

Ionization in low-energy atomic collisions

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The ionization processes which occur in the collisions of atoms at thermal energies are reviewed. The various experimental methods used to study ionization are discussed; these methods include spectroscopy of decaying plasmas, particle-beam methods for studying particle collisions, Penning electron spectroscopy, mass-spectrometric detection of reaction products, and methods for selectively exciting the atoms involved in collisions. Information on the cross sections and rate constants of Penning processes, associative ionization, and ionization involving a resonantly excited atom is reported. Results are reported on the spectra of the electrons freed in these ionization processes and on the probabilities for various particular reactions. Theoretical models for ionization in low-energy atomic collisions are discussed.

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INTRODUCTION

The ionization processes that occur in low-energy collisions of atoms strongly affect the properties of low-temperature plasmas, since they lead to the formation of charged particles in the plasma. A classic example of such an ionization process is the Penning process,^{1,2} which is the ionization that occurs in a collision of a metastable atom with an atom of a different species whose ionization potential is lower than the excitation potential of the metastable atom. This process was discovered in 1937 by Kruithof, Penning, and Druyvesteyn.^{1,2} It was found that a small argon admixture (at a concentration of the order of 0.01%) in neon significantly lowers the discharge ignition potential. The reason is that free electrons are formed in collisions of metastable neon atoms with argon atoms. Accordingly, in neon with an argon admixture free electrons can be formed in order to ignite a discharge by simply exciting the neon atoms to a metastable state, rather than ionizing them, as would be necessary in the absence of an admixture. A low-temperature plasma contains a certain number of excited atoms; their collisions with gas atoms lead to the formation of free electrons, and this process may compete with the ionization of the gas through collisions of atoms with electrons.

The ionization processes that occur in low-energy atomic collisions are also important in the detection of impurity atoms or atoms of different isotopes of the same chemical element in a gas. Such atoms are detected through their excitation and subsequent conversion into ions,^{3,4} so that the ionization which occurs in a low-energy collision of an excited atom with a gas atom may play a certain role.

These processes are of interest beyond their practical importance. Over the past decade some new experimen-

tal methods for studying these processes have been developed; these new methods include the molecular-beam method, study of the spectrum of freed electrons, mass-spectrometric detection of reaction products, and spectroscopic study of these processes. Combined with methods for selectively exciting atoms, these methods have yielded multifaceted and detailed information on ionization processes. Some of these methods and the results which they have furnished have been reviewed in several recent papers; in the Soviet literature, for example, there are the reviews in Refs. 5–9. Our purpose in the present review is to give a comprehensive report on the ionization processes which involve excited atoms and to describe the physical picture of these processes.

Ionization in collisions of excited atoms can occur through the following reactions:



here the asterisk denotes an excited state of an atom. The first of these reactions is important when the excitation energy of atom A^* exceeds the ionization potential of atom B . When atom A^* is in a metastable state, this reaction is called the "Penning process." Reaction (2) is important if the collision velocity is comparable to or greater than the velocity of the excited electron in its atomic orbit. At thermal collision energies, this condition corresponds to highly excited atomic states. Information on the ionization of highly excited atomic states in collisions is reviewed in Ref. 10, and we shall consider this reaction no further in the present paper.

Reaction (3), which is "associative ionization," is important if the dissociation energy of the molecular ion which forms exceeds the ionization potential of the excited atom.

1. IONIZATION OF AN ATOM IN A COLLISION WITH A RESONANTLY EXCITED ATOM

Let us consider reaction (1) in the case of practical interest in which the excitation energy of atom A^* is higher than the ionization potential of atom B. Then the A^*-B quasimolecule is in an autoionization state regardless of the distance (R) between the nuclei, but the width of the autoionization level, $\Gamma(R)$, falls off with increasing distance between the nuclei the interaction which causes the decay of the autoionization state becomes progressively weaker. To find the cross section for the detachment of an electron during the collision, we note that $P(\rho, t)$, the probability for this process to occur by time t in a collision with an impact parameter ρ , satisfies the equation¹⁾

$$\frac{dP(\rho, t)}{dt} = -\Gamma(R)[1 - P(\rho, t)].$$

Solving this equation, we find the probability for reaction (1) in a collision with an impact parameter ρ :

$$P(\rho) = 1 - \exp\left[-\int_{-\infty}^{+\infty} \Gamma(R) dt\right]. \quad (4)$$

From this result we can find the cross section for reaction (1):

$$\sigma = \int_0^{\infty} 2\pi\rho d\rho \left\{1 - \exp\left[-\int_{-\infty}^{+\infty} \Gamma(R) dt\right]\right\}. \quad (5)$$

The cross section for reaction (1) is largest when atom A^* is in a resonantly excited state, i.e., when it can undergo a transition to the ground state as the result of dipole emission. In this case the interaction determining the width of the autoionization level is at its strongest and ionization occurs most readily. The corresponding problem has been solved elsewhere,¹¹⁻¹³ and it is described in some monographs.^{14, 15} Here we shall give a qualitative solution which will show how the result depends on the parameters of the problem.

The transition probability for reaction (1) per unit time for the case of a constant value of R is¹⁶ (this is the frequency of the Auger effect for the quasimolecule)

$$\Gamma(R) = 2\pi |V_{12}|^2 g_2,$$

where the subscripts 1 and 2 refer to the states $A^* + B$ and $A^* + e + B$ of the quasimolecule, and g_2 is the final-state density. The operator representing the interaction between atoms for a large distance between the nuclei is determined by the dipole-dipole interaction between the atoms and is given by

$$V = \frac{D_A D_B - 3(D_A \mathbf{n})(D_B \mathbf{n})}{R^3};$$

here \mathbf{n} is a unit vector along the R direction, $D_A = \sum_A e r_A$ is the operator representing the dipole moment of atom A, and $D_B = \sum_B e r_B$ is the operator representing the dipole moment of atom B (the sum is taken over all the electrons of the given atom). Hence we find the dependence of the width of the autoionization level of the A^*-B quasimolecule on the distance between the nuclei:

$$\Gamma(R) \sim \frac{(D_A)_1^2 (D_B)_2^2}{R^6} g_2.$$

¹⁾ Everywhere except where specifically stated otherwise we are using atomic units with $1/\hbar = m_e = e^2 = 1$.

Introducing the cross section for photoionization of atom B by a photon whose energy ω is equal to the excitation energy of atom A^* , we have¹⁷ $\sigma_{ph} \sim (\omega/c)(D_B)_{12}^2 g_2^2$, where c is the speed of light. Using this result, we find the behavior of the width of the autoionization level as a function of the parameters of the interacting atoms:

$$\Gamma \sim \frac{c\sigma_{ph}}{\omega R^6} (D_A)_{12}^2, \quad (6)$$

where the subscripts 1 and 2 correspond to the ground and resonantly excited states of atom A.

Equations (5) and (6) can be used to determine the reaction cross section as a function of the parameters of the problem. When elastic scattering of particles is inconsequential, we find $\sigma \sim \rho^2$ from Eq. (5), where $\int \Gamma dt \sim 1$. Since $\int \Gamma dt \sim (1/v)\rho \Gamma(\rho) \sim c\sigma_{ph}(D_A)_{12}^2/\omega\rho^5 v$ (v is the collision velocity), the transition cross section is

$$\sigma_{ion} \sim \left[\frac{c\sigma_{ph}}{\omega v} (D_{12})^2\right]^{2/5}. \quad (7)$$

In particular, for an S-P transition of the atom, an exact solution of this problem¹²⁻¹⁵ yields the following cross section for this transition:

$$\sigma_{ion} = 3.16 \left[\frac{c\sigma_{ph}}{\omega v} (D_{12})^2\right]^{2/5}. \quad (8)$$

Table I shows the cross sections for the ionization of atoms and molecules found from Eq. (8) for collisions with a helium atom in the 2^1P state at room temperature. These cross sections were calculated for a velocity $\sqrt{2T/\mu}$, where $T = 300$ K, and μ is the reduced mass of the colliding atoms. We used an oscillator strength of 0.276 for the $1^1S - 2^1P$ transition of the helium atom.¹⁸ It can be seen from this table that the large value of the ionization cross sections of the atoms justifies the method used to find them. Specifically, since the product $c\sigma_{ph}$ is usually of the order of characteristic atomic values, the cross section for this transition turns out to be of order $v^{-2/5}$; in other words, at low collision velocities this cross section is much larger than the characteristic atomic values. This result justifies the use of the asymptotic method which led to Eqs. (6) and (7).

This result holds if the width of the energy distribution of the freed electrons is far smaller than the average energy of these electrons, which is $\omega - J$ (ω is the excitation energy of atom A, and J is the ionization potential of atom B). The width of the electron distribution

TABLE I. Cross sections for the ionization of atoms and molecules as a result of collisions with resonantly excited 2^1P helium atoms at room temperature.

Atom or molecule which is ionized	Ar	Kr	Xe	H ₂	N ₂	O ₂
Photoionization cross section of the atom at a photon energy equal to the excitation energy of the helium atom, in units of 10^{-17} cm ²	3.51 ⁹	3.82 ⁰	3.22 ⁰	0.62 ¹	2 ²¹	2 ²¹
Cross section for ionization of the atom and molecule in a collision with a helium atom in the 2^1P state, in units of 10^{-15} cm ²	8.6	8.9	8.4	2.6	6.9	6.9
Capture cross section in (11) at room temperature, in units of 10^{-15} cm ²	10.8	12.4	14.5	8.54	11	10.6

is $\sim 1/\tau \sim \Gamma$, where τ is the average time required for the Auger effect of the $A^* - B$ quasimolecule. Since this time is equal to the collision time, $\sim \rho/v$, for the collisions which dominate the cross section, this requirement leads to

$$\sigma_{\text{ion}} \gg \frac{v^2}{(\omega - J)^2}.$$

Let us consider the ionization which occurs in the collision of an excited atom with a resonantly excited atom. If the energy of the resonant excitation is low, the photoionization of the excited atom may be treated as the transition of a weakly bound electron in the Coulomb field of the atomic core during the absorption of a photon. Then the photoionization cross section is given by the Kramers formula,²²⁻²⁶

$$\sigma_{\text{ph}} = g \frac{16\pi}{3\sqrt{3}} \frac{1}{cn^2\omega^3},$$

where ω is the energy of the absorbed photon, n is the principal quantum number of the excited state, and g is the so-called Gaunt factor, which is approximately unity and asymptotically approaches unity with increasing n . Substituting the expression for the photoionization cross section into (8), we find the cross section for ionization of the excited atom as a result of the collision with the resonantly excited atom:

$$\sigma_{\text{ion}} = \frac{4.5}{\omega^2 J} (gf_A)^{2/5}, \quad (9)$$

where f_A is the oscillator strength for this transition of atom A. This expression is also convenient for estimates in the case in which atom B is in the ground state in reaction (1).

In the derivation of Eqs. (7)–(9) we assumed that the colliding particles were moving along rectilinear trajectories; in other words, we ignored elastic scattering of the particles. This assumption breaks down at low collision energies.

The attractive potential between the colliding particles results in the capture of the excited atom by atom B. As a result of the capture, the particles close within a distance of the order of the atomic dimensions. At such distances between the nuclei the width of the autoionization level of the quasimolecule made up of the colliding particles is quite large, so that the autoionization state decays. If, because of the large level width, the autoionization state of the quasimolecule is able to decay over a distance greater than the atomic dimensions, then each capture event is accompanied by ionization of the atom by the excited atom. Consequently, if the cross section for capture in the collision of an excited atom with an atom exceeds the ionization cross section calculated from Eqs. (5)–(7), the observed ionization cross section will be equal to the capture cross section.

For a collision of an excited atom with an atom which is determined by the long-range van der Waals attractive potential $U = -CR^{-6}$, where R is the distance between nuclei and C is the van der Waals constant, the capture cross section is²⁷

$$\sigma_{\text{capt}} = \frac{3\pi}{2} \left(\frac{2C}{E} \right)^{1/3}, \quad (10)$$

where E is the energy of the relative motion of the

atoms. Since one of the atoms is in an excited state, we have¹⁴ $C = \alpha \bar{r}^2$, in atomic units, where α is the polarizability of atom B in the ground state, \bar{r}^2 is the square radius of the orbit of the excited electron of atom A*, and the average is over the states of this atom.

In a study of the events which occur in a gas, we are usually dealing with quantities which are averaged over a Maxwellian distribution of gas atoms. In practice, the quantity which is measured in this case is the reaction rate constant $\langle v\sigma \rangle$, so that the effective cross section for the reaction should be determined from the following expression, which is written in atomic units:

$$\sigma_{\text{capt}}(T) = \frac{\langle v\sigma_{\text{capt}} \rangle}{\langle v \rangle} = \frac{3}{2} \pi^{1/2} \left(\frac{3}{5} \right) \left(\frac{2C}{T} \right)^{1/3} = 5.36 \left(\frac{C}{T} \right)^{1/3}, \quad C = \alpha \bar{r}^2. \quad (11)$$

Table I gives the cross sections found from this expression for the capture of resonantly excited helium atoms by inert gas atoms at room temperature. These are the cross sections for the ionization reaction with which we are concerned here at room temperature.

Brodskii *et al.*²⁸ have measured the cross section for the reaction $\text{Hg}(^3P_0) + \text{Cs} \rightarrow \text{Hg}(6^1S) + \text{Cs} + e$ by comparing its rate constant with the photoionization cross section of the cesium atom. The cross section for this reaction turned out to be $(6-2) \cdot 10^{-14} \text{ cm}^2$, more than an order of magnitude greater than the cross sections calculated from Eqs. (8) and (9). In this case Eq. (11) yields a ionization cross section $\sigma_{\text{ion}} = (2.3-2.9) \cdot 10^{-14} \text{ cm}^2$ if it is assumed that the polarizability of the excited mercury atom lies in the range 100–200 a.u.

Another example is shown in Fig. 1: the cross section for the decay of a resonantly excited helium atom in a collision with a neon atom. This decay corresponds to the ionization of the neon atom, i.e., to reaction (1). We see that the experimental cross sections for this reaction²⁹⁻³² agree well with the cross section for the capture of the colliding particles, found from (11).

2. THE PENNING PROCESS

If the excited atom in reaction (1) is a metastable atom, the process is called the "Penning process." In a Penning process the excitation energy of the metastable atom is expended on ionizing the atom with which it collides. This process has received the most study among ionization processes during collisions of excited atoms, because metastable atoms have long lifetimes, and their densities in decaying plasmas are accordingly higher than those of other excited atoms.

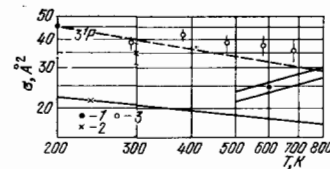


FIG. 1. Cross section for the decay of the excited state He (3P) in a collision with a neon atom. Points: Experimental. 1—Refs. 29 and 30; 2—Ref. 31; 3—Ref. 32. Curves: Theoretical. Solid curve—Ref. 33; dashed curve—Eq. (11).

