be noted that the contribution of this anisotropy is insignificant (usually $< 10\%$). If the molecule has a quadrupole moment $Q$, $\alpha$ is also anisotropic. The corresponding contribution to the interaction potential is determined by the equation

$$U_Q(r,\theta) = \frac{1}{2}\frac{Qq(3\cos^2\theta - 1)}{r^3}.$$

Estimates show that the contribution to the collision rate constant due to ion–quadrupole interaction ($\propto Q^{2/3}/\alpha^{1/2}$) is not very large in comparison with the Langevin constant ($\sim 10\%$). The contributions due to other types of interactions proportional to $-1/r^N$ (the exponent $N$ depends on the interaction type) are also relatively small.[45]

To summarise the above considerations, it should be noted that long-range interactions of ions with molecules and atoms are mostly determined by electrostatic forces represented as a sum of terms with different exponents $N$. The main contribution to the collision rate constant is given by the almost isotropic polarisation interaction ($\propto -1/r^4$). For polar molecules, the rotation of dipoles is not 'frozen' at long distances, and the contribution to the collision rate constant due to the ion–dipole interaction can be comparable with the Langevin constant only for a sufficiently large dipole moment ($> 3$ Debye units).

The Langevin model provides rather precise estimates of actual collision rate constants at translational energies of species from 0.01 to 1 eV. For a typical value of $k_L = 10^{-9}$ cm$^3$ s$^{-1}$, the cross-section $\sigma(\upsilon) = k_L/\upsilon = 3.3\times10^{-14}$ cm$^2$ at the initial ($\mathbf{r} = \infty$) velocity of the relative motion of species $\upsilon = 3\times10^{-14}$ cm s$^{-1}$. In this case, the maximum value of the aiming parameter $b^*(\upsilon)$ allowing a collision to occur is

$$b^*(\upsilon) = \left[\frac{\sigma(\upsilon)}{\pi}\right]^{1/2} = 10.5\,\text{Å},$$

while the 'orbiting' radius $r_c(\upsilon)$ defined from a condition where $U_{ef}(r,\upsilon)$ is a maximum (or the top of the 'centrifugal hump'), is

$$r_c(\upsilon) = \sqrt{2}b^*(\upsilon) = 7.4\,\text{Å}.$$

This value is much larger than the characteristic sizes of atoms and small molecules. A criterion for the collision to occur is that the initial translational energy exceeded $U_{ef}(r_c)$, *i.e.*, the image point passed above the 'centrifugal hump' into the region of short distances.

The value of $r_c$ may be regarded as an arbitrary border dividing the regions of interaction at short and long distances. The value of $r_c$ enables an approximate estimate of the position of the 'critical' surface (transition state) in the theoretical analysis of the processes with the use of statistical and quasi-equilibrium approaches. The actual position of this surface should be determined by the more precise variational methods. The corresponding criteria are found, for example, from the condition

$$\frac{\partial[W_{s-1}(E - U(r), r)]}{\partial r} = 0,$$

where $W_{s-1}(E-U(r),r)$ is the sum of the allowed states for all degrees of freedom, except for the reaction coordinate $r$, in the energy range $E-U(r)$; $E$ is the total energy.

At short distances, the interaction between the species cannot be represented as a sum of electrostatic interactions. In this case, one has to use various quantum-chemical methods (*ab initio* and modifications of the semiempirical methods). Nowadays, it is possible to calculate the optimum geometry of stable ionic complexes, their dissociation energies, frequencies of normal vibrational modes and rotational constants with sufficient precision using computer programmes. In turn, these data allow one to find equilibrium constants and other kinetic characteristics.

When comparing ion–molecule processes with those involving neutral species, it should be noted that the bond energy of the complexes $A^+B$, *i.e.*, products of association of a molecular ion formed from a stable molecule A and a stable molecule B, is often much higher than the bond energy of neutral van der Waals clusters AB. At short distances, charge delocalisation is typical; distribution of the effective charge between the species can be represented as $A^{+(1-\delta)} - B^{\delta+}$.

It is noteworthy that some stable complex ions, such as $(O_2)_2^+$, $(CO)_2^+$ and $(NO)_2^+$, have a zigzag structure, *i.e.*, the axes of the molecules $O_2$, CO and NO are not collinear but are parallel to each other and are coplanar. Let us also note that the multiplicity of the ground state of the $(O_2)_2^+$ complex equals four, which means that this state is formed with parallel spins of the ion (doublet) and the $O_2$ molecule (triplet).

The reactions of organic molecular ions with the precursor neutral molecules ($A^+ + A$) most commonly result in protonated ions $AH^+$ as the main products. In the association products of such ions (protonated dimers $AH^+A$), the species A appear non-equivalent, *i.e.*, they have different structures and effective charges. The structure of the complex ion should be represented as $A-H^+-A$, where one of the bonds is longer than the other by 40%–60%.

Thus, ion–molecule interactions are characterised by greater collision cross-sections than interactions of neutral species and wider 'potential wells' in the interactions at short distances. However, despite these features, the fundamental ideas of the theories used for three-body ion–molecule processes and those involving neutral species are alike. Still, the purely technical details can differ essentially in the calculations for particular systems.

## 3. Statistical methods for the calculation of the rate constants of three-body reactions

The statistical approaches have already been used for theoretical calculations of chemical reaction rates for nearly 70 years. The best known among them are the activated complex theory, the RRKM method (the quasi-equilibrium theory) and the statistical theory (phase space theory) taking the conservation of angular momentum into account. To date, these methods have been described in sufficient detail (see, *e.g.*, Refs 21–26).

The wide application of statistical methods to ionic processes started in the early 1950s after the statistical theory of mass spectra had appeared; this theory was used for the calculation of the energy distribution of fragmentation products (decomposition pathways) in the ionisation of molecules by electrons with different energies. Later, they found use in ion–molecule reactions.

The simplest form of the formula from transition state theory is

$$k(T) = \frac{k_B T}{h}\frac{Q^{\#}}{Q}\exp\left(\frac{-E_a}{k_B T}\right),$$

where $k_B$ is the Boltzmann constant, $h$ is the Planck constant, $T$ is the temperature, $E_a$ is the activation energy, $Q^{\#}$ is the partition function for the transition state, and $Q = Q_A Q_B Q_{tr}$ is the product of the partition functions for the reacting species A and B and the translational statistical sum of their relative motion. The microcanonical equation of the RRKM theory has the form

$$k(E) = \frac{W^{\#}(E - E_0)}{h\rho},$$

where $W^{\#}(E-E_0)$ is the number of states (vibrational and rotational) in the energy range $(E-E_0)$, $E$ is the total energy, $E_0$ is the dissociation energy and $\rho$ is the total density of vibrational-rotational states of the reagents.

