

STUDIES OF SHORT-RANGE INTERMOLECULAR FORCES

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This review presents the fundamentals of the method of determining the short-range interaction potentials of atoms and molecules by means of scattering of beams of fast particles. Original results obtained in recent years from studying more than 50 different systems are presented. The obtained potentials are analyzed and compared with independent semiempirical and theoretical calculations. The outlook for future studies is discussed.

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1. INTRODUCTION

IN principle, the properties of gases and liquids (which are the fundamental objects of macrophysics and the major working substances in technology) can be described quantitatively by studying the motion of the electrons and nuclei that constitute their atoms. In line with the evident inconvenience of such a detailed description, one uses cruder characteristics, but these permit one to exclude effectively from consideration the electronic structure of the material.

One of these convenient characteristics is the intermolecular forces, or intermolecular-interaction potentials of the particles. Introducing these characteristics permits one to separate the theoretical treatment of different macroproperties, and the atomic processes that govern them in gases, into two relatively independent parts: determining the forces themselves, and studying the statistical effect of pair collisions. Considerable progress has been made currently in the statistical part of the problem. Thus, quantitative study of the intermolecular forces provides a completed basis for determining various macroscopic properties of gases, and partially, of liquids.^[1]

In the broad sense, intermolecular and interatomic interaction forces are divided into two classes: short- and long-range forces. Long-range forces are manifested at distances of approach at which the electron clouds for the interacting atomic systems show no appreciable overlap, whereas the latter is specifically responsible for interaction at short distances.

The absence of overlap at great distances, and hence also the lack of any appreciable perturbation of the electron clouds, permits one relatively easily to calculate the corresponding forces from the atomic properties of the isolated systems. The literature currently contains considerable experimental and theoretical material on the long-range forces.^[2]

This simplifying circumstance does not exist for the short-range forces, which are the main topic of the treatment below. Hence the theoretical results obtained here are more limited, and the proportion of experimental data correspondingly greater. While digressing from discussing the methods and results of theoretical determination of the potentials of intermolecular forces, I shall first briefly examine the main fields of application of the information on these forces in gases. Then I shall treat the fundamental theoretical and technical aspects of determining intermolecular forces from data on scattering of molecular beams, and I shall summarize and discuss the results of studying the potentials of atom-atom, atom-molecular, and intermolecular interactions. In concluding, I shall try to mark the path of further development of studies of the short-range intermolecular forces.

2. USES OF DATA ON INTERMOLECULAR FORCES IN GASES

a) The first and most abundant source of information on intermolecular forces has involved analyzing changes in the thermodynamic and kinetic properties of gases. This is because people have been able to approach the solution of the inverse problem on the basis of statistical mechanics, i.e., to determine the forces from data on the cited properties.^[1] However, since the theory has not provided a way of deriving an explicit expression for the potential as a function of these properties, people usually have represented the potential by models in the form of functions that are convenient for mathematical operations, and which contain two or more parameters. The numerical values of the parameters of such a model potential are found by comparison of calculated and measured values, e.g., of the viscosity.

However, this procedure, which has been widely applied in analyzing low-temperature data, gives informa-

tion limited to the temperature range covered in the measurements. The upper limit corresponds to a temperature $\sim 1000^\circ\text{K}$, while the obtained information involves mainly the long-range forces. Since the role played by these forces declines with increasing temperature, while that of the short-range forces increases, extrapolation of the obtained potentials beyond the appropriate limits will lead to very large errors.^[3]

Development of the most recent technique has advanced the problem of determining the macroscopic properties of different gases at temperatures considerably greater than 1000°K . When one has independent information on the intermolecular forces in a distance range that is characteristic of the conditions at such high temperatures, one can determine the needed quantities by calculation alone, and avoid insurmountable difficulties of measuring them directly. This is exactly how they found in^[4] and recently in^[5] the transport coefficients of very hot air under the conditions behind the front of a shock wave arising during motion at ultra- and hypersonic velocities. One can calculate analogously also the characteristics of gas mixtures corresponding to planetary atmospheres.

In order to describe dynamic processes in the upper layers of the atmospheres of Earth and the planets, one also needs data on the kinetic properties (viscosity, diffusion, and heat conductivity) of the corresponding gas mixtures. Photodissociation by solar ultraviolet irradiation causes the steady-state composition of these mixtures to be far from thermal equilibrium, even at moderate temperatures ($\lesssim 1000^\circ\text{K}$). Direct measurement of the stated properties of such gas mixtures seems simply impossible, whereas the existence of data on the intermolecular forces opens a simple way to determine them.^[6]

b) The problem of energy exchange between the translational and internal degrees of freedom of molecules is attracting the attention of a large set of investigators. In the Fifties, this interest arose from the development of aerodynamics at ultrasonic velocities,^[7] and in recent years, the invention of gas-molecular and chemical lasers and upper-atmosphere studies have created a new stimulus to studying processes of shock excitation and deactivation of vibrations.^[8] Vibrational relaxation processes have a substantial effect on the rates of unimolecular decompositions and recombination reactions.

In the theory of vibrational relaxation, information on intermolecular interaction has proved to be the key to quantitative solution of the dynamic problem of shock excitation, and hence, study of these forces is of considerable interest.

c) The fundamental problem of the quantum-mechanical calculations is to establish the relation of the energy of a system of interacting atoms to their mutual arrangement. Development of the calculational technique has led to a considerable extension of the so-called *a priori* calculations of interaction energies of diatomic and more complex systems.^[2] As a rule, the final results for many-electron systems are obtained by approximations, and one cannot always estimate their effect on these calculations. Then, comparison of calculations with experimental determinations of interatomic forces can permit one to refine the calculations, and to

reject approximations that lead to appreciable discrepancies. Existence of information on the potential-energy surface is a prerequisite for quantitative theoretical treatment of the elementary process of atomic rearrangement or chemical transformation.^[9] The theory of scattering for a multidimensional potential has not yet been developed far enough to permit solving the inverse problem. However, use of a computer permits one to test the adequacy of a theoretical prediction of the potential surface by comparing the cross-sections for inelastic (see, e.g.^[10]) and elastic^[11,13] scattering as measured and calculated for this surface. Moreover, use of a computer allows one to find the parameters of the potential-energy surface that correspond to the additive approximation.^[12]

d) One of the interesting applications of intermolecular-potential data involves the vigorous development in recent years of the so-called hot-atom chemistry, i.e., studies of chemical reactions at energies substantially above thermal energies. There had been practically no information until recently on the behavior of the excitation functions (reaction cross sections) in the region beyond the reaction threshold.^[13]