TABLE II. Radiative transitions used in determining the density of metastable inert gas atoms.

Metastable state of the atom	Radiative transition used	Photon wavelength for this transition, Å
He (2^3S)	$2^3S \rightarrow 2^3P$	40830
	$2^3S \rightarrow 3^3P$	3889
	$2^3S \rightarrow 4^3P$	3188
He (2^1S)	$2^1S \rightarrow 2^1P$	20582
	$2^1S \rightarrow 3^1P$	5016
	$2^1S \rightarrow 4^1P$	3965
	$2^1S \rightarrow 5^1P$	4650
He ₂ ($^2\Sigma_u$)	$3^2\Sigma_u \rightarrow 3^2\Pi_u$	6402
Ne (3^3P_2)	$4^3P_2 \rightarrow 4^3D_3$	8115
Ar (4^3P_1)	$5^3P_1 \rightarrow 5^3D_3$	8106
Kr (5^3P_2)		

The Penning process is important in the plasmas of discharges in inert gases. It results in the breakup of metastable atoms and the formation of charged plasma particles, thereby affecting the electrical characteristics of the plasma. On the other hand, it is reflected in the decay time of a plasma containing easily ionized impurities. For example, the decay time of a helium or neon plasma (i.e., the characteristic recombination time of the charged particles in such a plasma) depends on small admixtures of other inert gases. As the number density of the admixture atoms is reduced, the breakup of the metastable atoms slows down, and the plasma survives for a longer time.

Study of a decaying plasma was the essence of the original method for measuring the rate constant for the Penning process. A weakly ionized plasma is produced at a certain time and then decays. From the absorption of the resonant emission corresponding to a transition from the metastable state to a resonantly excited state of the atom (Table II) it is possible to determine the time evolution of the number density of metastable atoms. Other plasma properties are also measured, and together the results give a picture of the decay of the weakly ionized plasma and reveal the characteristics of the events that occur in it. Two versions of this experiment are used to measure the rate constant for the Penning process. In one version,³⁴⁻³⁶ the weakly ionized plasma is produced at a certain time, and the time evolution of the properties of the plasma in the afterglow is measured. In the other version,³⁷⁻³⁹ a weakly ionized plasma containing metastable atoms is excited and maintained in a steady state at a certain point in space. In this second version, the gas is flowing, so that the plasma decay can be observed over distance from the excitation point. By measuring the properties of the decaying plasma along a tube through which a plasma is flowing it is possible to reconstruct the rate constant for the Penning process.

Developments in pulse-method apparatus have led to new versions of the decaying-plasma method for finding the rate constant for the Penning process. In Refs. 40-42, for example, the time dependence of the decay of the emission intensity accompanying the transition $N_2(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ was measured after the bombardment of a helium-nitrogen mixture by a nanosecond-pulse beam of high-energy electrons (~600 keV). Electronically excited molecular ions of nitrogen form as the result of a Penning process involving a metastable helium atom and a nitrogen molecule; the emission decay time is a

measure of the characteristic time for the breakup of these atoms by nitrogen molecules. By measuring this time at various nitrogen pressures it is possible to reconstruct the rate constant for the Penning process involving the nitrogen molecule.

By adding other atoms and molecules and finding the emission decay time as a function of the admixture number density it is possible to determine the rate constant for the Penning process involving these particles. From the absorption of the resonant emission corresponding to a transition from a given metastable state it is possible to determine the time evolution of the density of atoms in this metastable state. Then the rate constant for the Penning process involving the atoms in the given metastable state can be determined independently,⁴¹⁻⁴² so that the reliability of the result can be improved.

The most common method used to measure the rate constant for the Penning process is a beam method. In this method, the Penning process occurs when a beam of atoms containing metastable atoms collides with a gas or another beam of particles, which contains the atoms or molecules under study. The cross section for the process is determined from the current of ions or electrons formed in the reaction zone. This method has the indisputable advantage that the cross section for the process can be measured directly, and it is not necessary to measure an average rate constant, as it is in the decaying-plasma case. Furthermore, in the beam method the energies of the colliding particles can be varied over a broad range. Finally, the beam method permits measurements with atomic particles which do not exist in a gas phase and for which the beam method is thus the only method available for obtaining information of this sort.

We now discuss two versions of the beam method, which differ in the way in which the beam of metastable atoms is produced. In the first version, the metastable atoms are produced through the excitation of a thermal atomic beam. In the second version, the metastable atoms are formed as a result of the charge exchange of an ion beam with target atoms. The first version of the method clearly involves low collision energies, of the order of thermal energies. In the second version it is far more convenient to study collisions at high relative energies, of the order of electron volts and above.

Figure 2 shows a typical experimental arrangement⁴³ for the first version of the beam method. Penning pro-

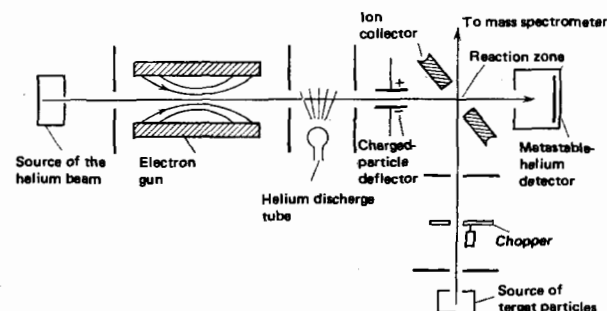


FIG. 2. Schematic diagram of the apparatus for the intersecting-beam method.

cesses are studied in the collision of a metastable helium atom with other atoms or molecules. The various experimental details can be modified; in some cases, for example, the metastable helium atoms are formed after the excitation of a thermal beam of helium atoms which passes through a zone bombarded by an electron beam. Another possibility is to produce a beam of helium atoms containing metastable atoms directly by extracting this beam from a region excited by a discharge. The beam formed beyond the electron gun contains helium atoms in the ground state and the 2^3S and 2^1S metastable states. The ratio of the number densities of 2^3S and 2^1S helium atoms can be varied by illuminating the atomic beam with a helium lamp. The emission spectrum of the lamp contains resonant photons which cause the $2^3S \rightarrow 2^3P$ and $2^1S \rightarrow 2^1P$ transitions. Since the radiative decay of the 2^1P atoms puts the excited helium atoms in the ground state, the illumination by the helium lamp leads to the loss of the 2^1S atoms from the beam. The electron gun and the discharge lamp produce a certain admixture of charged particles in the beam, which can be removed by sending the beam between capacitor plates.

The product is a thermal beam of helium atoms containing an admixture of metastable atoms in the 2^3S state and an adjustable number of atoms in the 2^1S state. The velocity of the beam atoms can be adjusted both at the beam source and by a velocity selector placed in the beam path. After passing through the reaction zone, the beam containing the metastable atoms reaches a detector, which is usually a metal plate (gold or steel). The metastable atoms incident on this plate cause secondary electron emission. The electron current is used to determine the flux density of metastable atoms in the beam, which must be known in order to determine the absolute cross section for the reaction under study.

The atoms or molecules of the target with which the beam containing the metastable atoms collides are themselves in the form of a beam or make up a low-pressure gas in a collision chamber. A thermal beam of target atoms or molecules is produced in the usual way; it is modulated by a chopper and may pass through a selector to produce a beam with a given velocity. An ion collector in the reaction zone measures the total current of ions which form. In addition, these ions can be sent to a mass spectrometer, so that the relative yields of the various particular reactions can be determined.

We turn now to a second version of the beam method, in which the beam of excited atoms is produced by the charge exchange of ions with target atoms or molecules. The method of overtaking beams is the most convenient for measuring cross sections in the Penning process. To demonstrate the capabilities of this method, we consider the reaction



which was studied by Neynaber *et al.*⁴⁴ A beam of metastable helium atoms was produced by charge exchange of 4-keV helium ions. At the same time, a beam of H_2 molecules was produced by charge exchange of H_2^+ ions

with hydrogen molecules. The two beams were injected in the same direction, in such a manner that one "overtook" the other.

The idea underlying the overtaking-beam method is that if the velocities of the particles in the two beams are approximately equal then it is possible to arrange extremely low energies of the relative motion of the particles, even if the absolute energies of the beam particles are relatively high. Consequently, beams with energies in the kiloelectron-volt range can be used to study the processes which occur at relative collision energies of only a fraction of an electron volt.⁴⁵

Going back to reaction (12), we denote by $E_1 = M_1 v^2/2$ the energy of the helium nuclei in the laboratory frame of reference, so that M_1 is the mass of the helium nucleus, and v is the velocity of these nuclei. If the hydrogen atoms have the same velocity, their energy in the laboratory frame will be $E_2 = M_2 v^2/2$, where M_2 is the mass of the hydrogen molecule. We now assume that we are able to vary the beam energy for molecular hydrogen near E_2 . If this energy is $E_2 + \Delta E_2$, then the relative velocity of the beams is $\Delta v = (1/M_2 v) \Delta E_2$, and the energy of the relative motion of the particles in the center-of-mass frame is

$$\epsilon = \frac{11 \Delta v^2}{2} = \frac{M_1}{M_1 + M_2} \frac{\Delta E_2}{E_2} \Delta E_2. \quad (13)$$

For some numerical estimates, we use the values $E_1 = 4$ keV and thus $E_2 = 2$ keV from the experiments of Ref. 44. We assume $\Delta E_2 = 10$ eV; then the energy of the particles in the c.m. frame is $\epsilon = 0.01$ eV. The value adopted here for ΔE_2 is completely reasonable, since the energy spread in the beam of helium ions and molecular hydrogen does not exceed 1.5 eV. Accordingly, by using beams with energies in the kiloelectron-volt range in the overtaking-beam method we can study processes which occur at thermal and higher energies. The relative energy of the colliding particles can be varied simply by changing the energy of one of the beams of original ions, by changing the accelerating potential.

Yet another convenience of the overtaking-beam method is that it is possible to produce a high concentration of metastable atoms of a given species in the beam. This is done by choosing an appropriate target, in which the charge exchange leads to the preferential formation of atoms in the desired metastable state. For example, charge exchange of helium ions in sodium vapor produces a helium-atom beam 94% of which consists of metastable helium atoms in the 2^3S state.⁴⁶ The overtaking-beam method has yielded much information about the cross sections for Penning processes—both on the dependence of the cross section on the collision energy and the effects of the various particular reactions—and also the absolute cross sections for the Penning process.

Tables III and IV show the experimental cross sections for the Penning process at thermal energies. Shown here are cross sections found by averaging the results of the specified papers and the statistical error found from an analysis of the various results. In those cases in which the scatter in the results from different measurements is large we give the range of measured

TABLE III. Cross sections for the Penning process at thermal energies, in units of 10^{-16} cm^2 .

Collision with	Ar	Kr	Xe	H	Na	Ca	H ₂
Metastable atom:							
He (2 ³ S)	7±4 34-38, 47-50	8.9±0.9 41, 47, 48, 52-54, 55, 59, 61	12±2 41, 47, 49, 52-54, 59, 63, 61, 63, 60	22 53	14 55 53 64	6,5 76, 77	2.3±1.4 37, 39, 41, 47, 49, 52-54, 56, 61, 62
He (2 ¹ S)	25±10 37, 38, 47, 55, 56	34±20 38, 47, 56	40±30 37, 38, 47, 54, 50	33 58, 59	17 70	22 77	2.7±0.8 37, 39, 41
Ne (3P ₂)	3.1±0.8 34-38, 41, 54, 71, 72	1±15 54, 71, 72	12±5 54, 71, 72	—	—	—	0.2-3.5 43, 45, 54, 72
Collision with							
	N ₂	O ₂	CO	NO	CO ₂	N ₂ O	SF ₆
Metastable atom:							
He (2 ³ S)	5.3±1 37, 38, 41, 47, 46, 52-54, 55, 60, 63, 65	14±2 37, 38, 41, 49, 56, 51-53, 56, 58	8±2 37, 38, 47, 52, 60, 55, 57	17±1 54, 51	51±6 39, 41, 49, 52, 56, 60, 67	36±2 36, 41, 50, 61	28±8 38, 41
He (2 ¹ S)	11±4 37, 38, 50	25±12 37, 38, 56, 65	16±7 37, 38, 56	36±3 38, 56	70±10 38, 56	38 58	53 38
Ne (3P ₂)	1.3-10 41, 54, 56, 72, 78	0.9-2.5 71, 72	3-11 54, 72	21 72	11 72	25 72	38 41

values. There are large discrepancies among the results found by different methods. For example, the cross section for the Penning process for the collision He(2³S)-Ar at room temperature is found from a statistical analysis of data^{38, 42, 47, 75} from afterglow measurements to be $6.6 \pm 0.8 \text{ \AA}^2$. On the other hand, the beam method^{55, 56} yields $19 \pm 3 \text{ \AA}^2$ for this process at room temperature at a collision velocity equal to the average thermal velocity. It is difficult to blame the discrepancies on the different methods used to average the cross section over the velocity, although this averaging operation undoubtedly leads to some differences in the results because of the strong velocity dependence of the cross section for this process (see Fig. 5 below).

It is particularly interesting to compare the cross sections for the Penning process for different metastable states of an atom but for the same other particle in the collision. Here we are primarily concerned with metastable helium atoms. Table V shows the ratio of the cross section for the Penning process for metastable helium atoms in the 2¹S and 2³S states. The source of metastable helium atoms usually contains a mixture of atoms in the 2³S and 2¹S states, and there is the separate problem of distinguishing the reactions

TABLE IV. Cross sections for the Penning process (in units of 10^{-15} cm^2) at temperatures of 500-600 K.

Metastable atom	He (2 ³ S)	Ne (3P ₂)	Ar (3P ₂)	Kr (3P ₂)
Collision with:				
Zn	3.6±0.7 74, 79, 80	4.2 ⁷⁴	5.3 ⁷⁴	9.3 ⁷⁴
Cd	7.2±2.5 74, 79, 80 2.6 ^{73*}	4.6 ⁷⁴ ; 2.3 ^{73*}	6.5 ⁷⁴	11 ⁷⁴

*) The measured cross section corresponds to the formation of the ground-state ion.

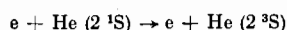
TABLE V. Ratio of the cross sections for the Penning process for metastable helium atoms in the 2¹S and 2³S states for thermal collision energies.