The most reliable results are obtained in the calculations of the rate constants with the use of phase space statistical theory that takes conservation of the total angular momentum ($J$) into account. This approach was used for calculations of the rate constants of three-body ion – molecule reactions (see, *e.g.*, Refs 49 – 51). An analogue of the Lindemann scheme of the association process is presented by the following scheme within the framework of the statistical model:[52]

$$A^+ + B \xrightarrow{k_f(E-E_0)} AB^{+*}(E-E_0, J),$$

$$AB^{+*}(E-E_0, J) \xrightarrow{k_d(E-E_0, J)} A^+ + B,$$

$$AB^{+*}(E-E_0, J) + M \xrightarrow{k_s} AB^+ + M.$$

The rate constants of the reactions are presented in a microcanonical form, but a two-dimensional one,

$$k(E - E_0, J) = \frac{W^{\#}(E - E_0, J)}{h\rho}$$

and then used in this form in the expression for the overall reaction rate. For example, the association rate constant at small pressures is represented as:[52]

$$k_t = k_f \beta k_c \int_0^{\infty} dE \int_0^{J^*(E-E_0)} \frac{F(E - E_0, J)}{k_d + k_c \beta [M]} dJ, \qquad (6)$$

where $\beta$ is the stabilisation probability, $k_c$ is the rate constant for the corresponding collision, $F(E-E_0,J)$ is the function of distribution over the states taking the conservation of the angular momentum of the $AB^{+*}$ complex into account, and $J^*$ corresponds to the greatest possible angular momentum for the current value of $E$.

For the sake of clarity, the stabilisation rate constant in the formula (6) is presented not in the microcanonical, but in a simplified form $k_s = \beta k_c$, *i.e.*, as the product of the stabilisation efficiency per collision of the $AB^{+*}$ complex with the species M by the rate constant for the corresponding collision. The relationships for the calculation of $F(E-E_0,J)$, $k_d(E-E_0,J)$ and the effective constant are reported in Ref. 52. Formula (6) is a stricter analogue of the expression (4).

The statistical approach was used to obtain the temperature dependence of the association rate constant at the low pressures limit. This constant was found to be mainly determined by the difference in the rotational degrees of freedom of the complex and the reagents ($S$)

$$k_t \simeq T^{-S/2}.$$

A correction ($X$) is introduced in order to take the contribution of vibrations into account, which depends on temperature and is estimated from the ratio of the statistical vibrational partition functions

$$k_t \simeq T^{-(S/2+X)}.$$

The effect of X becomes noticeable at rather high temperatures.

The use of the statistical theory requires detailed data on the activated complex and rather complicated calculations. The success of its application for particular systems often depends on how successfully the parameters of the complex are chosen and how meticulously the distribution functions are calculated.

It should be noted that even rather simple approaches can sometimes be used successfully for the interpretation of the experimental results. For example, the simplified statistical approach has been used [53] for the reaction

$$C_3H^+ + H_2 + He \longrightarrow C_3H_3^+ + He.$$

Statistical methods were used to find the boundaries of the area of experimental results processing where the dependences should conform to the behaviour at the low pressure limit for the ion – induced dipole [54] and ion – dipolar molecule association reactions.[55]

A stricter description of the three-body association process involving complex molecules is based on the solution of the two-dimensional master equation [such as equation (6)]. The corresponding approaches have been considered in detail;[56] the methods of its solution with account of the specificity of the ion – molecule interaction can be found in Refs 57 – 59.

The approach with the use of the master equation allows one to take into account the contribution of weak stabilising collisions, where the third body M accepts a relatively small fraction of energy from $AB^{+*}$. The remaining energy is sufficient for the decomposition of the complex, while complete stabilisation requires several collisions of this kind.[56 – 59]

For unimolecular decomposition of the $AB^{+*}$ complex with the characteristics $E-E_0$ and $J$, the two-dimensional master equation taking into account both the change in the internal state of the complex and its decomposition into the original species, has the following form at any pressure:

$$k_{uni} g(\varepsilon, J) = \omega \int\int [P_{2D}(\varepsilon, J \to \varepsilon_1, J_1) g(\varepsilon_1, J_1) - P_{2D}(\varepsilon_1, J_1 \to \varepsilon, J) g(\varepsilon, J)] d\varepsilon_1 dJ_1 - k_d(\varepsilon, J) g(\varepsilon, J), \qquad (7)$$

where $k_{uni}$ is the rate constant of the process, $\varepsilon = E-E_0$, $\omega$ is the frequency of collisions between $AB^{+*}$ and the species M, $P_{2D}(\varepsilon,J \to \varepsilon_1,J_1)$ are the probabilities of transitions between the states $(\varepsilon,J \to \varepsilon_1,J_1)$ induced by collisions, and $g(\varepsilon,J)$ and $g(\varepsilon_1,J_1)$ are the populations of the states with a given energy and angular momentum. The separation of variables method was used to simplify equation (7):[57]

$$P_{2D}(\varepsilon,J \to \varepsilon_1,J_1) = P_\varepsilon(\varepsilon,\varepsilon_1) P_J(J,J_1),$$

and present the functions in a form convenient for calculations.

Let us note some features of the use of the statistical theory for ion – molecule association. One of them concerns taking into account rotational freezing if the species B is a dipole. At long distances between $A^+$ and B, the species B is considered as a rotor, while at a distance shorter than some critical value $r_{cr}$ estimated from the relationship

$$\frac{\mu_d q \cos\theta}{r_{cr}^2} \leqslant k_B T,$$

where $\mu_d$ is the dipole moment, it becomes an oscillator. For example, $r_{cr}$ = 13 Å for the HCN molecule, and $r_{cr}$ = 23 Å for acetonitrile. The expressions for the partition functions of the oscillator and the rotor are different. There is an approach which takes the 'hidden rotor' into account.[57]

Yet another specific feature is the rather large moment of inertia of the transition state ($I^*$). Many of the methods for the calculation of the association rate constants from approximate solutions of the two-dimensional microcanonical master equation, which are used for the calculation of the association rate

constants of neutral species, can give wrong results when applied to ion–molecule processes. The approaches used for neutral systems are valid if the ratio of the moments of inertia of the transition state and the reagent is $I^*/I < 6$. This inequality usually holds for reactions of neutral species. If the inequality is not valid, the role of weak collisions increases. This factor can be taken into account using the reported procedures.[57]