Use of fragments from nuclear reactions (e.g., $^3\text{He}(n, p)\text{T}$), with subsequent deceleration of the fast T atoms by an inert moderator, or of "hot" photolysis products (e.g., $\text{HI} + h\nu \rightarrow \text{H} + \text{I}$) permits one to study reactions at energies $E \gtrsim 1 \text{ eV}$. Determination of the non-equilibrium energy distribution function for these particles involves calculating the energy losses in elastic collisions, information on the interaction potential can also be used directly in a stochastic analysis of the experimental data on the yield of products.^[14,15]

e) Data on the so-called crossings of potential curves are of considerable interest in physical (and chemical) kinetics. As we know, these crossings create channels for various inelastic processes in atomic collisions.^[9,16] The difficulty of predicting these crossings theoretically and the opportunity of experimentally observing scattering features associated with them opens up one of the most interesting applications of studies of intermolecular forces.

In closing the discussion of some of the applications of data on intermolecular forces that show the importance of studying them, I should comment on the goal of the experimental program of determining the potentials. Naturally, this program cannot be limited to getting numerical values, but must be directed toward establishing the relation between the interaction potentials at short and intermediate distances and the atomic characteristics of the interacting systems.

3. FUNDAMENTAL CLASSICAL AND QUANTUM RELATIONS OF THE THEORY OF ELASTIC SCATTERING

a) Expressions for elastic-scattering cross sections. In studying scattering experimentally, one usually finds either the attenuation of intensity ΔI of the beam, or the flux $I(\alpha)$ into a detector deviating from the beam axis by the angle α .

Interpreting the measured quantities in terms of differential cross sections $\sigma(\theta)$, and correspondingly, in terms of interaction potentials $V(r)$, requires that we

establish the relationships between them. Let us consider this problem, and restrict the treatment here to small scattering angles ($\theta \ll 1$, $V(r) \ll E$). In this treatment, I propose not to discuss the scattering theory in detail,^[17-19] but only to give a summary of the formulas that are useful for experimenters.

The angular distribution of particles scattered from a beam incident on a scatterer is customarily described by the differential scattering cross-section $\sigma(\theta, E)$. The latter is defined^[17] by the condition that the number of particles dN scattered in the angular range from θ to $\theta + d\theta$ for a beam of flux density J_0 is $dN(\theta) = 2\pi J_0 \sigma(\theta, E) \sin \theta d\theta$.

In scattering experiments we are dealing with the flux collected by the detector. For the idealized geometry of an infinitely narrow beam and a concentric detector (an aperture or annular slit), the flux of particles collected by the detector can be written, respectively, in the form

$$I_0 - I(\theta_{\max}) = \Delta I(\theta_{\max}) = I_0 \left\{ 1 - \exp \left[-2\pi n L \int_{\theta_{\max}}^{\pi} \sigma(\theta, E) \sin \theta d\theta \right] \right\},$$

$$I(\theta_{\min}, \theta_{\max}) = I_0 \exp \left[-2\pi n L \int_{\theta_{\min}}^{\theta_{\max}} \sigma(\theta, E) \sin \theta d\theta \right];$$

here θ_{\min} and θ_{\max} are the minimum and maximum deflection angles of particles that reach the detector, and I_0 is the intensity of the beam, which is passing through a homogeneous target of density n and length L .

The quantity Q_{trunc} that enters into the expression for $\Delta I(\theta_{\max})$:

$$Q_{\text{trunc}} = 2\pi \int_{\theta_{\max}}^{\pi} \sigma(\theta, E) \sin \theta d\theta,$$

characterizes the cross section for loss of particles from the beam, and is sometimes called the truncated "total" cross section. For the total cross section, which characterizes the total flux of scattered particles, $\theta_{\max} \rightarrow 0$.

In the classical treatment, the number of particles deflected by an angle in the range from θ to $\theta + d\theta$ equals the number of particles intersecting an annular cross section near the (spherically-symmetric) scatterer contained between circles of radii b and $b - db$ (b is the impact parameter). Thus we arrive at the relation

$$\sigma(\theta, E) = (b/\sin \theta) |db/d\theta|, \quad (1)$$

where we take the absolute value of the derivative because $\sigma(\theta, E)$ is always positive in sense. Correspondingly, the total cross section in the classical approximation is defined by the expression

$$Q = 2\pi \int_0^{\infty} b db.$$

This expression diverges for real potentials; as we know, one can eliminate the divergence of the total and the differential cross sections in the quantum treatment.