Other particle	Ar	Kr	Xe	H	K	Na	H ₂
Cross-section ratio							
$\frac{\sigma_p(2^1S)}{\sigma_p(2^3S)}$	3.1 ³⁸ 8.3 ⁴⁷ 1.3 ⁵⁵ 1.34 ⁶⁰ 1.7 ⁷⁶ 1.1 ^{81, 82} 1.7 ^{83, 84}	3.6 ³⁸ 6.2 ⁴⁷ 1.3 ⁶¹ 1.5 ⁶² 2.4 ⁸³	3.7 ³⁸ 7.4 ⁴⁷ 1.3 ⁶¹ 1.6 ⁶² 2.4 ⁸³ 0.9 ⁸⁰	1.5 ⁶⁸ 0.9 ^{69*}	1.2 ⁷⁰	1.1 ⁷⁰	1.5 ³⁸ 0.65 ³⁷ 0.87 ⁶⁶ 0.67 ⁶¹ 0.57 ⁶² 0.89 ⁶⁵ 1.4-1.7 ⁸⁴
Other particle							
	N ₂	O ₂	CO	NO	CO ₂	N ₂ O	SF ₆
Cross-section ratio							
$\frac{\sigma_p(2^1S)}{\sigma_p(2^3S)}$	2.4 ³⁸ 1.37, 70, 81 1.35 ⁶⁶	2.8 ³⁸ 1.46 ⁶⁶	3.1 ³⁸ 1.29 ⁶⁶ 0.9 ⁸¹ 1.0 ⁸⁴	1.8 ³⁸ 0.99 ⁶⁶ 0.9 ⁸¹	1.9 ³⁸ 0.93 ⁶⁶ 0.90 ⁸⁴	1.23 ⁶⁶ 0.90 ⁸⁴	2.5 ³⁸

*) The collision energy was 0.37 eV.

which involve each of these metastable species.

Many approaches have been taken to solve this problem. Dunning and Smith,⁸¹ for example, determined the species of metastable atom from the differences in the electron currents which arise when the metastable atoms are incident on a gold plate. Schmeltekopf and Fehsenfeld³⁸ determined the species of metastable atoms by exploiting the high efficiency of the reaction



in the presence of thermal electrons. The number density of thermal electrons was varied by adding SF₆, to whose molecules thermal electrons readily attach. In Refs. 70, 82, and 84 the ratio of the cross sections for these processes was determined from the spectrum of ionization electrons. This method has some further advantages, in that results can be found for each electronic state of the resulting ion separately. For example, Čermak⁸⁴ found that the ratio of the cross sections for the singlet and triplet states of helium in the Penning process for the collision of a metastable helium atom with an HCl molecule was 0.37 if the HCl⁺ ion formed in the X²I state or 0.32 if this ion formed in the A²Σ⁺ excited state. If a COS molecule participates, this ratio is 0.65 if the COS⁺ ion forms in the X²I electronic ground state, 0.78 if the ion forms in the B²Σ⁺ state, or 0.48 if the ion forms in the C²Σ⁺ state.

There is a large scatter in the ratios of the Penning cross section for processes involving metastable helium atoms in the 2¹S and 2³S states (Table V). The various experimental methods for detecting the metastable helium atoms have apparently been afflicted with large errors. Figure 3 shows the ratio of the Penning cross section for the process involving He(2¹S)+Ar to the cross section for the process involving He(2³S)+Ar as a function of the collision velocity.

Let us examine the mechanism for the Penning process. Figure 4 shows the molecular terms between which the transition occurs in the Penning process. These terms can be used to draw a physical picture of the Penning process. The energy level of the quasi-

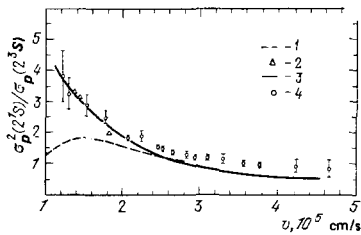


FIG. 3. Ratio of the cross sections for the Penning process for helium atoms in the 2^3S and 2^1S states, colliding with an argon atom, plotted as a function of the collision velocity. Experimental data: 1—Ref. 83; 2—Ref. 87; 3—Ref. 88; 4—Ref. 89.

molecule which is made up of the colliding particles in Penning process (1) lies in the continuum, since the excitation energy of the metastable atom exceeds the ionization potential of the other particle in the collision by virtue of the definition of the Penning process. Consequently, the quasimolecule which forms from the colliding particles is in an autoionization state, and its decay rate is related to the width of this autoionization level, $\Gamma(R)$, at the given distance between nuclei, R (Fig. 4). Since the level width is determined by the interaction of the colliding particles, the width increases sharply as the atoms move closer together; the decay thus occurs essentially near the distance of closest approach, where repulsive forces act between the colliding particles.^{92, 93}

The probability for ionization as the result of a collision with an impact parameter ρ is determined by Eq. (4). A particular characteristic of the Penning process is that in most of the cases which have been studied the cross sections for the Penning process are much lower than the kinetic cross sections for the collision of these particles in a gas.⁹⁴ To demonstrate this fact we show in Table VI the ionization probabilities inferred from the measurements by Bolden *et al.*⁵² for the Penning cross section in a collision of a 2^3S metastable helium atom with certain other atoms and molecules. These results support our assertion.

We can thus write the Penning cross section for relatively low collision velocities as follows, according to Bates *et al.*⁹⁵:

$$\sigma_p = f_w P_i \sigma_{\text{capt}} \quad (14)$$

Here σ_{capt} is the cross section for the capture of a metastable atom by the particle with which it collides; P_i is the probability for ionization as the colliding particles move closer together; and f_w is the probability

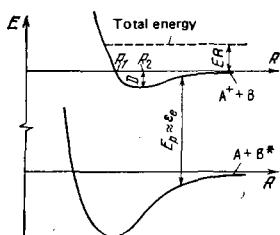


FIG. 4. Molecular terms in the Penning process.

TABLE VI. Cross section for the Penning effect and ionization probability in a close collision for the 2^3S metastable state of the helium atom at thermal energies.⁵²

Other particle	Ionization cross section, \AA^2	Ionization probability
Ar	7	0.11
Kr	8	0.12
Xe	14	0.15
H ₂	1.5	0.08
N ₂	5	0.07
CO	8	0.12
O ₂	15	0.23
NO	16	0.24

that the given process is allowed by the total electron spin of the system consisting of the colliding atoms [for example, in the collision of two metastable helium atoms, $\text{He}(2^3S) + \text{He}(2^3S)$, ionization is forbidden if the total spin is 2 or if the total electron spin in the final channel, $\text{He} + \text{He}^+ + e$, is 0 or 1; the probability that the total electron spin of the system is 0 or 1 in this case is $f_w = 4/9$].

Equation (14) describes a physical situation in which the ionization occurs when the colliding particles come extremely close together because they are captured in the attractive potential. Then the probability for ionization in the case in which the distance between the particles is small in comparison with the impact parameter of the collision can be assumed independent of the impact parameter; this conclusion justifies the use of Eq. (14) in this case.

Let us find a more general expression for the Penning cross section, assuming that the ionization probability in each collision of the particles is much smaller than unity. We shall work from the results reported by Miller⁹⁶ and Smirnov.⁹⁷ Since the ionization probability is small, an expansion can be carried out in Eq. (4), which becomes

$$P_i = \int_{-\infty}^{+\infty} \Gamma dt = \frac{2}{v} \int_{r_0}^{\infty} \left[1 - \frac{\rho^2}{R^2} - \frac{U(R)}{E} \right]^{-1/2} \Gamma(R) dR, \quad (15)$$

where $r_0(\rho)$ is the distance of closest approach of the nuclei, $U(R)$ is the interaction potential between the particles, v is the relative collision velocity, and E is the energy of the particles in the c.m. frame.

We can then find the cross section for the Penning process, $\sigma_p = f_w \int_0^{\infty} 2\pi\rho d\rho P_i(\rho)$, by substituting the expression for P_i into this equation and by changing the integration limits on the double integral which results^{96, 97}:

$$\sigma_p = \frac{4\pi f_w}{v} \int_{R_0}^{\infty} R^2 \Gamma(R) \sqrt{1 - \frac{U(R)}{E}} dR, \quad (16)$$

where R_0 is the distance of closest approach in the case of a zero impact parameter, and $U(R_0) = E$.

The change in the order of integration which was made in the derivation of Eq. (16) was based on the single-valued relationship between the distance of closest approach of the nuclei, r_0 , and the collision impact parameter ρ . This equation is thus valid if the process generally occurs in a repulsive interaction potential

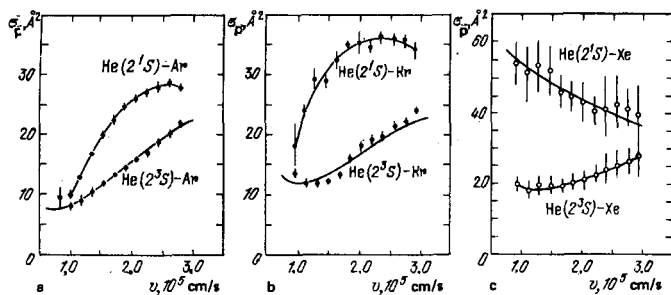


FIG. 5. Cross section for the Penning process for the collision of a metastable helium atom in the 2^3S state (lower curves) and in the 2^1S state (upper curves) with various atoms as a function of the collision velocity. a—argon atoms; b—krypton atoms; c—xenon atoms.

of the atoms in the initial channel. It does not hold if this process is determined by the capture of the colliding particles. In the energy range under consideration here, the Penning cross section increases monotonically with increasing collision energy. As the collision energy is increased, progressively smaller distances between the particles can be achieved, and at these short distances ionization is highly probable because of the large width of the autoionization level. Figure 5 shows the Penning cross section as a function of the collision velocity for the collision of metastable helium atoms with inert gas atoms.⁸³ We see that at thermal collision velocities the case described above holds for these particles.

In the limit of high collision velocities, at which the quantity $R_0^2 \Gamma(R_0)$ decreases with increasing collision energy, the Penning cross section is determined by rectilinear trajectories. For such collisions the lower integration limit can be replaced by zero, and the interaction potential of the particles can be ignored in comparison with the collision energy. Equation (16) can thus be transformed to

$$\sigma_p = \frac{4\pi}{v} f_w \int_0^\infty R^2 \Gamma(R) dR, \quad (17)$$

which tells us that the cross section for the Penning process is inversely proportional to the collision velocity. This dependence has been confirmed by experiment (Fig. 6).

We thus see that the width of the ionization level, $\Gamma(R)$, for the initial reaction channel has an important

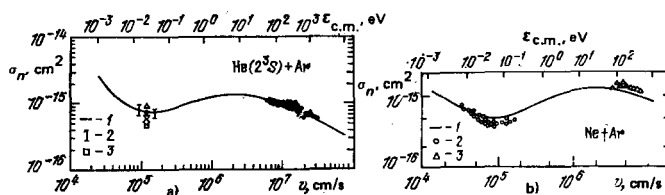


FIG. 6. Dependence of the cross section for the Penning process on the particle collision velocity. a: $\text{He}(2^3S) + \text{Ar}$. 1—Calculations of Ref. 107; 2—experimental data from Ref. 93; 3—experimental data from Refs. 102 and 103; other data— from Table IV. b: $\text{Ne}(3P_2) + \text{Ar}$. 1—calculations of Ref. 107; 2—experimental data from Refs. 104–106; 3—experimental data from Ref. 102.

TABLE VII. Width of the autoionization level of the system $\text{He}(2^3S) + \text{Ar}$ and parameters in the approximation of the width by the function $\Gamma(R) = Ae^{-\alpha R}$.

	Reference	Parameters of		Values of		
		A	α	$R=4$	$R=5$	$R=6$
Experiment	83	$3.3 \cdot 10^3$	2.56	0.12	$8.9 \cdot 10^{-3}$	$6.9 \cdot 10^{-4}$
	88	$7.4 \cdot 10^3$	2.80	0.40	$6.1 \cdot 10^{-3}$	$3.7 \cdot 10^{-4}$
	89	$4 \cdot 10^3$	2.78	0.06	$3.7 \cdot 10^{-3}$	$2.3 \cdot 10^{-4}$
	100	$5.3 \cdot 10^3$	2.80	0.07	$4.4 \cdot 10^{-3}$	$2.7 \cdot 10^{-4}$
	101	$1.2 \cdot 10^3$	2.64	0.03	$2.2 \cdot 10^{-3}$	$1.6 \cdot 10^{-4}$
Theory	107	1	1.50	$2.5 \cdot 10^{-3}$	$5.5 \cdot 10^{-3}$	$1.2 \cdot 10^{-4}$

effect on the Penning cross section. Expressed in the corresponding units, this width is equal to the decay frequency of the autoionization level of the quasimolecule for a fixed distance between the nuclei. Since the decay frequency of the autoionization level is governed by the interaction of the valence electrons of the colliding particles, the width $\Gamma(R)$ falls off sharply with increasing distance between nuclei. Table VII shows the parameters used to approximate $\Gamma(R)$ at distances responsible for the ionization in the Penning process $\text{He}(2^3S) + \text{Ar}$ along with values of this width in this distance range. These results were found through an analysis of the corresponding experimental data.

Specific calculations of the rate constant for the Penning process, which can be used to determine both the width of the autoionization level of the quasimolecule (an intermediate result) and the particle integration potential at various distances between the nuclei have been carried out.^{98, 99, 107–115} The greatest difficulties of these calculations are in determining the width of the autoionization level of the quasimolecule in that range of nuclear separations in which this width is small. The width is sensitive to the approximations used to calculate it, so that a given theoretical calculation can be applied only to simple systems, for which it is relatively reliable. Figure 7 illustrates the situation with a plot of the decay frequency of the autoionization state, $\Gamma(R)$, as a function of the distance between the nuclei for the simple Penning process $\text{He}(2^3S) + \text{H}$. This frequency was calculated in Refs. 95, 108, 113, and 115, and in Ref. 116 it was determined from an analysis of experimental data. The theoretical capabilities here can be judged on the basis of the agreement between the results from different studies.