## III. Experimental methods for the study of three-body ion–molecule reactions

Mass spectrometric methods are the most popular and convenient ones for the study of three-body ion–molecule reactions. The ratio of the number of three-body collisions ($Z_3$) to the number of two-body ones ($Z_2$) is proportional to the concentration of the species M in the reactor

$$\frac{Z_3}{Z_2} = \frac{k_t[M]}{k_f}.$$

Therefore, one has to increase the pressure in the region where these processes occur to increase the yield of the products. At a pressure of $10^{-8}$ Torr in the mass spectrometer, the effective time of formation of, *e.g.*, a neon molecular ion in the reaction

$$Ne^+ + 2Ne \longrightarrow Ne_2^+ + Ne$$

is $\sim 10^3$ years.[60]

The contribution of two-body ion–molecule reactions to the mass spectra obtained with mass spectrometers with conventional ion sources becomes appreciable at pressures of $\sim 10^{-6}$ Torr and a characteristic reaction time of *ca.* several microseconds. The study of three-body processes requires much higher pressures, *viz.*, at least $10^{-2}$ Torr. This implies that the reaction zone and the zone where ion separation according to their masses occurs should be separated, and in the second area the vacuum required for the analysis (no less than $10^{-6}$ Torr) should be provided.

In ordinary mass spectrometers, small ionisation chambers (with a characteristic size of 1 cm and even smaller) with rather narrow diaphragms (to minimise the gas flow into the high-vacuum zone) are used as a reactor.

Primary ions are usually formed under the action of a fast-electron beam. Diffusion of primary ions to the ionisation chamber walls is accompanied by various reactions. In the vicinity of the diaphragm, the ions are carried away by the gas flow into the high-vacuum zone, separated according to their masses by the mass analyser and detected. The processes occurring in the ionisation chambers at higher pressures have been considered elsewhere.[7, 61, 62]

The ratio between the current of secondary ions $I_2$ formed in three-body reactions [see reaction (1)] to the current of primary ions $I_1$ at low degree of conversion is determined by the expression

$$\frac{I_2}{I_1} = k_t[B][M]\tau,$$

where $k_t$ is the reaction rate constant (with the assumption of the low pressure limit) and $\tau$ is the lifetime of ions in the ionisation chamber. If B = M (it is for such systems that ordinary mass spectrometric methods are most commonly used), then

$$\frac{I_2}{I_1} = k_t[B]^2\tau.$$

This formula is used to determine the rate constants of three-body reactions from the experimental results. Of greatest difficulty is the determination of $\tau$, as the residence time of ions in the ionisation chamber is determined by many factors: diffusion, drift in the field of the space charge of ions, 'penetration' of the extracting field into the chamber, gas flow and geometric parameters of the chamber.

The problem can be simplified by using the pulse method suggested by Tal'roze and Frankevich.[63] These methods are mainly used for the study of ion–molecule reactions at elevated pressures in the ionisation chamber.[64–67]

Ionisation is carried out by a short pulse of electrons. The time dependences of the intensity of ion currents with different masses (over a sufficiently long time period) are studied with the use of a multichannel pulse analyser.[64–66] Ionisation pulses are repeated with a certain frequency, and acquisition of data on the time dependence of the current for each type of ions is performed. This is necessary to obtain reliable results as regards the signal-to-noise ratio. Processing of the kinetic dependences of the ion mass spectra obtained in such a way enables one to find the reaction rate constants.

However, the pulse method suffers a number of drawbacks, the main one of which is that a large excess of the buffer gas is not allowed. If B = M, the mechanism of stabilisation of the complex is much more complicated, as the substitution of the species B, *i.e.*,

$$BA^{+*} + B \longrightarrow B + AB^{+\#}.$$

can contribute to certain extent.

Instead of the actual reaction time, the kinetic dependences include its analogue which is averaged in a rather complicated way.

The flow and drift mass spectrometry methods are the most reliable. The use of these methods for the study of the ion–molecule reaction kinetics has been reviewed rather thoroughly (see Refs 68 and 69).

The flow method (this is also called the flowing after glow method) makes it possible to study the reactions of ions thermolysed in the excess of a buffer gas (He, Ar, $N_2$, *etc.*) at temperatures from 80 K to several hundred degrees (Kelvin scale) and pressures from tenths of a Torr to several Torr.[70–73]

In this method, the region where the primary ions are formed is spatially separated from the reaction zone, which begins where the neutral reagent is added to the flow of the buffer gas containing primary ions that had already been thermolysed. The reaction zone is ended by a nose cone with an orifice in the top, which withdraws a part of the flow for the ionic composition analysis. The time period during which the reactions are studied is determined by the flow rate and the place of injection of the neutral reagent and amounts to several milliseconds.

A useful modification of this method is the injection of ions, which have previously been separated by mass with another mass spectrometer, into the flow [the so-called SIFT (selected ion flow tube) technique]. The main drawback of the SIFT technique is that the conditions of injection from the low pressure zone into the reactor do not allow increasing the pressure in the latter above 1 Torr. Thus, despite the main advantage that only one type of primary ions is considered, the procedure for the processing of the kinetic result is simplified and the reliability is enhanced, the possibility of monitoring the changes in the reaction order occurring at pressures above 1 Torr for many three-body reactions is lost.

A similar principle for studying ion–molecule reactions underlies the drift methods. The motion of ions along the reactor is determined by the rate of the ion drift in an electrical field ($v_d \gg v_f$) generated by a potential difference between the guard rings located along the drift tube rather than by the gas flow rate. The drift methods allow one to study the dependences of the reaction rates on the energy of the relative translational motion of the colliding partners[74–76] which can vary over a wide range (from the value close to that of ambient-temperature motion to several electron-volts in the centre-of-mass system) by varying the electrical field. At present, drift methods make use of the injection of mass-selected ions into the drift tube. This method is known as selected ion flow-drift tube (SIFDT) method.