One must use the quantum relations if the classical treatment proves to be insufficiently justified (for the experiments described below, this can happen, e.g., in scattering of H atoms by the light targets He and H₂).^[18] The differential cross section (the square of the modulus of the scattering amplitude) can be found from the

well-known quantum expression:

$$\sigma(\theta, E) = (4k^2)^{-1} \left\{ \left[\sum_l (2l+1) (2 \sin^2 \delta_l) P_l(\cos \theta) \right]^2 + \left[\sum_l (2l+1) \sin 2\delta_l P_l(\cos \theta) \right]^2 \right\}.$$

In the quasiclassical approximation and for the small-angle scattering ($\theta \ll 1$) to be treated hereinafter, this expression is convenient for calculations. This is because now $l = kb$, where k is the wave vector of relative motion ($k = (2\mu E/\hbar^2)^{1/2}$), $\delta_l = \delta(b)$ is the phase shift, whose value can be found for a known (or postulated) interaction potential, and $P_l = P(b, \theta)$ is the asymptotic expression of the highest-order Legendre polynomials:

$$P_l = J_0(kb\theta) \quad \text{for } \theta \leq (kb)^{-1},$$

$$P_l = (0.5\pi kb \sin \theta)^{-1/2} [\sin \varphi - (8kb)^{-1} (\text{ctg } \theta \cos \varphi + 2 \sin \varphi)],$$

$$\varphi = kb\theta + (\pi/4) \quad \text{for } \theta \gg (kb)^{-1}.$$

The discussed relations can be used directly for calculating $\sigma(\theta, E)$ on a computer.

The problem of determining the regions of applicability of the classical and quantum descriptions of scattering has been discussed widely in the literature.^[19,20] An expression was derived in^[20] on the basis of the well-known Massey criterion for the critical angle θ_c at which, strictly speaking, one should replace the classical by the quantum treatment. For a power-function potential $V = K/r^s$:

$$\theta_c = (\pi \hbar^2 / 2\mu)^{s/(2s-2)} [KC(s)]^{-1/(s-1)} E^{-(s-2)/(2s-2)},$$

$$C(s) = \pi^{1/2} \Gamma((s+1)/2) \Gamma(s/2).$$

However, it turns out in practice that the differences between the trends of the quantum and classical differential cross sections are small for monotonic potentials, even at angles below θ_c , in particular for a system of the H-H₂ type. We see this in Fig. 1, which shows the values of θ_c and the limiting angles (dotted line) used in calculating the classical truncated "total" integral cross section \bar{Q} . This difference is relatively small at angles $\theta \geq \theta_c/2\pi$ (i.e., to the right of the intersection with the dotted line). Hence we can conclude that using the classical relations in the angular range $\theta \geq \theta_c/2\pi$ when analyzing the measured integral cross sections leads to insignificant errors as compared with the rigorous quantum-mechanical description.

b) Calculation of the differential cross section from a known potential and solution of the inverse problem. As I shall show in the next section, the measurable quantities ΔI and $I(\alpha)$ are directly related to the differential cross section. Hence, analysis of an experiment

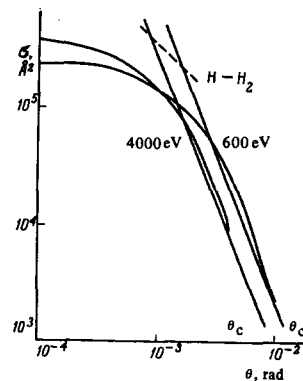


FIG. 1. Differential scattering cross section as calculated by the classical and quantum formulas for interaction of atoms having masses of 1 and 2 atomic-weight units.

poses the problem of calculating the cross section $\sigma(\theta)$ from the potential function $V(r)$. In turn, one must invert the experimental determinations of $\sigma(\theta)$, i.e., find from them the potential functions $V(r)$.

As we see from Eq. (1), one must resort to a deflection function $\theta(b, E)$ in the classical approximation for finding $\sigma(\theta, E)$. When $V \ll E$, the scattering angle θ (which is equal to the ratio of the transverse Δp_{\perp} and longitudinal p_{\parallel} momenta) is related to the impact parameter b by^[17]

$$\theta = \Delta p_{\perp}/p_{\parallel} = -bE^{-1} \int_b^{\infty} (dV/dr)(r^2 - b^2)^{-1/2} dr = -bE^{-1} \mathcal{P}(b). \quad (2)$$

One can find an explicit $\theta(b)$ relation only for a $V(r)$ of a particular type. In particular, for $V = K/r^S$, and $V = A \exp(-\lambda r)$, respectively,

$$\mathcal{P}_S = (K/b^{S+1}) \pi^{1/2} \Gamma((S+1)/2) / \Gamma(S/2), \quad \mathcal{P}_{\lambda} = A \lambda K_0(\lambda b),$$

where $\Gamma(s)$ is the gamma function of Euler, and K_0 is the zero-order modified Bessel function.

According to^[21], one can find the relation between θ and b for a potential of arbitrary type by transforming in (2) from integration to summation of the rapidly convergent series:

$$\theta E = -(\pi/m) \sum_{j=1}^{j=m/2} r_j (dV/dr)|_{r=r_j}, \quad r_j = b/\cos\{[(2j-1)/2m]\pi\}. \quad (3)$$

For real potentials, this summation gives accurate values with a number of terms in the series $m/2 \leq 15$. It can easily be calculated, even on a low-power computer.

In the quantum description of scattering, one of the problems consists in calculating the phase shifts. Simple analytical expressions for the phases exist in the quasiclassical approximation for power-function and exponential potentials;^[18] for a potential of arbitrary type, using the results of^[21], we can write

$$\delta(b) = -(k\pi/2mbE) \sum_{j=1}^{j=m/2} r_j^2 V(r_j), \quad r_j = b/\cos\{[(2j-1)/2m]\pi\}.$$

This relation permits one relatively easily to calculate the $\delta(b)$ relation, and then to use it in a tabulated or analytical form to find $\sigma(\theta, E)$.

Firsov^[22] has solved the problem of reconstructing the interatomic potential $V(r)$ from the experimental $\sigma(\theta, E)$ relation for monotonic $V(r)$ within the framework of classical mechanics. According to the results of^[22], one can determine $V(r)$ by the expression

$$V(r) = E \{1 - [\exp(\Phi(r/\pi))]^{-2}\}, \quad (4)$$

where

$$\Phi(r) = \int_{b_0}^{\infty} \frac{\theta(b) db}{(b^2 - b_0^2)^{1/2}}, \quad r = b_0 \left(1 - \frac{V(r)}{E}\right)^{-1/2},$$

and $\theta(b)$ is the classical deflection function.