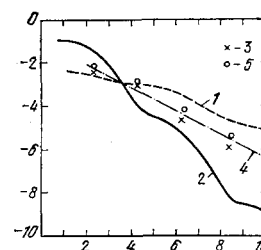


FIG. 7. Width of the autoionization state of the quasimolecule $\text{He}(2^3S) + \text{H}$ as a function of the internuclear distance. 1–4—Calculations; 1—Ref. 95; 2—Ref. 108; 3—Ref. 113; 4—Ref. 115, 5—From analysis of experimental results.¹¹⁶

Let us use this information to analyze the behavior of the cross section for the Penning process as a function of the collision velocity and the behavior of the rate constant for this process as a function of the temperature. Equations (14) and (16) describe two limiting physical situations. In the first case, the ionization which occurs in the Penning process is determined by the capture of the colliding particle in the attractive potential. In the second case, the range of distances between particles corresponding to attraction does not contribute to the cross section for the process. If the energy of the colliding particles in the Penning process, E , is much smaller than the depth of the potential well (D) corresponding to the interaction of the colliding particles, the cross section is given by Eq. (14). In this case the nature of the collision dynamics is such that at an impact parameter $\rho \leq \rho_{\text{capt}}$ (ρ_{capt} is that impact parameter at which the particles begin to move very close together) the distance of closest approach of the particles, r_0 , is approximately equal to r_{min} , which is the distance between the particles at which the interaction potential vanishes [$U(r_{\text{min}}) = 0$]. At $\rho > \rho_{\text{capt}}$ the distance of closest approach turns out to be of the order of the collision impact parameter. Since the condition $r_{\text{min}} \ll \rho_{\text{min}}$ holds²⁾ at $E \ll D$, at impact parameters smaller than ρ_{capt} the ionization is essentially independent of ρ and of the collision energy. At $\rho > \rho_{\text{capt}}$ the interaction between the particles which determine the transition is weak, so that this range of impact parameter does not contribute to the cross section. Consequently, the Penning cross section in this energy range, $E \ll D$, is determined by Eq. (14); the dependence of the cross section on the collision energy is the same as for the cross section for the capture of the colliding particles.

This behavior of the Penning cross section as a function of the velocity is supported by the experimental data. For example, the Penning cross section was measured in Refs. 104–106 as a function of the velocity for the collision of a metastable neon atom, $\text{Ne}(^3P_2)$, with argon, krypton, and xenon atoms at collision velocities in the range $(0.32 - 1.7) \cdot 10^5$ cm/s (the collision energy was less than 0.3 eV). The results show that the Penning cross section can be approximated by a function v^{-s} , where the exponent s is 0.62 in the case of the collision with the argon atom, 0.73 for krypton, and 0.87 for xenon. For a long-range interaction $U = -CR^{-6}$ this exponent should be 0.67.

We turn now to another limiting case, in which the ionization occurs in the region of a repulsive potential between the colliding particles. We will use Eq. (16) for the Penning cross section. We will assume that the most rapidly varying function in the integrand in this

²⁾In particular, for the model interaction potential $U(R) = -2D(R/R_0)^3 + D(R/R_0)^2$, which is frequently used, we have $r_{\text{min}}/\rho_{\text{capt}} = (1/\sqrt{3})(E/D)^{1/6}$ for $E \ll D$. Furthermore, the distance of closest approach of the particles for this potential is $r_0 = r_{\text{min}} [1 - (E/24D) + (E/24D)(\rho^2/r_{\text{min}}^2)]$, while the distance of closest approach in the case of the collision impact parameter ρ_{capt} is

$$r_0^{\text{capt}} = \sqrt{\frac{2}{3}} \rho_{\text{capt}} = \sqrt{2} \left(\frac{D}{E}\right)^{1/6} r_{\text{min}} \gg r_{\text{min}}$$

equation is $\Gamma(R)$. Expanding the other factors near the turning point, we find

$$\sigma_p = f_w \frac{2\pi^{3/2}}{v\alpha^{3/2}} \sqrt{\frac{U'(R_0)}{E}} R_0^2 \Gamma(R_0), \quad (18)$$

where $\alpha = d \ln \Gamma |dR|_{R_0}$, $E = U(R_0)$, and the resulting equation holds under the condition $\alpha R_0 \gg 1$. Equation (18) describes the increase in the Penning cross section with increasing collision energy. As the collision energy is increased by an amount dE , the relative change in the cross section due to the last factor is $d\sigma_p/\sigma_p \sim (d \ln \Gamma/dR)dR_0 \sim \alpha R_0$. Assuming that the interaction potential varies significantly when the distance between the particles is changed by an amount comparable to itself [i.e., $|U'(R_0)| \sim U(R_0)/R_0 \sim E/R_0$], and using the condition $E = U(R_0)$, we find the relation $dE \sim E dR_0/R_0$. This relation tells us that the relative change in the cross section due to the last factor is given in order of magnitude by $d\sigma_p/\sigma_p \sim \alpha R_0 dE/E$. Under the condition $\alpha R_0 \gg 1$, this change is greater than the relative change in the cross section caused by the other parameters; this other change is of the order of dE/E . In the parameter region $\alpha R_0 \gg 1$, therefore, the Penning cross section increases monotonically with increasing energy. It goes through a maximum at $\alpha R_0 \sim 1$. The last expression given for the collision energy is conveniently written in the form

$$U\left(\frac{1}{\alpha}\right) \sim E. \quad (19)$$

This analysis leads to the dependence of the Penning cross section on the collision energy which is shown schematically in Fig. 8. Region 1 corresponds to collision energies $E \ll D$ and is described by Eq. (14). The minimum in the cross section corresponds to a collision energy $E \sim D$. In region 2 the cross section for the Penning process is described by Eq. (18). Here the cross section is determined by the repulsive part of the interaction potential; $d \ln \Gamma(R_0)/d \ln R_0 \gg 1$. The maximum of the cross section corresponds to the condition $(d \ln \Gamma(R_0)/d \ln R_0) \sim 1$, which is the same as condition (19). In region 3 the cross section is dominated by collisions with rectilinear trajectories, and the cross section is determined by Eq. (17). We see that the cross sections for the particular Penning processes in Fig. 6 behave in the same way.

In studying a Penning process at thermal energies we must determine on which part of the curve in Fig. 8 we are working. It follows from Fig. 4 that in the case of a Penning process in a collision of metastable helium atoms with other atoms the process occurs primarily in the repulsive part of the interaction potential (region 2 in Fig. 8). This case corresponds to an increase in the Penning cross section with increasing collision energy or increasing temperature. A different result is

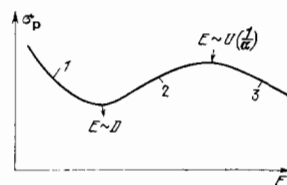


FIG. 8. Schematic cross section for the Penning process.

given by the calculations by Olson (Fig. 5a) and the measurement by Jones and Robertson⁹³ of the rate constant of the Penning process $\text{He}(2^3\text{S}) + \text{Ar}$ in the temperature range 100–600 K. According to these results, at thermal collision energies we are working near the minimum of the cross section for the Penning process (Fig. 8).

Further analysis of the experimental data on the process $\text{He}(2^3\text{S}) + \text{Ar}$, however, shows that the minimum of the cross section should fall at a far lower collision energy. The depth of the well for the $\text{He}(2^3\text{S})\text{-Ar}$ interaction potential, found from the experimental data of Refs. 87, 89, and 100, lies in the range 4–15 meV. We can expect to find the minimum of the cross section for this Penning process at the same energies. In particular, the calculations by Illenberger and Niehaus,⁸⁹ carried out with the parameters of the interaction potential found from an analysis of experimental data, predict that the cross section for the Penning process $\text{He}(2^3\text{S}) + \text{Ar}$ will have its minimum at a collision energy of 10 meV (100 K).

The situation is the same in the case of the collision of metastable helium atoms with molecules. For example, Cher and Hollingsworth¹¹⁷ found from the spatial distribution of the emission of a molecular ion in a flowing gas that the rate constant for the decay of the $\text{He}(2^3\text{S})$ state depends on the gas temperature in accordance with $k_p \sim T^{1+0.5}$ in nitrogen, oxygen, carbon monoxide, and carbon dioxide. According to measurements by Bogdanova and Marusin,¹¹⁸ the cross section for the Penning process $\text{He}(2^1\text{S}) + \text{Ar}$ varies from 3.5 to 10 \AA^2 as the temperature is changed from 120 to 575 K, while in the case of a collision of $\text{He}(2^1\text{S})$ and a xenon atom the Penning cross section varies from 38 to 54 \AA^2 over the temperature range 200–575 K.

Figure 9 shows the temperature dependence on the rate constant for the Penning process in the collision of a metastable atom with other atoms and molecules.

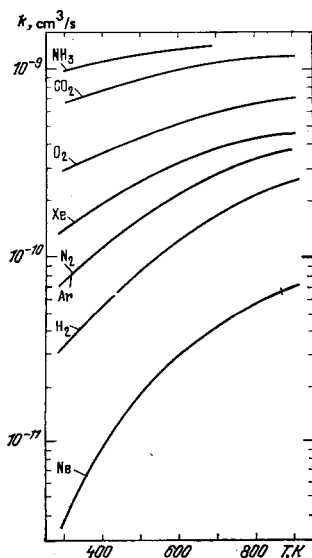


FIG. 9. Rate constant for the Penning process in the collision of a metastable 2^3S helium atom with other atoms and molecules.⁵⁸

These results confirm that the cross sections increase with the temperature; i.e., in the Penning process in the collision of metastable 2^3S and 2^1S helium atoms with other atoms and molecules at thermal energies, most of the ionization occurs in the repulsive region of the interaction between the particles.

The situation is different in thermal collisions of a metastable 3^3P_2 neon atom with heavier inert gas atoms¹⁰⁴⁻¹⁰⁶ (Fig. 6b). In these cases the cross section for the Penning process falls off with increasing collision energy (region 1 in Fig. 8) and behaves as the capture cross section does in the long-range interaction potential in the collision of atoms [see Eq. (14)].

It is interesting to examine the expression for the rate constant for the Penning process which occurs in a gas with a Maxwellian energy distribution of colliding particles. This expression takes a particularly simple form in the case in which the process occurs in the range of distances in which the colliding particles repel each other (regions 2 and 3 in Fig. 8). Using Eq. (16) for the Penning cross section, and taking the average of the rate constant for the Penning process over a Maxwellian particle distribution, we find the following result, after changing the order of the integration in the expression for the rate constant for the process:

$$k_p = \langle v\sigma_p \rangle = 4\pi f_w \int_0^\infty R^2 \Gamma(R) \times \exp\left[-\frac{U(R)}{T}\right] dR. \quad (20)$$

Equation (20) can also be derived on the basis of statistical considerations. The probability for finding an impurity atom at a distance between R and $R+dR$ from the metastable atom is, according to the Boltzmann law, $N_a \cdot 4\pi R^2 dR \exp[-U(R)/T]$, where N_a is the number density of impurity atoms. The frequency of the Penning process for a distance R between the atoms is $f_w \Gamma(R)$, so that the frequency for the Penning process, averaged over the distance between the nuclei, is

$$N_a k_p = N_a \int_0^\infty 4\pi R^2 dR \times \exp\left[-\frac{U(R)}{T}\right] f_w \Gamma(R),$$

which agrees with Eq. (20), derived above.

A special case of the Penning process is in the collision of two excited atoms. In this case the width of the autoionization level is relatively large because of the strong interaction between the particles, so that the ionization probability in a close approach is unity. The cross section for the Penning process is thus equal to the cross section for an elastic collision of the particles which brings them closer together. In particular, at low collision velocities, according to Eq. (14), the cross section for the Penning process is⁹⁵

$$\sigma_p = f_w \sigma_{\text{capt}}. \quad (21)$$

At high collision energies, at which the ionization probability becomes small in each collision, the cross section for the Penning process is determined by Eq. (17); i.e., the cross section falls off in inverse proportion to the collision velocity.

In the Penning process in a collision of two excited

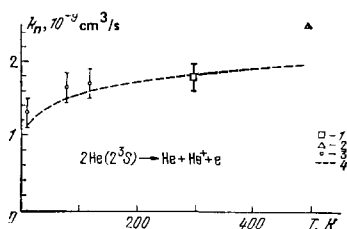


FIG. 10. Rate constant for the Penning process $2\text{He}(2^3\text{S}) \rightarrow \text{He} + \text{He}^+ + e$. 1-3—Experimental data; 1—Refs. 120-128; 2—Ref. 131; 3—Ref. 132. 4—Calculated from Eq. (23).

atoms the cross section is a monotonic function of the collision energy; specifically, it decreases with increasing energy (cf. Fig. 8). Among such processes, that which has been the subject of the most detailed experiments is the collision of two metastable helium atoms:



A statistical analysis of the cross sections measured in Refs. 120-128 yields a value of $(10 \pm 1) \cdot 10^{-15} \text{ cm}^2$ at a temperature of 300 K or at a relative collision energy of 0.033 eV. The value calculated for this cross section from Eq. (21), with the help of expressions (10) and (11) for the capture cross section, is^{14, 15, 129} the same, 10^{-14} cm^2 . Here we have used the value $C = 3300$ for the van der Waals constant for the interaction of two metastable helium atoms.¹³⁰ The value of the coefficient f_w in Eq. (14) for reaction (22) is $4/9$.

Figure 10 compares the measured rate constants for reaction (22) at various temperatures with the results calculated from Eqs. (14) and (10). In this case these equations yield

$$\sigma_p = \frac{4}{9} \bar{\sigma}_{\text{capt}} = 2.38 \left(\frac{C}{T} \right)^{4/3} = \frac{6.8 \cdot 10^{-14} \text{ cm}^2}{T^{4/3}}, \quad (23)$$

where the temperature is in degrees Kelvin.

At low collision energies the dependence of the cross section on the collision energy is the same as that for the cross section for the capture of one particle by the other. Accordingly, if we approximate the dependence of the Penning cross section on the velocity by the expression $\sigma_p \sim v^{-s}$ and assume that the capture results from the long-range van der Waals interaction between the particles ($U \sim R^{-6}$), then we have $s = 2/3$ according to Eq. (10). Table VIII shows the values found for this exponent from an analysis of the experimental data of Refs. 133-136. We have also included the parameters of the $\text{Ar}^* - \text{Na}$ collision in this table, because the rela-

TABLE VIII. The exponent s in the velocity dependence of the cross section for the Penning process ($\sigma_p \sim v^{-s}$) for a collision of two metastable atoms at low collision energies.

Colliding particles	s	Reference
$\text{He}^* - \text{He}^*$	0.76	133
$\text{He}^* - \text{Ne}^*$	0.82	134
$\text{Ar}^* - \text{Na}$	0.67	135
$\text{Ar}^* - \text{Kr}^*$	0.8	136

tively low binding energy of the electron in the sodium atom makes this collision similar in nature to the processes which occur with two excited particles. We see that the simple model used here gives a rather good description of the actual situation.

3. PENNING ELECTRON SPECTROSCOPY AND REACTION PRODUCTS IN THE PENNING PROCESS

A spectral study of the freed electrons yields much information about the physics of the Penning process and the corresponding characteristics. Research along this direction, which was begun by Čermak,¹³⁷ has evolved into the distinct field of "Penning electron spectroscopy." Extensive experimental work has been carried out in this field,^{70, 73, 82, 89, 137-152, 162, 172, 209} and it has been the subject of several reviews, e.g., those in Refs. 5 and 8. Before we examine the possibilities of this field and the results which it has yielded, we first determine the relationship between the spectrum of electrons liberated in the Penning process and the parameters of this process.