In the drift methods, there are nonequilibrium distributions of species according to their energies. These can be characterised as the translational collision temperature of an ion and a molecule, the effective temperature of the internal degrees of freedom of an ion (the relevant formulas can be found in Refs 74 and 77) and the

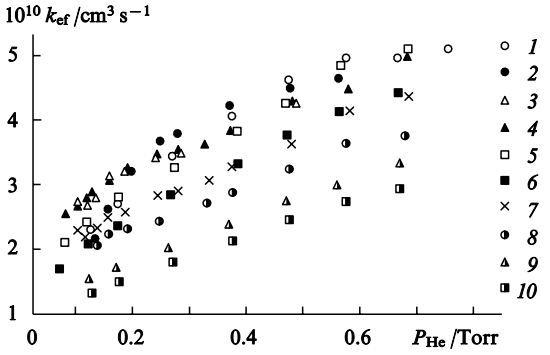



**Figure 2.** Dependence of the effective rate constant for the process (8) on pressure at different values of $E$.
$E$ /meV: (*1*) 41; (*2*) 42; (*3*) 47; (*4*) and (*5*) 49; (*6*) 59; (*7*) 61; (*8*) 75; (*9*) 87; (*10*) 100.

temperature of the neutral reactant, which is equal to the temperature of the reactor walls.

If the translational energy ($E$) in collisions of rather heavy species ($\geqslant$28 amu) is less than 0.1 eV and helium is used as the buffer gas, the effective temperature of the internal degrees of freedom of an ion does not differ much from the ambient temperature. This allows one to study correctly enough the dependences of the association rate constants on $E$ in the range from 0.04 to 0.1 eV.[78] Figure 2 can be regarded as an example, it presents the dependences of the effective rate constant for the reaction

$$O_2^+ + CH_3CN + He \longrightarrow O_2^+CH_3CN + He \qquad (8)$$

on the helium pressure, and Fig. 3 presents the dependence of the ratio of the rate constants for stabilisation in collisions of the complex with helium to the spontaneous reverse decay rate constant of the collisional complex at different $E$ values.

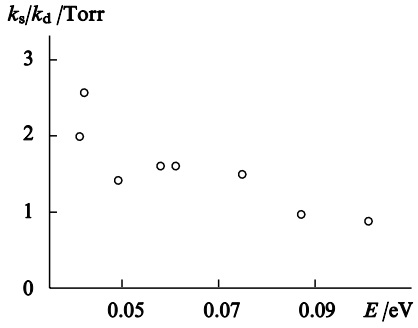



**Figure 3.** Dependence of the ratio of the rate constant for collisional stabilisation to the rate constant for the collisional complex decay on $E$ for the process (8).

The drift method allows one to study, over a wide energy range, the competition of the association channel with other channels, for example, endothermic charge transfer,[79] or with reactions accompanied by species rearrangement.[80]

At sufficiently high energy of species relative translational motion in the centre-of-mass system, the SIFDT method is very helpful for the studies of the collision-induced dissociation of stable ionic complexes $AB^+$, since the reaction zone contains no neutral reagent B and the reverse process, *viz.*, association, does not occur there. The dissociation of a series of complex ions has been studied in detail.[77]

A procedure with a modified flow reactor has been developed for the measurement of the rate constants for ion – molecule reactions at low temperatures in which the reactions were studied

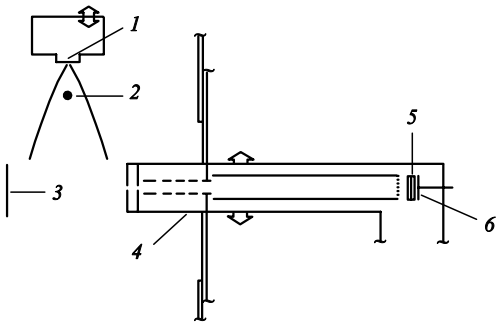



**Figure 4.** A scheme of an experimental set-up for low-temperature studies of ion-molecule reactions:[89]
(*1*) gas-dynamic nozzle with a pulse valve for gas flooding; (*2*) focus of ionising laser irradiation; (*3*) a plate for the deflection of ions to the input of the mass spectrometer; (*4*) time-of-flight mass spectrometer; (*5*) microchannel plates; (*6*) collector of secondary electrons.

in a cooled supersonic flow.[31,81–86] A strongly cooled flow is obtained by adiabatic gas expansion following its discharge through a nozzle or an orifice in a thin wall.

A scheme of this type of experimental set-up is shown in Fig. 4. The gas expands through a pulse nozzle. The ionising laser radiation is focused on the axis of the supersonic flow at a point located sufficiently close to the nozzle. The ions moving together with the supersonic flow react with molecules. When the ions reach the level of the repeller plate, the pulse electrical field directs them into the time-of-flight mass-spectrometer moved along the flow; the mass-spectrometer records the ion composition of the beam.

The yield of secondary ions in reactions can be increased not only by increasing the gas pressure, but also by increasing the time of ion residence in the reactor under low pressure conditions. Various types of ionic traps are widely used for this purpose in mass spectrometry.[87–93] In the flow and drift methods, the order of characteristic reaction time is $10^{-3}$ s, while in ionic traps this time can be many orders longer. In ion cyclotron resonance (ICR) spectrometers, the cell retention time for an ion can amount to several hours at a very high vacuum. However, kinetic measurements require higher pressures, but under these conditions the reaction time is usually less than a minute.

In radio frequency traps, such as QISTOR, effective retention of ions requires the presence of a buffer gas (usually, helium) at a pressure of $10^{-3}$ Torr. However, the ion translational energy in these traps is rather high ($>1$ eV), hence, they can be used only for studying the dissociation of complex ions that have been previously injected into them.

Yet more promising are multipole radio-frequency traps (of the 'ion guide' type)[93] in which the energy of ions is not high. The ionic-trap and ICR methods, like the drift method, allow variation of the translational energy of the reacting ions.

The ICR method is limited to small pressures. Therefore, it can be used for studying the association reactions of relatively complex species, with rather long complex lifetimes (of about a microsecond and more). Only the reagent can act as the stabilising species in this case. However, this method proved to be convenient for radiation stabilisation studies. This can be clearly demonstrated using the Lindemann scheme with allowance for radiative stabilisation with the rate constant

$$k_r = \frac{1}{\tau_r},$$

where $\tau_r$ is the radiation lifetime of the species.