Thus, if we know $\sigma(\theta, E)$, determining $V(r)$ reduces to the simple computational operation of finding $\theta(b)$ from the relation

$$b \theta = \left[2 \int_0^{\pi} \sigma(\varphi) \sin \varphi d\varphi\right]^{1/2}$$

and then taking the integral in (4) for different values of b_0 . Newton^[23] has derived a convenient expression for numerical calculations of $V(r)$ from a known $\sigma(\theta, E)$.

The range of distances over which one determines the interaction potential is unambiguously associated with the angular interval that one studies. Since it is difficult to determine $\sigma(\theta, E)$ in the angular range $\theta \leq 10^{-3}$, one can extend the range by merging with the results of determining $V(r)$ from measurements of the integral cross sections $\bar{Q}(E)$. When the classical description is inapplicable, the problem of finding $V(r)$ from $\sigma(\theta, E)$ also has a solution,^[23,24] but I shall not consider it here.

c) Scattering in the case of non-central interaction forces. In the discussion above, we have operated with cross sections and interaction potentials of spherically-symmetric systems. This approximation, which is well justified for the interaction potentials of atomic systems, must be made more precise in going over to treating atomic-molecular and intermolecular interactions.

Two fundamental approaches to describing the anisotropic interaction of molecular systems are known. They are, first, the one-center representation of a non-spherical potential as a series expansion in the spherically-symmetric components $V_l(R)$:

$$V(R, \gamma) = \sum_l V_l(R) P_l(\cos \gamma) = V_0(R) \sum_{l=1}^N [1 + \beta_l P_l(\cos \gamma)]; \quad (5)$$

Here R is the distance between the centers of gravity of the interacting particles. γ is the angle of relative orientation, $P_l(\cos \gamma)$ is the Legendre polynomial of order l , and β_l is an asphericity parameter. The other, many-centered representation is based on the so-called system of additive interatomic potentials, in which the interaction of the molecules AB and CD, for example, is written as follows:

$$V(R) = V(r_{AC}) + V(r_{BC}) + V(r_{AD}) + V(r_{BD}),$$

where R is the distance between the centers of gravity of the molecules, and r is the interatomic distance.

The interaction potential of the two molecules $\bar{V}(R, \gamma)$ averaged over the equally-probable orientations determines the effective spherically-symmetric potential that corresponds to a point force center. Analytic expressions^[25,26] are known for the additive system for the cases of inverse-power and exponential interatomic potentials. Furthermore, one can usually choose parameters of inverse-power or exponential functions for $\bar{V}(R)$ that permit a good approximation of the cumbersome analytic expressions.

Until recently, analysis of data on scattering by atomic-molecular systems was exclusively based on using isotropic potentials. That is, it corresponded to the approximation of point centers of repulsion (the PCR approximation). The fundamental defect of the PCR approximation, which was noted already in^[26], is that one correlates the measured cross section $\bar{Q}(E)$ averaged over the orientation with the cross section calculated for the averaged potential $\bar{V}(R)$.

For a known nonspherical potential $V(R, \gamma)$, the averaged total cross section can be described by the expression

$$\bar{Q}(E) = 2\pi \int_{(\gamma)} \int_{(\theta)} \sigma(\theta, \gamma, E) d \cos \gamma d \cos \theta. \quad (6)$$

Since theoretical calculations of a nonspherical potential of the type of $V(R, \gamma)$ are known only for individ-

ual systems, analysis of experiments involving measurement of total or differential cross sections of molecular scattering has proved possible only within the framework of using an additive-potential system. As will be shown below, one can actually avoid the PCR approximation on this basis by going over to an adequate treatment of the averaged cross sections. An additional attractive feature of this approach involves the possibility of decreasing the number of parameters of the potential, and effectively eliminating the indeterminate asphericity parameter β_l .

Within the bounds of validity of classical mechanics (we shall restrict ourselves here to precisely this case), in order to calculate $\sigma(\theta)$ according to Eq. (1) for a fixed E , one must find the deflection function $\theta(b) = \theta(b, \varphi_n, \chi_n)$. Here φ_n and χ_n ($n = 1, 2$) describe the orientations of the interacting molecules.

In describing the orientations of the colliding particles, it is convenient to use the xy plane of the coordinate system, with the z axis along the vector of the relative velocity v . The position of an axially symmetric molecule is determined with respect to this plane (for real conditions of experiment with fast beams, the orientations of the interacting molecules are frozen) by the two angles φ and χ (by three angles in the general case). Figure 2 shows, as it were, an instantaneous photograph of one of the possible relative orientations. Owing to the small scattering angles and the large relative velocities v of approach, this fixed orientation exists throughout the time of interaction of the molecules at the impact distance b as reckoned between the centers of gravity of the molecules.

For small scattering angles, the projections of the molecules AB and CD on the xy plane (see Fig. 2) permit one easily to relate* the distances of closest approach between the atoms A, B and C, D (the interatomic impact parameters in Fig. 2) to the angles φ_n and χ_n , the bond length r_{en} , and the intermolecular impact parameter b .

Assuming additive interatomic potentials is equivalent to assuming that the total transverse momentum Δp_{\perp} that determines the deflection angle is equal to the sum of momenta imparted during the interaction process on the (almost) rectilinear trajectory of each of the atoms. From Eq. (2) and the obvious expression (see Fig. 2)

$$\Delta p_{\perp} = k\Delta p_x + l\Delta p_y, \quad b_{ij} = kx_{ij} + ly_{ij}$$

we can derive the following expression for the total transverse momentum:

$$\Delta p_{\perp} = (2/v) (k \sum x_{ij} \mathcal{F}_{ij} + l \sum y_{ij} \mathcal{F}_{ij}),$$

$$\Delta p_{\perp} = (2/v) [(\sum x_{ij} \mathcal{F}_{ij})^2 + (\sum y_{ij} \mathcal{F}_{ij})^2]^{1/2} = (2/v) \Phi(b),$$

where

$$\Phi(b) = \sum b_{ij}^2 \mathcal{F}_{ij} + \sum_{\substack{i,j \\ i \neq j}} x_{ij} x_{i'j'} \mathcal{F}_{ij} \mathcal{F}_{i'j'} + y_{ij} y_{i'j'} \mathcal{F}_{ij} \mathcal{F}_{i'j'} \quad (1/2);$$

Here k and l are unit vectors that correspond to the x and y directions, \mathcal{F}_{ij} is defined by Eq. (2), with b_{ij} set as the lower limit.