If we assume that the width of the autoionization level of the quasimolecule, $\Gamma(R)$, is small in comparison with the typical electron energies in which we are interested, then by virtue of the Franck-Condon principle we can assume that the energy of an electron which is freed at a distance R between the nuclei is equal to $V(R)$, which is the difference between the energies of the $\text{A}^* - \text{B}$ and $\text{A} - \text{B}^*$ states (Fig. 1). Then we find the probability for the liberation of an electron with an energy between ε and $\varepsilon + d\varepsilon$ to be,

$$dP_1 = d\varepsilon \int d \left[1 - \exp \left(- \int_{-\infty}^{\varepsilon} \Gamma dt \right) \right] \delta(\varepsilon - V(R)),$$

for a collision with a given impact parameter, where the δ -function reflects energy conservation at the transition point. Under the assumption that the probability for the Penning process is low, we can then find an expression for the cross section for the process which leads to a free electron with an energy ε :

$$\frac{d\sigma_p}{d\varepsilon} = \int_0^{\infty} 2\pi\rho d\rho \int_{-\infty}^{+\infty} \Gamma(R) dt \delta(\varepsilon - V(R)),$$

where ρ is the impact parameter of the collision. Now changing the order of integration, and going through the same operations as in the derivation of Eq. (13), we find

$$\frac{d\sigma_p}{d\varepsilon} = \frac{4\pi}{v} \int_{R_0}^{R_c} R^2 \Gamma(R) \sqrt{1 - \frac{U(R)}{E}} \delta(\varepsilon - V(R)) dR; \quad (24)$$

Here $d\sigma_p$ is the cross section for the Penning process which results in the appearance of electrons with energies between ε and $\varepsilon + d\varepsilon$, E is the particle collision energy in the c.m. frame, $U(R)$ is the interaction potential of the particles in the initial state, R_c is the term intersection point, R_0 is the distance of closest approach in the case of a head-on collision [$U(R_0) = E$], and $V(R_c) = \varepsilon$.

We see that if the differential cross section for the Penning process in (24) is integrated over the energy of the emitted electron the result would be Eq. (16).

[In the derivation of Eq. (24) we set the factor f_w equal to unity to simplify the equations.] As in the derivation of Eq. (16), we have assumed that the ionization in the Penning process occurs primarily in the repulsive region of the interaction potential of the colliding particles. Equation (24) is easily generalized to the case in which we are interested—in which the energy scale of the liberated electron is comparable to the level width. In this case, according to the Breit-Wigner formula, the δ -function in Eq. (24) should be replaced by

$$\frac{\Gamma(R)}{2\pi \{[\varepsilon - V(R)]^2 + (1/4)\Gamma^2(R)\}^{1/2}}$$

We now assume that the depth of the well in the interaction potential of atoms A^* and B is small in comparison with the thermal energy of the colliding particles. Then calculations similar to those used in the derivation of Eq. (17) lead to the following expression for the electron energy distribution:

$$F(\varepsilon) = \frac{R_0^2 \Gamma(R_0) \exp[-U(R_0)/T]}{V'(R_0) \int_0^\infty \Gamma(R) R^4 dR \exp[-U(R)/T]} \quad (25)$$

Here $F(\varepsilon)d\varepsilon$ is the probability that an electron is freed with an energy between ε and $\varepsilon + d\varepsilon$, and R_ε is the distance between the nuclei at which the electron with energy $\varepsilon [V(R_\varepsilon) = \varepsilon]$ is freed. The function $F(\varepsilon)$ is normalized: $\int F(\varepsilon)d\varepsilon = 1$.

Using Eq. (25) and the experimental spectra of freed electrons for various gas temperatures, we can reconstruct the interaction parameters of the atoms involved in the Penning process. For example, it follows from this equation that the electron spectrum depends only slightly on the temperature if the Penning process is essentially completed in the region of attraction of the colliding particles, while the electron spectrum varies markedly with the gas temperature if the decay is essentially completed in the closest-approach region. Figure 11 shows the spectrum of electrons freed in the collision of metastable helium atoms with argon and xenon atoms.¹⁴² Figure 12 shows the electron spectrum from a collision of metastable helium atoms with mercury atoms.¹⁴² We see that the collision of a $\text{He}(2^1S)$ atom is an example of the first case, while the collision of a $\text{He}(2^2S)$ atom is an example of the second case.

Measurements of the electron spectrum can reveal the

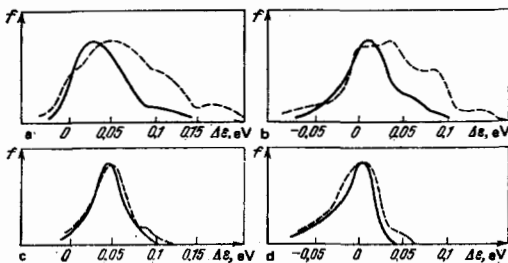


FIG. 11. Energy spectrum of the electrons freed in collisions of metastable helium atoms with atoms of argon and xenon.¹⁴³ $\Delta\varepsilon = \varepsilon - E_{ex} + J$; E_{ex} is the excitation energy of the metastable atom. a— $\text{He}(2^3S) + \text{Ar}$; b— $\text{He}(2^1S) + \text{Ar}$; c— $\text{He}(2^3S) + \text{Xe}$; d— $\text{He}(2^1S) + \text{Xe}$.

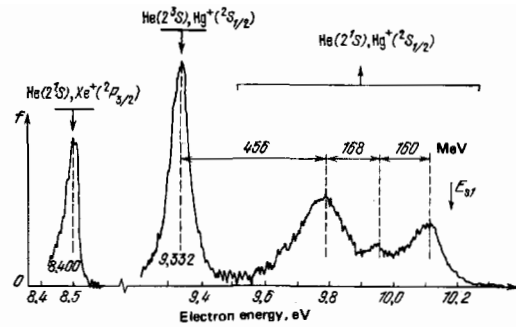


FIG. 12. Energy spectrum of the ionization electrons in the case of the collision of metastable helium atoms with mercury atoms.

state of the reaction products. For example, Table IX shows the relative values for the rate constant for the formation of a mercury ion in the corresponding electronic state in a collision of a metastable helium atom with a mercury atom.^{139, 142} These values correspond to the relative number of electrons emitted with the given energy, which corresponds to the state of the product ion under consideration. Electron-spectrum studies of the Penning process in the case of a collision of a metastable atom with a molecule show that the vibrational state of the resulting molecular ion usually corresponds to the Franck-Condon principle.

If the decay in the Penning process occurred at an infinite separation of the nuclei, the energy of the emitted electrons would be $E_{exc} - J$, where E_{exc} is the excitation energy of the metastable atom, and J is the ionization potential of the impurity atom. The average energy of the electrons resulting from the ionization, $\bar{\varepsilon}$, is shifted from this value, depending on the relative behavior of the terms of the colliding particles in the initial and final states. Table X shows the values of this energy shift for some specific collisions of metastable helium atoms with other atoms.¹⁴² Where this shift is negative, the repulsion between the particles in the final state is greater than their repulsion in the initial state; where the shift is positive, the opposite is true.

The possibilities of the method of Penning spectroscopy are determined by its accuracy. In experiments

TABLE IX. Relative cross sections for the Penning process in the collision of a metastable helium atom with a mercury atom corresponding to a given final state of the mercury ion.

State of metastable helium	2^3S			
	$^2S_{1/2}$	$^2D_{3/2}$	$^2D_{5/2} + ^2P_{1/2}$	$^2P_{3/2}$
State of the mercury ion formed				
Relative cross section for the process	1	0.38 ¹⁴³ 0.52 ¹³⁹	0.34 ¹⁴³ 0.40 ¹³⁹	0.15 ¹⁴³ 0.32 ¹³⁹
State of metastable helium	2^1S			
	$^2S_{1/2}$	$^2D_{3/2}$	$^2D_{5/2} + ^2P_{1/2}$	$^2P_{3/2}$
State of the mercury ion formed				
Relative cross section for the process	1.05 ^{139, 143}	1.27 ¹⁴³ 1.23 ¹³⁹	0.98 ¹⁴³ 0.94 ¹³⁹	0.29 ¹⁴³

TABLE X. Shift of the average energy of the electrons freed in the Penning process.

State of metastable helium atom	2 ³ S			
Ion formed	Ar ⁺ (² P _{3/2})	Kr ⁺ (² P _{3/2})	Xe ⁺ (² P _{3/2})	Hg ⁺ (² S _{1/2})
Shift of the average electron energy, in units of 10 ⁻³ eV	46	25	5	-50
State of metastable helium atom	2 ¹ S			
Ion formed	Hg ⁺ (² D _{3/2})	Hg ⁺ (² D _{5/2})	Hg ⁺ (² P _{3/2})	
Shift of the average electron energy, in units of 10 ⁻³ eV	-67	-83	-100	

by Hotop and Niehaus,¹⁴² the energy resolution in the measurements of the electron energy was 0.01–0.02 eV, i.e., slightly lower than the thermal energy.³⁾ It is thus possible to determine the composition of the final products of the Penning process even in the case in which the binding energy of the resulting molecular ions is comparable to the thermal energies. Table XI shows results found from data on the electron spectrum for the process



where A* is a metastable atom and B is an inert gas atom.

If the relative energy of the colliding atoms is assumed to be zero, then energy conservation tells us that the emission of an electron with an energy greater than $E_{exc} - J$ is accompanied by the formation of a molecular ion in process (26) (E_{exc} is the excitation energy of the metastable atom, and J is the ionization potential of the inert gas atom). The analysis becomes more difficult if the characteristic energy in the electron spectrum is comparable to the thermal energies of the colliding atoms. In this case, the reaction channel must be known for an unambiguous determination of the reaction channel from the electron spectrum.

Advanced experimental methods for studying the Penning process can yield even such details as the electron distribution over the emission angle with respect to the direction of the collision velocity. Measurements of this type were carried out in Refs. 146, 149, and 150 for the collision of metastable helium atoms with other atoms and with molecules. A beam of metastable atoms moving at a velocity comparable to the thermal velocity passed through a gas, so that the relative collision velocity was determined by the beam direction in the collisions of the metastable helium atoms with the heavier gas particles. The metastable helium atoms were in both 2³S and 2¹S states. The current of electrons emitted at various angles with respect to the beam direction was measured, and the

³⁾This resolution makes it possible to reconstruct the parameters of the molecular ion formed in the Penning process. In Ref. 91, for example, measurements of the spectrum of freed electrons led to the parameters of the molecular ions NeH⁺ and ArH⁺.

TABLE XI. Ratio of the cross section for the associative ionization corresponding to the formation of a molecular ion to the total cross section for the Penning process (%).

Metastable atom	Other particle		
	Ar	Kr	Xe
He (2 ³ S)	15 ^{82, 154}	17 ⁸²	11 ⁸²
	17 ^{82 *}	13 ¹⁵⁴	6 ¹⁵⁴
	14 ^{153 1)}	24 ^{82 *}	18 ^{82 *}
	12 ^{78 **)}	11 ^{153 1)}	
He (2 ¹ S)	21 ^{88, 9147}	13 ^{82, 8154}	2 ^{82, 6154}
	44 ^{82 *}	46 ^{82 *}	7 ^{82 *}
	4 ^{78 **)}		
Ne (² P _{0,2})	31 ⁷⁸	30 ⁷⁸	24 ⁷⁸
	34 ¹⁵⁸	34 ¹⁴⁸	23 ¹⁴⁸
		32 ¹⁵⁸	

Note. * Temperature of 90 K; ** temperature of 600 K; no asterisk—temperature range 320–430 K. 1) State of the meta-atom not identified.

energy of these electrons was also measured. This energy made it possible to determine which metastable state was responsible for the decay which resulted in the electrons. It was thus possible to determine the relative angular distribution of the electrons in the decay of systems including the 2³S and 2¹S helium atoms.⁴⁾

The data on the spectrum of ionization electrons refer to the collision of a metastable atom with another atom. When molecules are involved, the electron spectrum becomes more complicated,^{151, 152, 162, 172} since the ions which form may be in vibrationally as well as electronically excited states. Figure 13 illustrates the situation with the spectrum of electrons resulting from the collision of metastable helium atoms with carbon dioxide molecules.¹⁶² We see that in this case the electron spectrum contains, in addition to the resonances corresponding to the formation of a molecular ion in one of several electronic states, some rather poorly defined resonances which correspond to the formation of various vibrational states of the ion in this electronic state.

Since the Penning process involves a significant change in the electronic energy of the colliding and resulting atoms, molecules, and ions, this process may go by various paths. Let us examine the states and structure of the particles which are formed in the Penning process and determine the characteristics associated with the final reaction path. Some results of this type, found from an analysis of the electron spectrum, were given above.

From the standpoint of the identity of the resulting ion, the ionization which accompanies the collision of an excited atom with another atom can go by various reactions, (1)–(3). Reaction (1) is called "Penning ionization" if the excited atom is in a metastable state. Reaction (3), which results in the formation of a bound

⁴⁾In the case of argon,^{146, 149} for example, if we adopt a value of unity for the ratio of the number of emitted electrons for the decay of metastable helium atoms in the 2³s and the 2¹s states at an electron emission angle of 90°, then at an emission angle of 30° this ratio is 0.6, and at 130° it is 1.2.

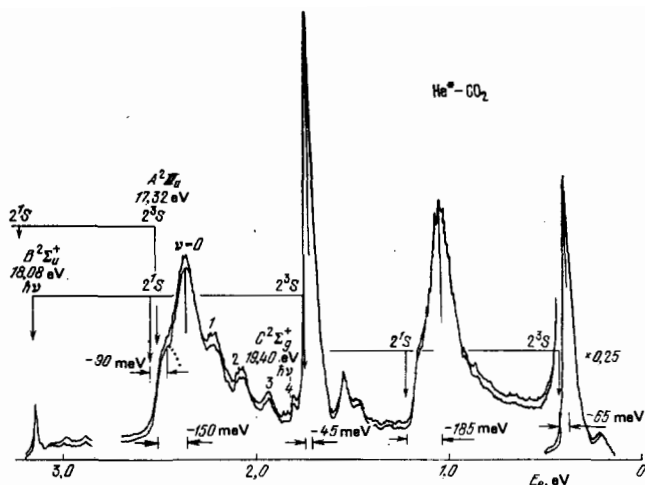


FIG. 13. Electron energy spectrum in the Penning process involving a metastable helium atom and a carbon dioxide molecule.

state of the heavy particles, is called "associative ionization." Since the ionization is accompanied by a simultaneous change in the chemical structure of the colliding particles, it is frequently called "chemionization." Tables XI–XV contain information on the relative importance of Penning ionization and associative ionization for several specific Penning processes.

The data in tables XI–XV were obtained experimentally by two methods. One involves the use of Penning electron spectroscopy, and in this method the ion species can be determined from the energy of the emitted electrons.^{70, 72, 141, 142} The other method uses mass spectrometry^{153–161} and makes it possible to determine the relative yield of a given ion species, either the absolute value of the cross section, or the rate constant for the Penning process for a given species of the ions that are formed.