The effective rate constant of association (represented as a second-order reaction) has the form

$$k_{ef} = \frac{k_f k_s[M]}{k_d + k_r + k_s[M]} + \frac{k_f k_r}{k_d + k_r + k_s[M]} \quad (9)$$

and has a nonzero value when [M] is extrapolated to zero. Experimental studies of the processes taking into account the competition between the collisional and radiative stabilisation are described in Refs 94–100. A more perfect statistical model for data interpretation [in comparison with that used to derive formula (9)] is reported elsewhere.[101, 102]

The results of the rate constant measurements for three-body ion–molecule reactions using the methods described above are tabulated in reference books.[103, 104]

## IV. Temperature dependences of association rate constants

As noted above, the temperature dependence of the association reaction is a negative power function

$$k \simeq T^{-n}. \quad (10)$$

At relatively low temperatures, where the energy difference between the vibrational levels is much greater than the thermal energy ($h\nu \gg k_B T$) for simple molecules, the contribution of the relative vibrational partition functions to the rate constant can be neglected. Under nonequilibrium conditions where the effective temperatures of the internal degrees of freedom for ions ($T_i$), neutral molecules ($T_m$) and collisional complexes ($T_c$) differ (as in the case of ion drift), the temperature dependence of the association rate constant at the low pressure limit has the form [76]

$$k \propto \frac{T_c^{r_c/2}}{T_{tr}^{3/2} T_i^{r_i/2} T_m^{r_m/2}},$$

where $T_{tr}$ is the temperature that characterises the energy of the relative motion of the colliding molecules; $r_c$, $r_i$ and $r_m$ are the numbers of the rotational degrees of freedom of a complex, an ion and a neutral molecule, respectively. It should be noted that the electrical field can affect the translational temperature of ions and their internal energy but not the temperature of neutral species. The validity of this formula was confirmed experimentally in studies of ion drift in an electrostatic field.

In the case of equilibrium temperature, the exponent $n$ is determined by the relationship

$$n = \frac{3 - r_c + r_i + r_m}{2}. \quad (11)$$

It should be noted that both the statistical theory, which takes conservation of the angular momentum into account, and the simplified theory, which disregards this, give identical expressions for $n$.[105]

It should be noted that the statistical theory is applicable only to the reactions occurring with the formation of an intermediate complex with a sufficiently 'deep potential well', which is the reason for its long lifetime necessary for the efficient energy exchange between the degrees of freedom. For example, the temperature dependence of the rate constant for the process

$$N_2^+ + N_2 + N_2 \longrightarrow N_4^+ + N_2 + 96.5 \text{ kJ mol}^{-1} \quad (12)$$

is rather well described by the statistical theory, $n = 2$, whereas for a similar process

$$NO^+ + N_2 + N_2 \longrightarrow NO^+N_2 + N_2 + 17.4 \text{ kJ mol}^{-1} \quad (13)$$

$n = 4$.

For complexes with a small bond energy, a transition from statistical to dynamic control of the lifetime of the intermediate complex takes place.[105, 106] In this case, the lifetime of the complex is given by the effective time of collision, *i.e.*, the time during which the species remain sufficiently close to each other. This value is estimated by numeric calculation of trajectories. The large exponent $n$ for the formation of the intermediate complex $(NO^+N_2)^*$ is a consequence of dynamic restrictions for the total rotational energy of the colliding species (at fixed energy, collisions are possible only at small values of the total orbital momentum).

As the molecules become more complex and/or the temperature increases, it is necessary to take the contribution of the vibrational partition functions of the colliding species and the intermediate complex into account. Relatively simple models of harmonic oscillators are used for the estimation of this contribution. The corresponding correction of the parameter $n$ in the formula (10) gives results which agree satisfactorily with the experiment.[107, 108]

The contribution of the aforementioned radiative processes to the stabilisation of complex molecules, *viz.*, association products, can increase considerably. The competition between the channels for complicated hydrocarbon ion–molecule complexes was considered in detail;[94, 109] it was shown that their ratio evaluated using the approach mentioned above agrees satisfactorily with the experiment. For very complicated systems, the assumption of the uniform energy distribution between the degrees of freedom of a collisional complex may no longer agree with the experimental results.[110]

## V. Some results of studies

A new type of isotope effect related to the involvement of several potential energy surfaces with different symmetry types in one process has been discovered in three-body ion–molecule association processes. The simplest of the processes studied is the association in helium [111]

$$He^+ + 2He \longrightarrow He_2^+ + He.$$

In a mixture with approximately equal concentrations of $^3$He and $^4$He, the molecular ions with the isotope composition $^3He^4He^+$ are formed with a higher efficiency than the $^3He^3He^+$ and $^4He^4He^+$ ions. The relative concentration of the mixed molecular helium ions [$^3He^4He^+$] exceeded approximately 2.5 times the statistical value, which would be observed if equal association rate constants independent of the isotope composition were assumed.

This isotope effect was rationalised as follows. Only for a half of collisions between the species of identical isotope composition is the interaction potential defined by the term $^2\sum_u^+$ of the ion $He_2^+$, which corresponds to attraction and passes through a minimum; for the other half of the collisions, the potential interaction energy corresponds only to the repulsive term $^2\sum_g^+$, and the species cannot approach for short distances where the formation of a bound state becomes possible (Fig. 5 *a*).

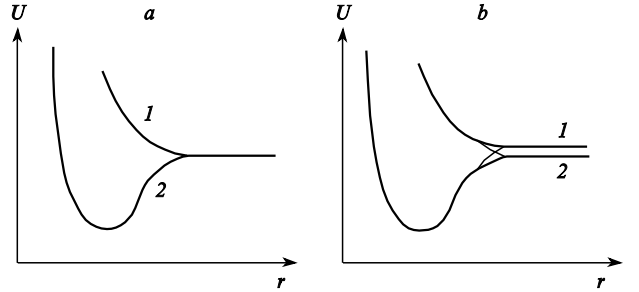



**Figure 5.** Dependences of the potential energy on the internuclear distance for the system $He^+ + He$.[111]
(*a*) the $^4He^+ + {}^4He$ system, (*1*) $^2\sum_g^+$, (*2*) $^2\sum_u^+$; (*b*) the $^3He^+ + {}^4He$ (*1*) and $^4He^+ + {}^3He$ (*2*) systems.

If the isotopes are different, at sufficiently long distances between the species, along with the term of the original species there is a term with a very small energy difference corresponding

to the charge transfer products, *i.e.*, there is a splitting of terms for the $^3He^+ + {}^4He$ and $^4He^+ + {}^3He$ systems (Fig. 5 *b*). It is assumed that the binding state of the molecular ion becomes available in every collision, as the transition to the binding term occurs in a nonadiabatic transition in the area indicated in the Figure.