The sought deflection function for elastic scattering of the molecules is found from

$$\theta(b, \varphi_n, \chi_n) = \Delta p_{\perp} / p_{\parallel} = \Delta p_{\perp} / \mu v = \Phi(b, \varphi_n, \chi_n) / E. \quad (7)$$

*B. M. Smirnov proposed the idea of treatment presented herein after.

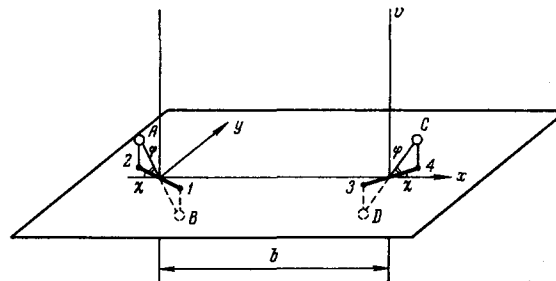


FIG. 2. Schematic diagram of the pattern of scattering at small angles, and the fundamental collision parameters of diatomic molecules.

When one has assigned the form of the interatomic potentials, Eq. (7) permits one to find the deflection function, and from it to find the differential cross section $\sigma(\theta, \varphi_n, \chi_n)$ for fixed orientations. Upon averaging $\sigma(\theta, \varphi_n, \chi_n)$ one can arrive at an expression for the cross section $\bar{\sigma}(\theta, E)$ that corresponds to the measured differential scattering cross section.

I have assumed in deriving Eq. (7) that the atoms in the molecules do not interact, and thus the collision did not excite molecular degrees of freedom (vibrations and rotations). In the next approximation, one can take account of the small (in the sense of a correction to Δp_{\perp}) effect of excitation. However, one must take into account the intramolecular forces to do this.

One can use a method analogous to the one for finding the deflection function $\theta(b, \varphi_n, \chi_n)$ described above for calculating the phase function $\delta(b, \varphi_n, \chi_n)$ and the quantum differential cross section for scattering in a many-centered force field.

4. EXPERIMENTAL STUDY OF INTERMOLECULAR INTERACTION

a) The method of elastic scattering of fast neutral beams. The elastic-scattering method has an advantageous position over other methods of determining intermolecular forces. This involves the fact that it contrasts with other methods in that one can directly determine the scattering probability (or cross-section) at a given angle, and unambiguously interpret these measurements in terms of interaction potentials.

One can use several variants of the elastic-scattering method: one can measure the total cross sections $Q(E)$, or the integral cross sections $\bar{Q}(E)$, or the differential cross sections. The choice of any particular variant is dictated on the one hand by the studied energy range, and on the other hand by the potentialities and convenience of technical performance of the experiment.

Usually when one uses fast beams, the scattering cross section is found from the attenuation ΔI of the beam intensity I_0 in a target of known density n and length l by using the expression

$$\Delta I = I_0 [1 - \exp(-n\bar{Q}l)] \approx I_0 n \bar{Q} l,$$

Here $\bar{Q}(E)$ is the (integral) cross section for loss of particles from the beam. In measuring differential cross sections, one usually determines the flux of particles $I(\alpha)$ arriving at a detector set at an angle α to the axis of the beam. The relation of $\bar{Q}(E)$ and $I(\alpha)$ to $\sigma(\theta)$ will be discussed below.

In a crude approximation, the interaction energy V at

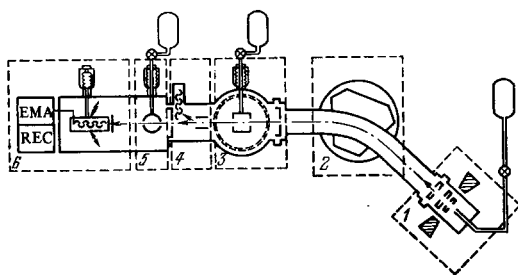


FIG. 3. Diagram of an apparatus to study scattering of fast beams of neutral atoms and molecules.

the point of closest approach r_0 , the energy E_{lab} of the impinging particle, and its deflection angle θ_{lab} ($\theta_{lab} < 30^\circ$) are connected by the simple relation $V(r_0) \approx E_{lab} \theta_{lab}$. One can conveniently use this relation to characterize experimental conditions (as we know, $E_{lab} \theta_{lab} = \theta E$).

Molecular-beam technique on the current level does not possess simple means of creating neutral particle beams that are homogeneous in energy in the range 1–10 eV. Hence, using beams of higher energies involves decreasing the absolute values of the deflection angles to be measured. Thus, for the practically convenient energy range $E_{lab} \sim 10^3$ eV, study of intermolecular forces in the range $V \sim 1$ eV implies that one must measure scattering at angles of $\theta_{lab} \sim 10^{-3}$ radians.

Amdur (see [27]) performed the first experiments to study scattering at such small angles. Thus far, several instruments have been built and described [27–29] for studying scattering of fast neutral beams.

The apparatus of [28] shows the greatest universality from the standpoint of choice of objects of study and methods. Figure 3 shows a diagram of it (EMA: electrometric amplifier; REC: recorder; the functions of sections 1–6 will be described below). The only way of getting monokinetic neutral beams of high energy ($E \geq 10^2$ eV) at acceptable intensity is charge transfer of accelerated ions. If the source must permit getting beams of any atomic particles whatever, then naturally mass selection must precede the charge transfer. Resonance or almost-resonance charge transfer of mass-selected ions makes it possible to convert an ion beam into a neutral beam with practically no perturbation of the initial trajectories and energies of the particles. These ideas are the basis of design of the apparatus shown in Fig. 3:

1) Electron-bombardment ion source that permits variation over a broad range of both the energy and the current of the ionizing electrons. The beam being formed is ribbon-shaped.