Table XII shows the relative probabilities for the formation of ions of a given species in collisions of metastable helium and neon atoms with molecules of various hydrogen isotopes. Most of these results were

TABLE XII. Relative yield of the ions of a given species (%) in collisions of metastable helium and neon atoms with molecules of hydrogen and its isotopes (A ≡ He, Ne). A mixture of 2³S and 2¹S states is involved in the processes in the case of the metastable helium atom; a mixture of the ³P₂ and ³P₀ state is involved in the processes in the case of the metastable neon atom.

Target molecule	Ion formed	Metastable atom	
		He*	Ne
H ₂	H ₂ ⁺	88 ^{78, 88} , 88.4 ¹⁴¹ , 88.6 ¹⁵⁵ , 91 ¹⁵⁶	77.8 ¹⁴¹
	AH ⁺	8.1 ⁷⁸ , 10 ⁸⁸ , 9.7 ^{141, 149} , 9 ¹⁵⁶	20.2 ¹⁴¹
	AH ₂ ⁺	1.5 ⁷⁸ , 1.6 ⁸⁸ , 1.9 ¹⁴¹ , 1.7 ¹⁵⁵ , 0.7 ¹⁵⁶	2.0 ¹⁴¹
HD	HD ⁺	87.3 ¹⁴¹	74 ¹⁴¹
	AH ⁺	4.7 ¹⁴¹	10.4 ¹⁴¹
	AD ⁺	7.1 ¹⁴¹	14.1 ¹⁴¹
	AHD ⁺	0.9 ¹⁴¹	1.5 ¹⁴¹
D ₂	D ₂ ⁺	99.3 ¹⁵⁵	—
	AD ⁺	—	—
	AD ₂ ⁺	0.7 ¹⁵⁵	—

TABLE XIII. Relative probability for the given reaction product in the Penning process involving a metastable Ne(³P_{0,2}) atom.

Target	NO		H ₂			N ₂		CO	
Ion in final reaction channel	NO ⁺	NeNO ⁺	H ₂ ⁺	NeH ⁺	NeH ₂ ⁺	N ₂ ⁺	NeN ₂ ⁺	CO ⁺	NeCO ⁺
Relative probability for ion emission, (%)	99.3 99 *	0.7 1 *	78 78 *	22 20 *	0 2 *	94.1	5.9	92.5	7.5

Target	O ₂		CO ₂		N ₂ O			
Ion in final reaction channel	O ₂ ⁺	NeO ₂ ⁺	CO ₂ ⁺	NeCO ₂ ⁺	N ₂ O ⁺	NO ⁺	O ⁺	NeN ₂ O ⁺
Relative probability for ion emission, (%)	99.7	0.3	99.4	5.6	76	17	6.3	0.7

*Results obtained in Ref. 70, corresponding to a temperature of 320 K. Values without an asterisk were obtained in Ref. 72 for a gas temperature of 435 K.

obtained by the mass-spectrometry method.^{141, 155, 156} We see that the isotopic effect is more noticeable in the case of a relatively low ion dissociation energy. The decrease in the relative probability for the formation of ions of the type AH₂⁺, when the protons are replaced by deuterons, can be explained in the following way¹⁵⁵:

The dissociation energy of the HeH₂⁺ ion is low (0.2 eV), so that the vibrational motion of the protons in this ion is nearly the same as that for the H₂⁺ ion. If the HeH₂⁺ ion is to be produced in the reaction He^{*} + H₂, the He and H₂⁺ particles in the final reaction must be bound, and the H₂⁺ ion must be in the vibrational ground state or in the first excited state in the case of D₂⁺. Imposing the Franck–Condon principle, we see that the probability for the formation of a molecular hydrogen ion in the vibrational ground state during the ionization of a hydrogen molecule in the vibrational ground state falls off when the protons are replaced by deuterons. There is a corresponding decrease in the yield of products of the type HeH₂⁺ for this reaction when protons are replaced by deuterons.

Ions of the type AD⁺ are slightly more likely to be formed than AH⁺ ions, since the number of vibrational and rotational levels of the AD⁺ ions is higher than that of the AH⁺ ions. The difference is magnified as that range of coordinates in which the classical laws of motion for the nuclei are violated becomes relatively more important for the reaction.

A study of isotopic effects can be of assistance in studying the nature of the Penning process. Certain

TABLE XIV. Relative probability of the corresponding reaction channel for the process A(³P_{0,2}) + NO.

Metastable atoms A	Ar		Kr	
	NO ⁺	Ar	Kr	Ar
Ion in final reaction channel	NO ⁺	81 ^{70 1}), 81 ^{78 2}), 80 ^{142 3}), 82 ^{160 3})	74 ^{70 1}), 64 ^{78 2}), 98 ^{142 3}), 65 ^{160 3}), 80 ^{160 4})	
	ANO ⁺	19 ^{70 1}), 19 ^{78 2}), 20 ^{142 3}), 18 ^{160 3})	26 ^{70 1}), 36 ^{78 2}), 1.5 ^{142 3}), 35 ^{160 3}), 20 ^{160 4})	

¹)Gas temperature of 320 K. ²)Gas temperature of 435 K. ³)Gas temperature of 300 K. ⁴)Gas temperature of 600 K.

TABLE XV. Relative yield of ions (%) for the Penning process $\text{He}^* + \text{H}_2\text{O}$, D_2O (He^* is a mixture of metastable He atoms in the 2^3S and 2^1S states; the temperature is 340 K).

Target		H_2O	D_2O
Ion in final reaction channel	H_2O^+ , D_2O^+	78	76
	OH^+ , OD^+	17.8	19.3
	H^+ , D^+	3.1	3.1
	HeH^+ , HeD^+	0.7	0.5
	HeO^+	0.2	—

conclusions regarding the nature of this process in the collision of metastable atoms with molecules can be drawn from the results reported by Penton and Muschlitz,¹⁵⁹ who measured the relative cross sections for the Penning effect in the collision of metastable helium atoms with H_2 , HD , and D_2 molecules. The metastable helium atoms were in singlet and triplet states, with the ratio of corresponding atoms varying from 0.9 to 2.

If the thermal collision energy is significantly lower than the dissociation energy of the hydrogen molecule, it can be assumed that the distance between the protons does not change in the course of the collision. When the isotopic composition of the nuclei is changed, there is no change in the interaction potential, so that the rate constant for the Penning process does not depend on the mass of the colliding nuclei, according to Eq. (20), and the cross section for this process is proportional, at a given temperature, to the square root of the reduced mass of the colliding particles. It follows that we have $\sigma_{\text{D}_2}/\sigma_{\text{H}_2} = 1.22$ and $\sigma_{\text{HD}}/\sigma_{\text{H}_2} = 1.13$, where the subscript specifies which molecule is ionized as a result of the Penning process. Measurements carried out under identical conditions yield¹⁵⁹ $\sigma_{\text{D}_2}/\sigma_{\text{H}_2} = 1.15 \pm 0.05$ and $\sigma_{\text{HD}}/\sigma_{\text{H}_2} = 1.03 \pm 0.05$. The discrepancy between the theoretical and experimental results is attributed to different distributions in the distance between the nuclei in the molecules.

It can be concluded from this analysis that a dependence of the characteristics of the Penning process on the isotopic composition of the molecules involved is seen in the case in which a threshold energy is required for this process; the threshold is very sensitive to the isotopic composition of the molecules. When the process occurs far from the threshold, its parameters depend only slightly on the isotopic composition of the molecules. This assertion is supported by the data in Table XV on the relative yields of various ions in a Penning process involving metastable helium and neon atoms and various isotopes of a water molecule.

It follows from general considerations that associative ionization can dominate the ionization which occurs in the Penning process if the relative collision energy of the particles is much lower than the dissociation energy of the product ion. In this case the kinetic energy of the relative motion of the particles in the final reaction is smaller than the attraction energy of the product particles if the electron is detached at a nuclear separation corresponding to strong attraction of the product particles (Fig. 4). With increasing collision energy, the probability for the formation of a bound state of the

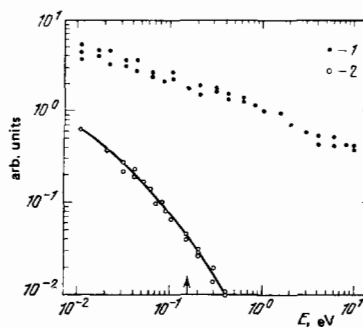
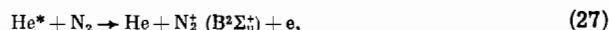


FIG. 14. 1—Dependence of the total cross section for the Penning process on the collision energy for the pair $\text{Ar}^* + \text{Na}$; 2—dependence of the cross section for associative ionization on this energy.¹³⁵

particles in the final channel decreases; i.e., the relative probability for the associative ionization falls off with increasing collision energy. This conclusion is confirmed by data from many experiments (see, for example, Refs. 44, 87, 88, and 133–137), which show that the relative cross section for associative ionization falls off with increasing collision energy and that that part of the total cross section for the Penning process which can be attributed to associative ionization falls off with increasing collision energy. At a collision energy comparable to or greater than the dissociation energy of the product ion, the cross section for associative ionization becomes extremely small.

This fact is illustrated in Fig. 14 by the relative cross section for associative ionization and the total cross section for the Penning process $\text{Ar}^* + \text{Na}$, plotted as functions of the collision velocity. The arrow shows the position at which the dissociation energy of the resulting molecular ion, NaAr^+ (0.15 eV according to Refs. 163 and 164) is equal to the kinetic energy of the relative motion.

Some information on the Penning process can be found by studying the emission spectrum of the product ion. In Refs. 40, 41, and 165–167, for example, studies were made of the process



where the helium atom is in a metastable state. Table XVI shows the cross sections for this process. Comparison with Table III shows that, according to Eq. (24), the probability for ionization accompanied by the formation of an excited ion in Penning ionization involving a metastable helium atom and a nitrogen molecule is of the order of some tenths.

Table XVII shows another example of this type,¹⁶⁸ in this case for the collision of a metastable helium atoms with a CO molecule. In this case the probability for the formation of the ion in the ground state is lower

TABLE XVI.

Metastable state of helium atom	Cross section for reaction (27), 10^{-16} cm^2
2^3S	5, 1 ⁶⁰ , 2, 0 ¹⁶⁶ , 1, 5 ¹⁶⁷
2^1S	4, 9 ¹⁶⁶ , 2, 5 ¹⁶⁷

TABLE XVII. Pathways for the reaction He(2³S)+ CO (Ref. 168).

Final product	Relative yield, (%)	Rate constant of process, 10 ⁻¹¹ cm ³ /s
e + He + CO ⁺ (B ³ Σ)	53	5.3
e + He + CO ⁺ (A ³ Π)	17	1.7
e + He + CO ⁺ (X ³ Σ)	26	2.6
e + He + O + C ⁺	4	0.4

than that for the excited state. Table XVIII shows partial cross sections for the Penning process in the collision of a metastable helium atom with metastable metal atoms, corresponding to the formation of an ion in various states. These results were obtained in a study of the afterglow in a decaying plasma.⁸ In these cases the excitation energy of the colliding atoms was quite high, so that the formation of many states of the ion was energetically allowed.

The excitation potential of the metastable helium atom is higher than the potential for the appearance of doubly charged ions of several elements. In the case of a collision of a metastable helium atom with atoms of these elements, therefore, doubly charged ions form along with singly charged ions. This process was observed for several elements in Refs. 169-171. Table XIX shows the relative probabilities for the formation of doubly charged ions in the Penning process (in comparison with singly charged ions) for several cases in which the formation of doubly charged ions is energetically allowed.

Turning to the polarization of the resulting electrons, we see that it must be the same as the spin polarization of the metastable atoms in the case of a collision with an atom or a molecule with zero spin.¹¹⁹ This assertion has been confirmed experimentally¹⁹⁰ in collisions of metastable 2¹S helium atoms with Ar atoms and with the molecules H₂, N₂, CO₂, and N₂O. In the case of a collision of a metastable helium atom with a CO molecule the observed polarization of the ionization electrons is lower than the initial polarization of the metastable helium atom by about 30% (the error in the measurement of the polarization in that experiment was 10%).

4. ASSOCIATIVE IONIZATION

Associative ionization, reaction (3), is of particular interest if direct ionization is energetically forbidden in

TABLE XVIII. Partial cross sections for the Penning process in the collision of a metastable 2²S helium atom with metastable metal atoms.⁸

Initial state of atom	Product ion and its state	Partial cross section, 10 ⁻¹⁵ cm ²
Hg (6 ³ P ₂)	Hg ⁺ (7 ² P _{1/2})	10
Zn (4 ³ P ₂)	Zn ⁺ (6 ² S _{1/2})	1.5
	Zn ⁺ (5 ² P _{1/2})	2
	Zn ⁺ (5 ² P _{3/2})	1
Cd (5 ³ P ₂)	Cd ⁺ (5 ² F _{7/2})	0.40
	Cd ⁺ (7 ² P _{3/2})	0.40
	Cd ⁺ (6 ² D _{5/2})	1.5
	Cd ⁺ (6 ² D _{3/2})	1.0
	Cd ⁺ (4 ² F _{7/2})	2.5
	Cd ⁺ (4 ² F _{5/2})	2.0
	Cd ⁺ (7 ² S _{1/2})	0.35
Cd ⁺ (6 ² P _{3/2})	2.5	

TABLE XIX. Characteristics of Penning process (28).

Target atom and its electronic configuration	Metastable helium atom	Difference between the excitation potential of the metastable helium atom and the potential for the appearance of the doubly charged ion, eV	Relative probability for the formation of a doubly charged ion at a collision energy of 0.1 eV, (%)
Ba (6s ²)	He (2 ³ S)	4.60	1
	He (2 ¹ S)	5.39	1.8
Y (4d5s ²)	He (2 ³ S)	1.20	2
	He (2 ¹ S)	1.99	2
Ce (4d5f6s ²)	He (2 ³ S)	3.50	2.8

a collision of an excited atom with another atom, i.e., if the excitation potential of atom A* in (3) is lower than the ionization potential of atom B. This energy deficiency in the associative ionization can be made up from the dissociation energy of the resulting molecular ion. In this case, associative ionization is the sole ionization reaction in a collision of an excited atom with another atom. In particular, this situation arises in the collision of excited and unexcited atoms of the same species.

Ionization in a collision involving excited atoms was first discovered by Mohler and Boeckner¹⁷³ in 1930 in the photoexcitation of cesium vapor. The formation of molecular ions, however, was not identified. Associative ionization was first observed in 1951 by Hornbeck and Molnar.¹⁷⁴ This process is the basic mechanism for the formation of charged particles in gases excited by electromagnetic radiation (in particular, by resonant radiation).