The quantum-mechanical restrictions for symmetry (more exactly, the restrictions due to the identity of species) forbid a transition into the ground state from the $^2\sum_g^+$ state for identical isotopes. Thus, the isotope effect depends not only on the masses of the species involved in the process, but also on this type of quantum-mechanical restrictions.

Let us compare, for example, the kinetic isotope effect related to the mass difference with the isotope effect due to the symmetry (identity or nonidentity) of the species for the process

$$^{20}Ne^+ + {}^{22}Ne + He \longrightarrow {}^{20}Ne{}^{22}Ne^+ + He.$$

This process has not been studied experimentally yet. The interest in it is due to the fact that the difference between the ionisation potentials of $^{20}Ne$ and $^{22}Ne$, which determines the energy difference of terms, is much smaller than that for helium. In addition, the hyperfine structure for ions is absent (its possible effect has not been discussed) because the nuclei of these isotopes have no magnetic moments.

The magnitude of the isotope effect due to the mass difference only is estimated as $\sim 3\%$. Assuming, as in the case of helium, that upon collision of homonuclear species the potential of interaction between them is determined with equal probability by the terms $^2\sum_u^+$ and $^2\sum_g^+$ and that for every collision of heteronuclear species the potential corresponds only to the binding term, we find that the ratio of the association rate constant $k_{20-22}$, estimated taking into account the mass difference and the nonidentity of the nuclei, to the rate constant $k_{st}$ found ignoring these effects is

$$\frac{k_{20-22}}{k_{st}} = 2.06.$$

The even greater magnitude of the kinetic isotope effect for the $^3He - {}^4He$ mixture is due to the fact that the symmetry restrictions manifest themselves not only in the complex formation step but also in its stabilisation step.

Let us note that the isotopes formed in the three-body association can then participate in fast bimolecular switching reactions of the type

$$^3He\,{}^4He^+ + {}^4He \longrightarrow {}^4He\,{}^4He^+ + {}^3He,$$

$$^{20}Ne\,{}^{22}Ne^+ + {}^{20}Ne \longrightarrow {}^{20}Ne\,{}^{20}Ne^+ + {}^{22}Ne\,.$$

There are no symmetry restrictions for these reactions, and they can rapidly result in an equilibrium isotope distribution in the molecular ions. Therefore, the isotope effect described above is observable only at relatively small degrees of conversion determined by the ratio between the association and switching rate constants.

This type of kinetic isotope effect has been also found experimentally in three-body reactions involving molecular species. The theoretical explanation of the effect in this case is much more complicated than in the case of systems involving atomic species.

The enrichment in the $^{17}O$ and $^{18}O$ isotopes upon the formation of the $O_4^+$ ions in the reaction $O_4^+ + O_2 + M$ was studied.[112] It was found that the isotope effect strongly depends on the energy of the ionising electrons used for the formation of the primary $O_2^+$ ions. The relative enrichment of the dimers in the labelled molecules (in comparison with the statistical enrichment) was found to be $\sim 10$ at $E_i$ close to the $O_2$ ionisation threshold (12.077 eV). However, the enrichment at an energy of the electrons above 40 eV decreases to a virtually statistical value.

In addition, the yield of ionic dimers $O_4^+$ from $O_2^+$ ions formed by electrons at $E_i$ close to the ionisation threshold is much lower than that from ions obtained at higher electron energies. All this is explained [112] by the above-mentioned symmetry restriction upon the formation of a bound electronic state of $O_4^+$ in a collision of $O_2^+$ with $O_2$ ($^3\Pi_g$). The restriction disappears if $O_2^+$ (or $O_2$) is a heteronuclear species.

The efficiency of the $(CO_2)_2^+$ formation in the $CO_2^+ + CO_2 + M$ reaction also increases as the energy of ionising electrons is increased.[113] The symmetry-induced kinetic isotope effect was also studied for this process with the use of $^{13}C$ and $^{18}O$ labels. If the heavy oxygen label $^{18}O$ is used, an increase in the ionising electron energy from 25 to 100 eV results in a gradual decrease in the heavy isotope enrichment factor from 27 to 8. For $^{12}C$ and $^{18}O$, the heavy isotope enrichment factor is $\sim 5$ and virtually does not depend on the energy of the ionising electrons.

It is of note that the kinetic isotope effect is also manifested in the clusterisation of ions $(CO_2)_n^+$ where one of the $CO_2$ molecules is replaced by another species with a closed electron shell. For example, the isotope effect was observed in the formation of cluster ions in reactions of $ArCO_2^+$ complexes (see Ref. 114). It was shown that the $CO_2$ molecules containing heavy isotopes $^{17}O$ and $^{18}O$ are incorporated into the $ArCO_2^+$ clusters 20 times more efficiently than a statistical combinatorial estimate would predict. The studies of the symmetry-induced kinetic isotope effect in three-body ion – molecule reactions have been reviewed.[115]

Let us discuss the results of the experiments at ultralow temperatures in a cooled gas-dynamic flow. Figure 6 presents the temperature dependence of the rate constant for the reaction

$$Kr^+ + 2Kr \longrightarrow Kr_2^+ + Kr. \qquad (14)$$

In a wide range from moderate ($\sim 300$ K) to low temperatures ($\sim 0.1$ K), the rate constant cannot be described by the relationship (10) with an index $n$ which does not depend on $T$. It was found that $n = 1.8$ at low temperatures, while at moderate temperatures $n$ is much smaller. The average value $\langle n \rangle$ over the entire temperature range studied is equal to 1.2. It should be recalled that the theoretical $n$ value for the association of monatomic species should be equal to 0.75.

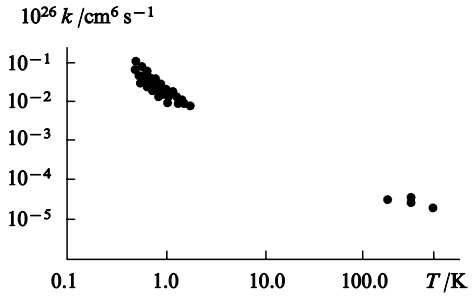



**Figure 6.** Temperature dependence of the rate constant for reaction (14).[116]

Similar deviations from the theoretical dependence are also observed for other reactions involving monatomic species:

$Ar^+ + 2Ar \longrightarrow Ar_2^+ + Ar$, $n = 1.4$, $\langle n \rangle = 1.0$;

$Ar^+ + 2Ne \longrightarrow ArNe^+ + Ne$, $n = 2.4$, $\langle n \rangle = 0.8$;

$Kr^+ + 2Ar \longrightarrow KrAr^+ + Ar$, $n = 1.8$, $\langle n \rangle = 1.2$;

$Xe^+ + 2Xe \longrightarrow Xe_2^+ + Xe$, $n = 2.3$, $\langle n \rangle = 1.1$;

$Xe^+ + 2Kr \longrightarrow XeKr^+ + Kr$, $n = 2.3$, $\langle n \rangle = 1.3$.