2) Magnetic (120°) analyzer for selection of ions of the beam over the mass interval from 1 to 400 atomic-weight units at energies from several hundred eV to 4–5 keV.

3) Charge-transfer section using gas or vapor (alkali-metal) targets.

4) Section containing the deflecting capacitor and monitor to control constancy of the beam flux.

After charge transfer and removal from the mixed beam of ions by using a parallel-plate deflecting capacitor, the neutral beam is collimated by a narrow slit.

The resonance defect (as defined by the energy difference of the terms of the system $A^+ - B$ and $A - B^+$ at infinity) can decrease strongly as the particles approach. However, in contrast to resonance charge transfer, the charge transfer realized here will be accompanied by an appreciable deflection of the particles. Collimation of the neutral beam makes it possible to eliminate the contribution from charge transfer involving an undesired amount of resonance defect.

5) Section containing the scattering target, with an ionization gauge for measuring the pressure in the target and an automatic supply system. The target is set on a movable stage for adjustment of its position. In order to increase the accuracy of relative measurements of cross sections, a special valve is used to supply gas to the target. It periodically switches the gas supply, either to the scattering chamber, or into the working volume. This method makes it possible to take account automatically of scattering by the background, and by using the high stability of delivery through the valve, it avoids constant recording of the pressures in the target. One can then determine the absolute values of the measured cross sections only in special, separate calibration measurements.

6) Section containing the detector and recording system. The detector used is an open secondary-electron multiplier set on a movable platform. Along with measuring the profile of the incident beam, it permits one to measure fluxes of particles scattered in the range up to 10° (in the laboratory system), i.e., differential scattering cross sections. The lower energy limit of measurement and the upper angular limit of deflection are mainly determined by the sensitivity of the secondary-electron multiplier. The major opportunity for sharply increasing the sensitivity involves use of a channel multiplier as the detector. The measuring system includes an electrometric amplifier whose output is connected to a digital voltmeter. The latter is used for (amplitude-frequency) conversion of the signal, with subsequent measurement of the amplitude with a scaler (PP-09M).

The automation of measurements attainable with this system makes possible a considerably greater speed with heightened accuracy. As a whole, the described apparatus makes possible:

1) obtaining well-collimated beams of neutral particles (and ions) of fixed mass and energy ($j^0 \sim 10^{-11}$ A-cm $^{-2}$, $j^+ \sim 10^{-10}$ A-cm $^{-2}$);

2) varying the energy of the particles in the beam over the range $3 \times 10^{-2} - 5 \times 10^3$ eV;

3) reliable measurement of the angular distribution and attenuation of the scattered beam, with exact measurement of the density of the scattering gas directly in the target;

4) obtaining beams of metastable atoms of the noble gases and molecules (N_2 , etc.) with a controllable admixture of the ground state by using special charge-transfer targets.

b) The problem of interpreting the measured quantities. The directly measured beam attenuation $\Delta I(E)$ and the angular distribution $I(\alpha)$ of the scattered particles can be transformed into $\sigma(\theta)$ (and from $\sigma(\theta)$ into $V(r)$) only under ideal geometric conditions in which one can neglect the finite dimensions of the detector, the scattering target, and the beam cross section, and corre-

spondingly, the fact that one is collecting a spectrum of scattering angles. Usually the conditions are such that the detector cannot isolate from the scattered flux only those particles deflected by angles from θ to $\theta + d\theta$. An actual detector collects particles scattered over a finite range of angles, and here the efficiency of collection (actual solid angle) is a function of the deflection angle. This feature of the detector is manifested both in measurements of attenuation (loss from the beam), and also in measurements of the angular distribution of the scattered flux. Hence the problem arises of determining $\sigma(\theta, E)$ from the measured quantities $\Delta I(E)$ or $I(\alpha)$.

A natural connection between the quantities $\sigma(\theta)$, $\Delta I(E)$, and $I(\alpha)$ is a characteristic such as the efficiency of collection of the scattered particles. This is because $\sigma(\theta)$ characterizes the total number of scattered particles, while ΔI and $I(\alpha)$ are respectively the measured fraction of particles lost from the beam and the fraction of scattered particles entering the detector.

One can conveniently describe the efficiency of the detector with the function $\eta(\theta, l)$ introduced by Kusch.^[30] It determines the probability normalized to unity that a particle scattered by the angle θ at a point removed from the detector by the distance l will enter the detector (in the laboratory system, when $\theta \ll 1$, the deflection angle θ_{lab} is directly proportional to θ). On the other hand, $1 - \eta$ gives the probability of loss from the beam. In its physical meaning, $\eta = N_d(\theta)/N(\theta)$ is the ratio of the number of particles scattered by the angle θ and entering the detector to the total number of particles scattered by the same angle.

We shall examine a method of determining the function $\eta(\theta, l)$, while mentioning another approach to analyzing the measurements that was developed by Amdur's studies, and which has been described in detail in^[27]. In this approach, the measured quantity $\bar{Q}(E)$ is correlated with the cross-sections $\langle \bar{Q} \rangle$ averaged over the angle, as caused by a finite thickness of the target, the area of the detector, and the shape of the intensity distribution over the cross section of the beam. In averaging, one assumes that the relation of \bar{Q} to the angle θ has a quite definite form (that corresponds to an interaction potential having an inverse-power function dependence on the distance). This permits one to perform the integration in closed form. These calculations have been performed for a beam and detector both of round^[27] and of rectangular^[31] cross section.