The physics of associative ionization can be understood with the help of Fig. 15, which shows the electronic terms of the molecular ion AB and one of the terms corresponding to the interaction of an excited atom A* with another B. These terms intersect at a certain distance between the nuclei, R_c and at shorter distances the A* + B system is in an autoionization state. This state may decay, forming a molecular ion and a free electron.

Associative ionization is important in the formation of charged particles in a hot gas or a weakly ionized plasma in cases in which the excitation energy is too low for direct ionization of the atoms. For example, the formation of charged particles in flames in which hydrocarbons are burnt results primarily from the reaction¹⁷⁵⁻¹⁸⁰



In hot air the charged particles form by the reaction¹⁸¹⁻¹⁸⁷

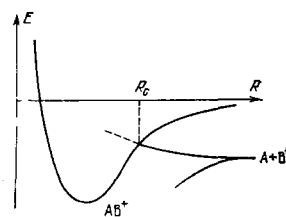


FIG. 15. Behavior of the terms in associative ionization.

Associative ionization is important in the development of sparks and lightning. The first step in the breakdown of a gas at atmospheric pressure is an ionization wave, which propagates toward the positive electrode and creates a conducting channel with relatively few charged particles and a relatively low number density. Then the ionization wave propagates in the opposite direction, creating a relatively high density of charged particles. As a result, a conducting channel forms in the gas, and it is along this channel that the voltage discharge occurs. The second step of the breakdown, corresponding to the propagation of an ionization wave toward the negative electrode, cannot be explained on the basis of the motion of ions, because the velocity is high (10^9 cm/s). This step of the breakdown results^{188, 189} from the appearance of excited atoms as a result of absorption of photons moving toward the positive electrode. The photons themselves appear in emission by atoms excited by electron impact. An excited atom leads to the formation of a free electron, which causes a rapid breeding in the external electric field. Consequently, if the emitted photon moves toward the negatively charged electrode, then after a certain time interval an electron avalanche will return to the region from which the photon was emitted. As a result, an ionization wave (streamer) moves opposite the electron current direction and increases the charged-particle density, i.e., creates a conducting channel.

In the interaction of a monoenergetic electron beam with a gas, ions also appear at an electron energy insufficient for direct ionization of the gas particles. This appearance is a consequence of associative ionization: The electron beam excites gas atoms, which form molecular ions in collisions with ground-state atoms. The threshold electron energy in this case is determined by the threshold for the excitation of those states from which molecular ions can form through associative ionization. Table XX shows the potentials at which several molecular ions appear, i.e., the lowest energies of the electrons in the beam at which the formation of the ions is observed in the gas or gas mixture. In all the cases studied, this potential is below the ionization potential of the host-gas atom.

The original methods for studying associative ionization made use of this electron-impact method for exciting a gas.^{74, 191-208} The gas is excited by a monoenergetic electron beam capable of ionizing the gas atoms.

TABLE XX. Potentials for the appearance of molecular ions.

Molecular ion	Potential for its appearance, eV	Ionization potential of atoms, eV
Hej	23.3±0.4 ^{174, 198, 195}	24.59
HeNe ⁺	23.0±0.4 ^{195, 198}	
HeAr ⁺	17.9 ¹⁹⁵	
HeKr ⁺	19.9 ¹⁹⁸	
Nej	20.9 ^{174, 198}	21.56
NeAr ⁺	16.8±0.4 ^{192, 199}	
NeKr ⁺	16.6 ¹⁹³	
NeXe ⁺	16.0 ¹⁹⁸	
Arj	14.9±0.2 ^{174, 191, 202, 204}	15.76
ArKr ⁺	14.0 ²⁰²	
ArXe ⁺	13.5 ^{202, 205}	
Krj	13.1±0.4 ^{174, 195, 198, 204}	
KrXe ⁺	12.2 ²⁰⁵	14.0
	12.3 ¹⁹⁸	
Xej	11.3±0.4 ^{192, 202, 204}	12.1
Cs ₂ ⁺	2.82 ²⁰¹	
		3.89

The following reactions occur in the gas:



Shown above the arrow is the rate constant or the characteristic time of the given reaction. The change in the number density of particles of a given species satisfies

$$\frac{dN_1}{dt} = N_e N_a k_i, \quad \frac{dN_2}{dt} = N^* N_a k_r, \quad (31)$$

$$\frac{dN^*}{dt} = N_e N_a k_e - N^* \left(\frac{1}{\tau_r} + k_r N_a \right), \quad (32)$$

where N_1 and N_2 are the densities of atomic and molecular ions, N^* is the density of excited atoms, and N_a and N_e are the densities of atoms and electrons, respectively. This system of equations was written under the assumption that a molecular ion can form from only a single excited state.

Solving system (32) for the instant at which the electron pulse ends, we find

$$\frac{N_2}{N_1} = \frac{k_r \tau_r N_a}{1 + k_r \tau_r N_a} \frac{k_e}{k_i} \left\{ 1 - C \exp \left[- \left(\frac{1}{\tau_r} + k_r N_a \right) t \right] \right\}, \quad (33)$$

where the constant C depends on the length and shape of the electron pulse. We now apply a constant electric field, and by extracting the ions from the gas we measure the ratio of the currents of molecular and atomic ions. We choose a weak electric field, so that the ratio of ion currents will be proportional to the ion density, and by measuring this ratio we can determine the properties in which we are interested.

The usual procedure is to measure the ratio of the total currents integrated over the entire duration of the experiment. Changes can be made in the gas density, the energy of the beam electrons, the length of the electron current pulse, and the delay time before the application of the electric field and the extraction of ions from the gas. Measurements for various values of these parameters make it possible to reconstruct the radiative lifetime of the state, τ_r , and the rate constant for electron-impact excitation of that state of the atom which is active in associative ionization.

If there are several excited states of the atom for which associative ionization is effective, then a sum should be taken over these states on the right side of Eq. (33). Whether such states can be revealed by this method depends on not only the associative-ionization cross section for these states but also the resolution of the particular experimental apparatus. For example, a study of helium by this method has revealed four excited levels which lead to associative ionization.¹⁹⁹ These levels can be identified from their radiative lifetime and from the dependence of their excitation cross section on the electron energy.²⁰⁶ This method for studying the quantitative characteristics of associative ionization cannot compete with advanced methods for studying this process (see Table XXII). For this reason, this method has essentially fallen into disuse.

TABLE XXI. Parameters of associative-ionization process (34) in the collision of two resonantly excited alkali metal atoms.

Species and state of colliding atoms	Heat of reaction, eV	Temperature, K	Rate constant for process (34), 10^{-13} cm ³	Average cross section for process, 10^{-16} cm ²	Reference
Li (2 ³ P)	-0.74	900	—	$5 \cdot 10^{-3}$	210
Na (3 ³ P)	0	500	—	100	211
		Beam $v = 3.8 \cdot 10^4$ cm/s	—	0.5	212
		550	380 ± 40	38	213
K (4 ³ P)	0.1	450	9 ± 2	1.3	214
Rb (5 ³ P)	0.2	470	3.2 ± 0.4	0.7	215
Cs (6 ³ P)	0.33	425	2 ± 0.2	0.54	216
		500	1.6	0.5	217
		500	2.5	0.65	218

In this case an electron beam is used to produce excited atoms. Another possibility is to use photoexcitation of a gas. Although this method can produce only atoms having a certain symmetry of levels, because of the selection rules, it does make it possible to avoid various secondary processes which occur in the case of electron-impact excitation of atoms. In this case the excited atoms are formed in only a single state, and this is a definite advantage. This method is becoming particularly popular because of the appearance of a convenient excitation source: the tunable laser.

In this method, the atoms undergo a single or double photoexcitation, and the current of the resulting molecular ions is measured. Two versions of this method have been adopted. In one version, a study is made of the associative ionization which results from the excitation of resonant states of gas atoms by resonant radiation. The associative ionization occurs in the collision of two resonantly excited atoms. In the second version, the associative ionization occurs in the collision of an excited atom with a ground-state atom. The first version has been adopted most widely for collisions of two resonantly excited atoms of alkali metals. Table XXI shows the characteristics of the reaction



where $M(^2P)$ is an alkali metal atom in a low-lying, resonantly excited state. When two metastable mercury atoms participate, the associative ionization $[2Hg(6^3P_2) \rightarrow Hg_2^+ + e]$ occurs far more efficiently than in the case of a collision of alkali metal atoms. The cross section for associative ionization corresponding to this process is ⁵⁾ $5 \cdot 10^{-14}$ cm² (Ref. 219).

In addition to producing excited atoms through photoexcitation, it has become common to study associative ionization by measuring the spectral characteristics of

⁵⁾This value is not only much greater than the cross section for the molecular mercury ion but also larger than the cross section in (11) for the capture of two excited mercury atoms. The latter cross section can be taken as an estimate of the upper limit on the associative-ionization cross section. According to estimates, the constant of the van der Waals interaction of two metastable mercury atoms is $C \approx 10^3$, from which we find from (11) that the capture cross section in a collision of these atoms at room temperature is $\sigma = 1.5 \cdot 10^{-14}$ cm². This value is significantly lower than the measured cross section for associative ionization.

TABLE XXII. Average cross section for associative ionization at a temperature of 320 K.

Excited state of helium atom	3 ³ S	3 ¹ S	3 ³ P
Potential for ionization from this state, eV	1.87	1.67	1.58
Associative-ionization cross section, A ³	$< 0.04^{220, 221}$ 0.07^{222} $< 0.3^{223}$	$< 0.1^{220, 221}$ $< 3.7^{223}$	$1.6^{220, 221}$ 1.9^{222} $< 4^{223}$
Excited state of helium atom	3 ³ D	3 ¹ P	3 ¹ D
Potential for ionization from this state, eV	1.52	1.50	1.42
Associative-ionization cross section, A ³	$4.5 \pm 0.5^{220, 221}$ 2.8^{222} 2.4 ± 0.5^{223}	$3.1 \pm 1.0^{220, 221}$ 1 ± 1^{223}	$20 \pm 4^{220, 221}$ 15 ± 4^{223}

gas-discharge plasmas. In this case the initial excitation occurs in a gas discharge, and a further selective excitation of certain particular states is caused by the resonant light source. The result is the formation of excited atoms in a given state. Associative ionization involving these atoms leads to the formation of molecular ions, which are detected. It can be seen that the measurement arrangement in this method is similar to that of the method just discussed, but since additional excitations arise in the gas discharge and disrupt the selectivity in this method, it requires a careful study.

Table XXII shows the average cross sections for associative ionization in a collision of helium atoms in excited and ground states. These cross sections were measured in a gas discharge in which metastable helium atoms (in the 2³S and 2¹S states) were excited by resonant light.²²⁰⁻²²³ The associative ionization is seen to occur most efficiently from the 3¹D state, because of the positions of the He₂⁺ and He₂⁺ terms. Figure 16 is a diagram of the electronic terms²²⁴ along which the nuclei move in the dissociative ionization from the He(3¹D) state. This state has the largest associative-ionization cross section among the group of states under consideration.

It is not difficult to see the nature of the transition for this case. As the nuclei come closer together, the system of colliding particles, originally on the He(3¹D) + He term, switches to a repulsive term, which intersects a term of the molecular ion. It is the transition

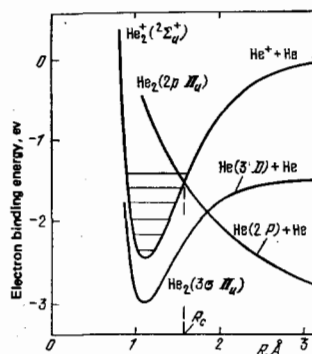


FIG. 16. Position of the potential curves of the helium molecules and molecular ion responsible for the process $He(3^1D) \rightarrow He_2^+ + e$.

to this state which leads to the ionization.

The measured average cross section for associative ionization is roughly three times the quantity πR_c^2 , where R_c is the point at which the repulsive term intersects the continuum boundary (Fig. 16). Then the kinetic energy of the nuclei at the point at which the molecular ion forms (i.e., at a distance between the nuclei of approximately R_c) is much higher than the thermal energy of the nuclei. In this case, therefore, the associative ionization is determined by the capture of the colliding particles as a result of the attractive force acting between them.⁶⁾

Let us derive an expression for the cross section for associative ionization in the case in which this ionization occurs on the repulsive part of the interaction potential. This process is similar to the Penning process, but the autoionization state decays at an internuclear separation $R < R_c$. The cross section for associative ionization is thus determined by Eqs. (15) and (16), in which the infinite upper limit on the integral should be replaced by the term intersection distance R_c . Then we find the following expression for the cross section for associative ionization:

$$\sigma_{ac} = \frac{4\pi}{v} f_w \int_{R_0}^{R_c} R^2 \Gamma(R) \sqrt{1 - \frac{U(R)}{E}} dR; \quad (35)$$

where E is the energy of the relative motion of the nuclei, v is the relative collision velocity, $U(R)$ is the interaction potential of the particles in the initial channel, R_0 is the distance of closest approach in a head-on collision, so that $U(R_0) = E$, $\Gamma(R)$ is the width of the autoionization level, and f_w is the probability for the system to be in the initial channel.

We can write an expression for the associative-ionization cross section near the threshold. Assuming that the width of the autoionization level is independent of the internuclear separation near the threshold, and introducing $U' = \partial U / \partial R / R_c$ and E_{thr} (the threshold energy), we find $E - U'(R) = |U'| (R - R_0)$ and $E - E_{thr} = |U'| (R_c - R_0)$. Substituting these expressions into (35), we find the threshold energy dependence of the cross section:

$$\sigma_{ac} = A \frac{(E - E_{thr})^{3/2}}{E}, \quad A = \frac{4\pi \sqrt{2\mu} R_c^2 \Gamma}{3 |U'|}; \quad (36)$$

where μ is the reduced mass of the colliding particles.

In complete analogy with Eq. (20), the rate constant for this process is

$$k_{ac} = 4\pi f_w \int_{R_0}^{R_c} R^2 \Gamma(R) dR \exp \left[-\frac{U(R)}{T} \right]. \quad (37)$$

⁶⁾The average capture cross section for the pair $\text{He}(3^1D) - \text{He}$ at a temperature of 500 K is $2.8 \cdot 10^{-15} \text{ cm}^2$ according to Eq. (11). Here we have used the $\gamma^2 = 200$ for the square of the radius of the orbit of a valence electron, in accordance with the general formula²²⁵ for hydrogen-like atoms. We see that the capture cross section is slightly larger than the associative-ionization cross section. For a collision of the type $\text{H}(2s) + \text{H}_2$, the average capture cross section at 300 K is $9.3 \cdot 10^{-15} \text{ cm}^2$ according to Eq. (11). This value agrees with the measured cross section for associative ionization,²²⁶ $9 \cdot 10^{-15} \text{ cm}^2$.

as follows from Eq. (35). If the decay occurs basically near the level intersection point, where the interaction potential of the particles in the initial channel can be approximated by a straight line, $[U(R) - U(R_c)] = |U'| (R_c - R)$, Eq. (37) can be rewritten as

$$k_{ac} = 4\pi f_w R_c^2 \Gamma \frac{T}{|U'|} \exp \left[-\frac{U(R_c)}{T} \right]. \quad (38)$$

Here we have made use of the circumstance that Γ , the width of the autoionization level, is independent of the internuclear distance near the intersection point.