The values of $n$ are given for $T \simeq 0.1$ K.

For the above process (12) involving molecular nitrogen in the same wide temperature range, the expression (10) at $n = 2$ describes well the experimental temperature dependence of the rate constant (Fig. 7). It would be interesting to study analogous temperature dependences for $n$ at low $T$ for the formation of weakly bound complexes, for example, for the reaction (13) for which $n$ is anomalously high at moderate temperatures.

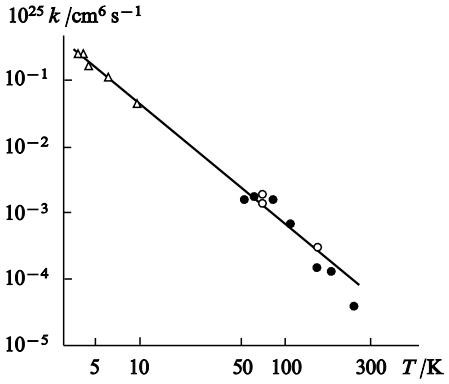



**Figure 7.** Temperature dependence of the rate constant for reaction (12).[116]
The points refer to the data from different authors.

The radio frequency ion trap method with cooled walls was used to measure the rate constants for clusterisation and fragmentation

$$H_i^+ + 2H_2 \rightleftharpoons H_{i+2}^+ + H_2$$

at 10 K for odd $i$ in normal hydrogen $n$-$H_2$ with an equilibrium ratio of the *ortho*- and *para*-isomers and in hydrogen enriched in the *para*-component, $p$-$H_2$.[92] The data obtained are presented in Fig. 8. The difference between the curves for $n$-$H_2$ and $p$-$H_2$ is due to the rotational energy of the molecule with total nuclear momentum $J = 1$ in the *ortho*-modification of molecular hydrogen. The bond energy of the $H_2$ molecule with the $H_i^+$ cluster changes from several kcal mol$^{-1}$ at small $i$ to a value comparable with the heat of evaporation of liquid hydrogen (0.2 kcal mol$^{-1}$).

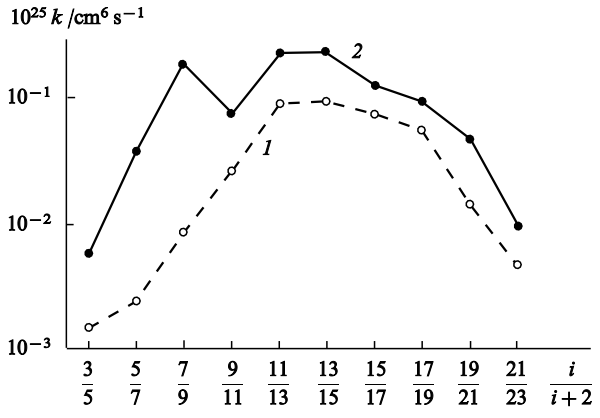



**Figure 8.** Dependence of the rate constant for the formation of odd hydrogen ionic clusters in the reaction $H_i^+ + 2H_2$ on the relative size change $i/(i+2)$ of an ionic cluster $H_i^+$ at low temperatures.[92] The points in the curve *1* were obtained in an experiment with an equilibrium concentration of the *para*- and *ortho*-modifications in $H_2$, those in the curve *2*, in hydrogen enriched with the *para*-component.

This example demonstrates a transition from clusters with sufficiently strong chemical bonds to clusters with van der Waals bonds with an increase in the number of species.

Experiments also give information on the cluster structure. For example, a decrease in the association rate constant with an increase in the cluster size at $i = 9$ is due to the beginning of formation of the second shell around the $H_5^+$ skeleton. The rate decrease at $i > 15$ is due to a decrease in the efficiency of stabilisation by the third body.[41, 73]

The effect of the particular features of the complex structure on the association rate constant is demonstrated in Fig. 9, which

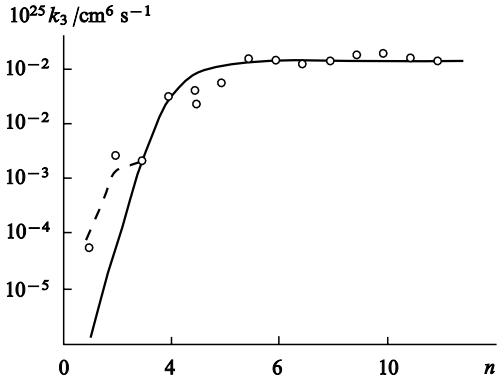



**Figure 9.** Dependence of the rate constant for reaction (15) on the number of atoms in an ionic copper cluster.[73]
The points refer to the experiment; the curve gives the calculation in accordance with the RRKM theory under the assumption of a 'soft' transition state. The dotted line connects the calculated points obtained for a 'hard' transition state for $n = 1$ and 2.

shows the experimental dependence of the association rate constant for copper ionic clusters $Cu_n^+$ with CO molecules

$$Cu_n^+ + CO + He \longrightarrow Cu_n^+CO + He \qquad (15)$$

on the magnitude of $n$.[73] On going from the $Cu^+$ ion to its dimer $Cu_2^+$, the rate constant increases by about an order of magnitude. However, the rate constant decreases somewhat on going from $Cu_2^+$ to $Cu_3^+$. This rather unexpected result is related to the specific features of the trimer electronic structure, which are unknown.‡ The passage from $Cu_3^+$ to $Cu_4^+$ again results in an increase in the reaction rate constant by an order of magnitude.

Further increase in the cluster size results in a slower increase in the rate constant, which approaches a steady level at $n = 7$.

The agreement between the calculated and experimental points for the rate constants of the reactions of the $Cu_n^+$ ions with $n \geqslant 3$ is good, but the experimental points for $Cu^+$ and $Cu_2^+$ 'fall out'. If another type of transition states (so-called hard ones) are assumed for the $Cu^+CO$ and $Cu_2^+CO$ complexes, the agreement for these points with the calculated data is improved considerably.