In terms of detector efficiency, these calculations actually correspond to defining some aperture angle θ_a for which the efficiency $1 - \eta$ of the detector is taken to be unity when $\theta_{lab} \leq \theta_a$, while it is zero when $\theta_{lab} \geq \theta_a$. The integral cross sections $\bar{Q}(E)$ to be measured are replaced by cross-sections truncated at θ_a . A defect of this approach is its limitation to the case of inverse-power potentials and the introduction of rather artificial limits of applicability of the obtained potential parameters K and s .

For measurements of angular distributions of scattered particles, Filippenko^[32] has given an analysis and method of accounting for errors that arise in interpreting the measurements in terms of differential cross sections. However, this author restricted the treatment to the case of small and equal heights of the beam and the detector slit. Hence, the obtained results are in-

applicable to ribbon-shaped beams.

If we use the detector efficiency $\eta(\theta)$ introduced above, then we can achieve a more adequate approach to analyzing the measurements.^[33,34] In contrast to^[27,32], one can account for geometric factors in this method, quite independently of the nature of the interaction.

One can easily express the attenuation ΔI , or flux of particles that miss a detector coaxial with the beam, and the flux $I(\alpha)$ into a detector shifted from the axis of the beam by the angle α , in terms of the differential cross section $\sigma(\theta, E)$ and the detection efficiency $\eta(\theta)$. In the notation of^[37], these expressions have the form

$$\Delta I = 2\pi n I_0 \int_0^\pi \sigma(\theta, E) \sin \theta d\theta \int_{l_0+\Delta l}^{l_0-\Delta l} A(l) [1 - \eta_0(\theta, l)] dl,$$

$$I(\alpha) = 2\pi n I_0 \int_0^\pi \sigma(\theta, E) \sin \theta d\theta \int_{l_0+\Delta l}^{l_0-\Delta l} A(l) \eta_\alpha(\theta, l) dl.$$

If we introduce the function

$$f_{0,\alpha} = \int_{\Delta l} A(l) \eta_{0,\alpha}(\theta, l) dl / \int_{\Delta l} A(l) dl,$$

called the apparatus function, we arrive at the following convenient relations connecting the measured quantities with the sought cross section $\sigma(\theta, E)$:

$$\bar{Q}(E) = 2\pi \int_0^\pi \sigma(\theta, E) [1 - f_0(\theta)] \sin \theta d\theta, \quad (8)$$

$$I(\alpha) = B \int_0^\pi \sigma(\theta, E) f_\alpha(\theta) \sin \theta d\theta, \quad (9)$$

Here B is a numerical coefficient that contains experimentally measured quantities ($n, \Delta l, I_0$, etc.).

The functions $f_{0,\alpha}$ have been calculated^[33,34] on a computer for a number of the possible combinations of detector widths, beam profiles, and round and rectangular geometries.

Figure 4 shows the results of calculating f_0 , from which we see that the apparatus function depends rather strongly on the deflection angle, and it can be only crudely approximated by a step function corresponding to the aperture angle θ_a that had been used in^[27,31]. (ρ is the dimensionless deflection angle.^[34] The notations on the curves of the universal relationships correspond to different types of intensity distributions (see^[34]). Use of the functions f_0 and f_α and Eqs. (8) and (9) allows one to convert the measured quantities $\Delta I(\bar{Q}(E))$ and $I(\alpha)$, and to get the $\sigma(\theta, E)$ relationship. Also, if one compares the measured and calculated

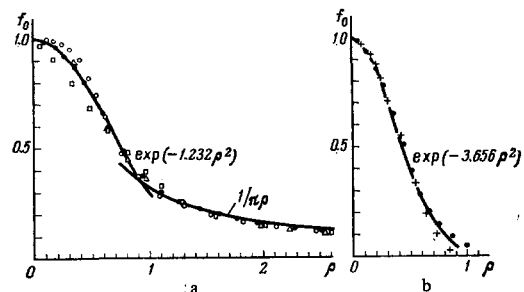


FIG. 4. Apparatus functions $f_0(\rho)$ describing the efficiency of detection of particles scattered at a given reduced angle ρ for a detector of rectangular (a) and round (b) geometry.

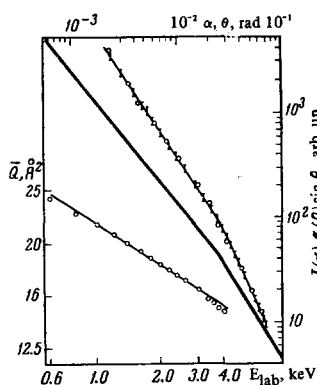


FIG. 5. An example of fitting values of $\bar{Q}(E)$ and $I(\alpha)$ as calculated by Eqs. (9) and (10) (circles) and measured (fine lines) for the N_2-N_2 system upon using the apparatus functions f_0 and f_a , the interatomic-potential parameters from Table V (p. 53), and the differential cross section $\sigma(\theta)$, which is shown by the heavy line.

values of ΔI and $I(\alpha)$, one can find the parameters of a potential of any presumed type. Thus, for non-central molecular interaction potentials, one can express Eq. (8), using (7), in the form (e.g., for diatomic molecules):

$$\bar{Q}(E) = 2\pi \int_{(b)} db \iint_{(\varphi)} d^2\varphi \iint_{(\chi)} b(\theta, E, \varphi_n, \chi_n) |1 - f_0(\theta)|^2 d^2 \cos \chi. \quad (10)$$

If we assume a potential of the type $V = A \exp(-\lambda r)$ for the interatomic interactions, then by using a Monte Carlo procedure we can calculate $\bar{Q}(E)$ for fixed values of A and λ . Thus, the true values of A and λ have been determined by fitting measured and calculated $\bar{Q}(E)$ relations. The fivefold integral in (10) (fivefold in the case of diatomic molecules, and sevenfold in the general case) was calculated with the BÉSM-4 computer with a statistical accuracy of 1–3%. Here the number of calculated trajectories was as great as 10^4 . Figure 5 shows a typical example of the agreement of calculated and measured $\bar{Q}(E)$ and $I(\alpha)$ relationships for the N_2-N_2 system.