The average cross section for associative ionization is smaller than $\pi R_c^2 \exp[-U(R_c)/T]$, where πR_c^2 is the maximum possible cross section, and the exponential function is the probability that the particles will enter a region in which the process can occur as they move closer together. We can thus write an upper limit on the rate constant for the associative ionization:

$$k_{ac} < \sqrt{\frac{8T}{\pi\mu}} \pi R_c^2 \exp \left[-\frac{U(R_c)}{T} \right], \quad (39)$$

where μ is the reduced mass. We thus have a condition for the applicability of Eq. (38), which was derived under the assumption that the probability for associative ionization is low for each collision impact parameter:

$$\Gamma \ll \frac{|U'|}{\sqrt{T\mu}}. \quad (40)$$

The same condition can be found directly from the requirement $\int \Gamma dt \ll 1$. To show this, we write

$$\int \Gamma dt \sim \frac{\Gamma \Delta R}{v} \sim \Gamma \Delta R \sqrt{\frac{\mu}{T}},$$

where $\Delta R \sim T/|U'|$ is the width of the region well below the intersection point which basically determines the cross section for associative ionization. Now requiring that the probability for associative ionization be low in each collision ($\int \Gamma dt \ll 1$), we find condition (40).

Among the various associative-ionization processes involving highly excited atomic states, that which has been studied most thoroughly is



which involves alkali metal atoms. For an experimental study of this process, Klyucharev *et al.*^{8, 227-230} measured the ion currents in the vapor of the alkali metal during selective excitation of the atoms in a given excited state by resonant light. The maximum cross sections for associative ionization correspond to values $n \sim 10$ for the principal quantum number of the excited atom. These values fall in the region of states under consideration. The theory for reaction (41) is considerably simpler than that for the general case of associative ionization: On the one hand, the system of colliding particles is symmetric in this case, and on the other the electron is highly excited, and the process is determined by a Coulomb interaction of an electron with an atomic core. Consequently, the theory of Refs. 8, 227, 231, and 232 yields general expressions for the rate constant for process (41) in this case, and a comparison of theory with experiment can reveal the mechanism for and the characteristics of the processes in question.

To outline a theory for reaction (41), we assume that

the transitions occurs in the repulsive region. We represent the quasimolecule A^*-A in the initial and final channels by the state of the electron in the field of the molecular ion A_2^+ . Then the initial channel corresponds to an odd state of the molecular ion and to a bound state of the electron, while the final channel corresponds to an even state of the molecular ion A_2^+ and to a free electron. The change in the electron energy is $\Delta(R)$, where $\Delta(R)$ is the exchange-interaction potential of atom A and ion A^+ when separated by a distance R . For large values of n the electron binding energy is $1/2n^2$, so that the intersection point is given by

$$\Delta(R_c) = \frac{1}{2n^2}. \quad (42)$$

Let us determine the values of n at which we can expect the maximum cross section for a given temperature. For large n we have

$$\Gamma \sim \frac{1}{n^3}. \quad (43)$$

the expression for the width of the autoionization level contains the square of the excited-electron wave function ψ_n and is determined by distances small in comparison with the size of the orbit of this electron. Since $\psi_n(0) \sim n^{-3/2}$, the dependence on the principal quantum number is given by Eq. (43). Using this expression in (38) and noting that $U(R_c) \sim \Delta(R_c) \sim 1/n^2$, we find that the maximum of this expression can be expected at

$$n \sim \frac{1}{\sqrt{T}}, \quad (44)$$

which corresponds to $n \sim 10$ at room temperatures. In other words, associative ionization occurs most efficiently from the high-lying levels. In accordance with (39), we have an estimate for the maximum rate constant for associative ionization:

$$k_{ac}^{max} \leq 10^{-9} \text{ cm}^3/\text{s}.$$

Figure 17 shows the theoretical dependence of the rate constant for associative ionization on the principal quantum number for the case of rubidium and cesium atoms in the ground state and a highly excited state.²³²

Another example of process (41) was studied by Gress *et al.*²³³:

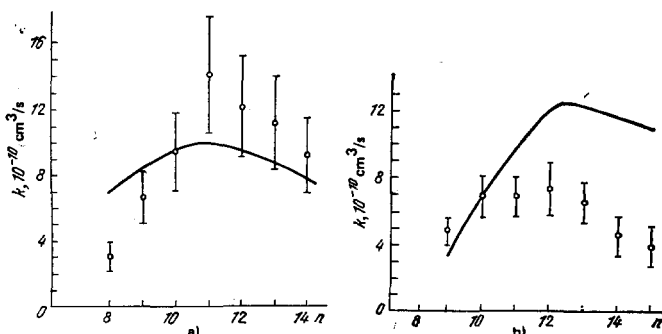


FIG. 17. Cross section for associative ionization at a temperature of 520 K a: $Rb(np) + Rb(5s) \rightarrow Rb_2^+ + e$; b: $Cs(np) + Cs(6s) \rightarrow Cs_2^+ + e$. Solid curve—Theory of Ref. 231; circles—experimental data of Refs. 227 and 228.

It was found that for the range of principal quantum numbers considered, $n=4-8$, the cross section for associative ionization at room temperature falls off with increasing principal quantum number. If we assign a unit value to the relative cross section for reaction (45) with $n=4$, we find that with $n=5$ its value is 0.32, at $n=6$ its value is 0.24, and at $n=7$ and $n=8$ its value is 0.23.

Using the information which has been obtained on the cross sections for associative ionization at low collision energies, we can divide these reactions into two groups, using different models to describe the two groups. In the first group, the associative ionization occurs in the region of attraction between the colliding particles. Then the cross section for this process is not greatly different from the particle-capture cross section, given by (11). In the second case, the process occurs on the repulsive part of the interaction potential of the colliding atoms. Then the ionization occurs near the turning point, and the cross section is given by Eqs. (35) and (36).

The most promising method for measuring the cross section for associative ionization is a beam method. In this method, the process occurs in a region in which beams of colliding atomic particles intersect, and the cross section for the process is determined from the current of charged particles extracted from the reaction zone. This approach embodies all the advantages of the beam method: the ability to carry out measurements with particles which do not exist in a gas phase and the possibility of determining the dependence of the cross section on the relative collision velocity. At the present state of the beam method the primary difficulty in measuring the associative-ionization cross section is in producing a beam of electronically excited particles. Different approaches have been taken to solve this problem, depending on the particular situation.

A convenient process in this regard is the associative ionization involving lanthanide and transuranium atoms. These atoms have relatively low ionization potentials, but they form very strong molecular bonds with gas atoms or molecules. Consequently, associative ionization is energetically allowed when the lanthanide or transuranium atoms are in the ground state. This circumstance is of major assistance in experiments in

TABLE XXIII. Characteristics of the associative ionization of uranium and thorium atoms with oxygen atoms and of oxygen molecules^{237, 238, 241}.

Reaction	Heat of reaction, eV	Cross section, 10^{-14} cm^2
$U + O \rightarrow UO^+ + e$	2.1	16.2 ± 0.4
$U + O_2 \rightarrow UO_2^+ + e$	4.1	0.17 ± 0.03
$U + O_2 \rightarrow UO_2^+ + O + e$	3.0	2
$UO^+ + O_2 + e$	1.0	2
$Th + O \rightarrow ThO^+ + e$	2.8	10.3 ± 3.2
$Th + O_2 \rightarrow ThO_2^+ + e$	2.8	0.15 ± 0.03
$Th + O_2 \rightarrow ThO_2^+ + e$	1.7	$2 \cdot 10^3$
$ThO_2^+ + O + e$	1.7	0.1
$ThO^+ + O_2 + e$	1.7	4
$ThO_2^+ - O^-$	3.2	0.02
$ThO^+ + O_2^-$	2.2	0.01

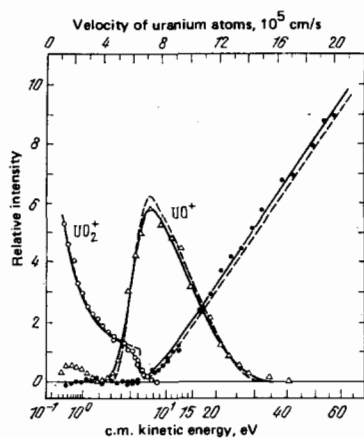


FIG. 18. Distribution in ion species in the collision of uranium atoms with oxygen molecules, plotted as a function of the relative collision energy.

which a beam of metal atoms produced by one of various possible methods intersects a beam of atomic particles, with which the metal atoms react. This method has been used to measure the cross sections for associative ionization in collisions of certain atoms of the lanthanides, actinides, and other metals (Ti, Cd, Zr, etc.) with atoms and simple molecular particles.²³⁴⁻²⁴¹ Table XXIII illustrates the results with the cross sections for associative ionization involving uranium and thorium, from Refs. 237, 238, and 241. Here the beam of uranium or thorium atoms is characterized by the evaporator temperature, which was slightly above 2000 K. The oxygen molecules and atoms correspond to a temperature comparable to room temperature.

Figure 18 shows the relative cross sections for the formation of various uranium ions in the reaction $U + O_2$, plotted as a function of the kinetic energy of the uranium atoms.²³⁹

As the collision energy is increased, the probability for the formation of simple ions naturally increases. The dissociation energy of the molecular ion UO^+ is about 8 eV. This value can be taken as a typical value of the kinetic energy of the colliding particles—a value separating the region of preferential formation of the molecular ion from the region of preferential formation of the atomic ion. The possible formation of electronically excited atomic particles shifts this boundary to a higher energy.

Figure 19 shows the energy distribution of the elec-

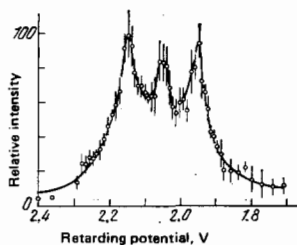


FIG. 19. Energy spectrum of the electrons freed in the associative ionization $U + O_2 \rightarrow UO_2^+ + e$. The data are shown here in terms of the retarding potential; the electron energy distribution can be found from these data.

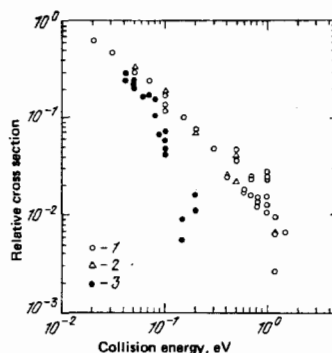


FIG. 20. Cross section for associative ionization in a collision of a metastable helium atom with a nitrogen or oxygen atom.²⁴⁴ 1— $He^* + N \rightarrow HeN^+ + e$. The nitrogen atoms in the beam are formed in the charge exchange of N^+ in krypton; 2—the same process, but the nitrogen atoms are produced in the charge exchange of N^+ with xenon atoms; 3— $He^* + O \rightarrow HeO^+ + e$.

trons freed in the reaction $U + O_2 \rightarrow UO_2^+ + e$ for low collision energies.²⁴² The zero on the electron energy scale corresponds to a cutoff potential of about 2 V. The electron spectrum thus consists of three peaks, which correspond to different vibrational states of the UO_2^+ ion, which are separated by 0.08 eV (Ref. 243). We see that this process results in the appearance of primarily slow electrons, with an energy small in comparison with the heat of the reaction, 4.1 eV. It follows that the molecular ion is formed in an excited state.

It is more difficult to use the beam method to measure the cross section for associative ionization when excited particles are involved. In this case the approach taken is to make use of the fact that the collision of unexcited particles does not result in ionization. A beam of atoms contains some atoms which are in an excited state, and these excited atoms are alone responsible for the ionization. This approach makes it possible to determine the relative cross sections: the dependence of the cross sections on the collision velocity and the probability that the reaction will go by a given path. There are serious difficulties in determining the absolute cross sections in this approach, and the results are usually afflicted by large errors.

The beam method for measuring the cross sections for associative ionization involving excited atoms is widely used in studying reactions involving metastable atoms of an inert gas (Sec. 2). Figure 20 illustrates the situation with the dependence of the cross sections for the reactions



on the collision energy. The helium atom is in a metastable state and is formed through charge exchange of helium ions with appropriate targets.

A similar method can be used to study reactions involving other metastable atoms. For example, experiments²⁴⁵ on the reaction



show that this reaction occurs most efficiently when the nitrogen atom is in the 2D state and the oxygen atom is

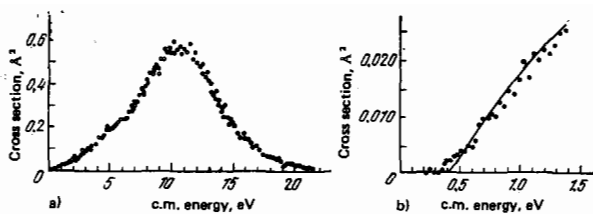


FIG. 21. Cross section for the process, a: $N(^2D) + O(^3P) \rightarrow NO^+ + e$; b: Threshold behavior of the cross section. Solid curve—Equation (36).

in the 3P ground state. In beams of these atoms produced by charge exchange of ions with arbitrary targets a certain fraction of the atoms are in these states. It is thus possible to study the characteristics of this process, which can be written most specifically in the form

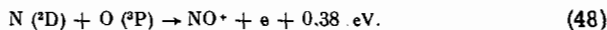


Figure 21 shows the cross section for this process as a function of the collision energy.²⁴⁵

Methods are currently being developed to excite atoms in beams with a tunable laser. This approach raises new possibilities for using beam methods to measure associative-ionization cross sections when these processes involve resonantly excited atoms. In particular, measurements of this type have been carried out²¹² for the reaction $2Na(^3P) \rightarrow Na_2^+ + e$, and further development of this direction can be expected.⁷

CONCLUSION

Detailed and fundamentally new information on ionization processes at thermal collision energies of the atoms has been obtained in recent years. Interestingly, the primary stimulus for the progress in this field came not from applications but from the development of sophisticated experimental apparatus which has proved quite successful in these problems. The experimental results have contributed to the appearance of models for the processes and to corresponding theoretical developments. The experimental tools for studying these processes presently include spectroscopy of decaying plasmas, beam methods for studying particle collisions, Penning electron spectroscopy, methods for selectively exciting atomic particles, including laser-spectroscopy methods, and mass-spectrometry methods. Refinements of these experimental methods and combinations of the different methods will lead to further progress in this field.

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