The rates of three-body association processes usually decrease with an increase in the temperature and translational energy of ions. There is only a single publication [117] where the effective rate constant for the reaction

$$C_6H_6^+ + 2C_6H_6 \longrightarrow C_{12}H_{12}^+ + C_6H_6$$

is reported to be independent of the translational energy of the ions over a wide energy range. However, in this case it cannot be ruled out that the $C_{12}H_{12}^+$ ions are products of associative ionisation of highly excited benzene molecules [118]

$$C_6H_6^{**} + C_6H_6 \longrightarrow C_{12}H_{12}^+ + e;$$

the rate of this process is not affected by electrical fields that accelerate the ions.[117]

However, some data indicate that the efficiency of association in certain systems is increased with an increase in the translational energy of the colliding species. For example, it was found that collisions of accelerated fullerene ions with inert gas atoms produce long-lived excited complexes with a noble gas atom inside the molecular cage of the fullerene.[119, 120] These are threshold processes that occur only at sufficiently high collision energies.

‡ A semiempirical calculation by one of the authors suggests that for $Cu_2^+CO$ the almost T-shaped structure of the $(Cu-CO-Cu)^+$ complex in which the carbon atom is arranged between the two copper atoms has the lowest energy.

The formation of long-lived excited complexes in bimolecular processes also occurs in collisions of ions of large biological molecules with small molecules like $NH_3$ and $CH_4$.[118] Probably, association is possible in these systems, and its efficiency increases with an increase in the translational energy of ions.

Of the three-body ion – molecule processes, the association processes have been studied most thoroughly to date. However, three-body exchange reactions, which have been little studied thus far, are of considerable interest. There are reasons to believe that at higher gas pressures three-body reactions resulting in the same products as bimolecular ones

$$A^+ + B + M \longrightarrow C^+ + D + M$$

can compete successfully with some slow exothermic bimolecular reactions of the type

$$A^+ + B \longrightarrow C^+ + D\,.$$

The reactions

$$SF_5^+ + H_2O + M \longrightarrow SF_3O^+ + 2HF + M,$$

(rate constant $3 \times 10^{-27}$ cm$^6$ s$^{-1}$) and

$$SF_5^+ + H_2O \longrightarrow SF_3O^+ + 2HF,$$

with a rate constant less than $10^{-11}$ cm$^3$ s$^{-1}$ can serve as examples.[14, 121]

The detailed mechanisms of these processes have not been sufficiently studied yet. Studies of the dependence of the reaction rate on pressure [122, 123] and temperature [124] revealed an abnormal behaviour of the [$SF_5 + H_2O$] complex. This complex can probably exist in different configurations with considerably different reactivities.

## VI. Conclusion

Intense studies on ion – molecule reactions in gases have already been continuing for almost half a century after V L Tal'roze discovered these reactions in mixtures of hydrocarbons in the early 1950's. About 15 years later, intense studies of three-body reactions began in parallel with bimolecular reactions; the contribution of the former becomes important upon increasing the pressure in the reaction region. At present, there is a rather extensive experimental data base on the rate constants for such reactions; however, its bulk is about 30 times smaller than that of a similar base for bimolecular ion – molecule reactions.

After the discovery of ion – molecule reactions, it was considered that all of them are fast if this is allowed by their thermochemistry. The main reason in favour of this was the assumption that the activation barriers appearing in the rearrangement of species (characteristic of reactions between neutral species) are already inside the 'potential well' arising due to strong electrostatic ion-dipole or polarisation attraction. In addition, it was shown that the majority of ion – molecule reactions result in an intermediate long-lived complex, and this mechanism is more typical than the 'direct' mechanisms.

It was thus concluded that exothermic ion – molecule reactions are a specific type of process different from similar reactions between neutral species. However, many exceptions from this concept were found later. The presence of energy barriers and the effect of various types of internal excitation on the reaction rates were observed. In view of this, it was concluded that there is no fundamental difference between the mechanisms of ion – molecule reactions and reactions of neutral species.

In fact, the energy barrier exists in the direction of the reaction coordinate, while the potential well originating from electrostatic attraction between an ion and a molecule corresponds to another coordinate describing the distance between the species. The effect of the electrostatic attraction can be demonstrated in a simplified form as a decrease in potential energy relative to the level of dissociation into the original species. The difference between the total energy and the energy barrier level (which, in rare cases, can even be negative) for ion – molecule system is most commonly different from that for neutral species. However, this is most likely a quantitative parameter, and the theoretical approaches for the consideration of ion – molecule reactions do not differ fundamentally.

It is of note that the role of the ion – molecule attraction should not be overestimated. The electrostatic interactions cannot be extrapolated for the short distance range. When the reacting partners approach each other, considerable redistribution of the effective charge in a system of colliding species occurs, and the character of interaction alters.

However, owing to redistribution of the effective charge, which can occur even at rather long distances between the partners, the properties of the reagents (geometry, bond energies, vibration frequencies) also change. This charge redistribution is more typical of ion – molecule collisions than of collisions involving neutral species (except for the systems with a weakly bonded electron).

Activation is usually non-typical of ion – molecule association reactions. However, specific effects related to the presence of charge in the system manifest themselves in full measure. This corresponds to a deeper global minimum of the potential energy surface for the interaction between the reagents, *i.e.*, an increase in the dissociation energy. The potential well becomes much wider, which results in an increase in the number of internal energy levels. As a result, the rate constants for ion – molecule association appear to be much higher than those for similar systems of neutral species. Upon this is further superimposed the effect of larger collision cross-sections due to long-range interaction.

Despite the similarity of the theoretical approaches for three-body processes involving only neutral and ion-neutral species, the calculation details differ in the practical calculations, where it is necessary to use certain approximations. For ion – molecule association processes, anisotropic effects are essential (an example of their calculation within the framework of the statistical theory was described above). Calculations of potential energy surfaces (which commonly have local minima in addition to global ones in ion – molecule systems) and the corresponding trajectory calculations are also important.

Rather recently, a quasi-classical method has appeared, *viz.*, SACM (statistical adiabatic channel model), for the calculation of ion capture by molecules.[125] Rather accurate algorithms of trajectory calculations for these processes [126 – 129] and three-body collisions [130] have also been developed. However, a strict theoretical consideration of low-temperature experiments requires the development of purely quantum models.

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