We note that the calculated $\bar{Q}(E)$ relationships for a choice of monotonic interatomic potentials prove always to be monotonic, and practically linear when $\ln \bar{Q}$ is plotted against $\ln E$. Hence, in principle, experimentally observed non-monotonic $\bar{Q}(E)$ relations (showing a break) should correspond to non-monotonic interatomic potentials. Figure 5 also shows an example of conversion of the measured angular distribution $I(\alpha)$ for the same N_2-N_2 system, and its result is the differential cross-section $\sigma(\theta, E)$ shown in the same diagram. The experimental $\sigma(\theta, E)$ relation can be used to determine

the parameters of the anisotropic potential. In order to do this, one can, by varying the parameters A and λ , compare the measured values of $\sigma(\theta, E)$ with the calculated values by the relation

$$\bar{\sigma}(\theta, E) = \iint_{(\varphi)} d^2\varphi \iint_{(\chi)} (\Delta b^2 / \Delta \theta^2) d^2 \cos \chi;$$

Here the integrand arises from Eq. (1), $\Delta \theta^2 = (\theta_1^2 - \theta_2^2)$ is determined by the size of the fixed interval $\Delta b = b_1 - b_2$, and $b(\theta, \varphi_n, \chi_n)$ can be calculated by Eq. (7).

5. FUNDAMENTAL RESULTS OF STUDYING INTERMOLECULAR FORCES

a) Interaction of noble-gas atoms. Studies of the interaction of noble-gas atoms seems to be the simplest, both from the methodological standpoint and from that of interpreting the measurements. It was precisely for these systems that the first data were obtained in the fifties; the purely repulsive interaction of the atoms permitted Amdur to make a reliable interpretation of the obtained $\bar{Q}(E)$ relations in terms of a potential of the type $V = K/r^s$.

We also began our experimental program of studies with the noble gases, since comparison permitted us to estimate the reproducibility of the independently obtained data. Table I^[35,36] summarizes the obtained parameters K and s for a potential $V = K/r^s$ and A and λ for a potential $V = A \exp(-\lambda r)$ for atoms of the noble gases. Comparison of the energies calculated by the parameters of Table I with the values from the experimental study^[27] and the calculations^[37,38] shows close agreement for practically all systems. The agreement of independent experimental determinations of $V(r)$ performed in apparatus having substantially different geometries is convincing evidence of the reliability of the data obtained by the method of scattering of fast beams.

In the treatment of the first measurements on the noble gases, which was carried out by calculating the effective aperture by the method of^[27], the assumption was made that an inverse-power potential with constant parameters K and s is valid over the range of approach distances corresponding to the entire set of deflection angles in the detector. We can expect the potential to change in slope over the experimentally-realized broad

Table I

System	K, eV-Å ^s	s	Δr, Å	System	K, eV-Å ^s	s	Δr, Å
He-He	2.8	3.9	0.87-1.23	He-Kr	45.3	5.52	2.67-2.04
He-He	4.33	5.86	0.79-1.35	He-Xe	35.2	5.2	1.73-2.2
Ne-Ne	78	7.65	1.7-2.18	Ne-Ar	99.5	6.58	1.93-2.49
Ar-Ar	171	6.06	2.27-3.12	Ne-Kr	437	7.65	2.25-2.52
Kr-Kr	1382.5	7.7	2.4-3.02	Ne-Xe	210	6.76	2-2.56
Xe-Xe	463	6.35	2.48-3.09	Ar-Kr	855	6.92	2.4-3.1
He-Ne	10.3	5.61	1.3-1.65	Ar-Xe	292	5.9	2.48-3.27
He-Ar	22.6	5.15	1.63-2.06	Kr-Xe	875	7.1	2.44-3

System	A, keV	λ, Å ⁻¹	Δr, Å	System	A, keV	λ, Å ⁻¹	Δr, Å
He-He	{ 0.542	7.05	0.20-0.35	Kr-Kr	{ 4.8	3.49	1.0-2.25
	{ 0.212	4.30	0.35-1.50		{ 0.67	2.6	2.2-3.0
Ne-Ne	{ 4.55	4.51	0.60-1.35	Xe-Xe	{ 7.15	3.46	1.2-1.8
	{ 440	6.20	1.35-1.80		{ 1.64	2.64	2.8-3.3
Ar-Ar	{ 2.54	3.56	0.8-2.3				

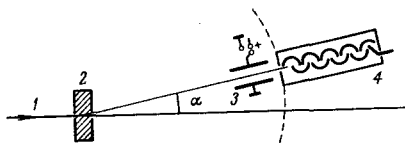


FIG. 6. Diagram of the measurement of the angular distributions of scattered particles.

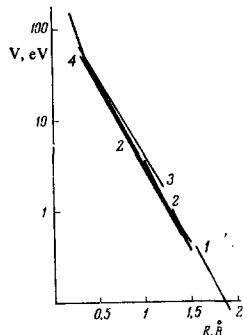


FIG. 7. Comparison of the theoretical and experimental determinations of the interaction potential of He atoms.

range of approach distances, i.e., the exponent s will not be constant. We^[40] undertook a series of measurements of the angular distribution $I(\alpha)$ of the flux of scattered particles in order to test the correctness of the assumptions that the parameters K and s are constant, and to eliminate the discrepancy between Amdur's measurements for the He-He system and the theoretical calculations.^[39] Figure 6 shows a diagram of these measurements (Here 1 is the fast-particle beam, 2 is the target, 3 is a deflecting condenser to remove particles that have changed their charge state upon scattering,^[40] and 4 is the detector.) The $\sigma(\theta)$ relationships reconstructed from the measured $I(\alpha)$ by using the apparatus function show that the exponent remains constant (the $\sigma(\theta)$ relationship is linear on a log-log plot) over a limited range of angles (and correspondingly also a limited range of impact parameters). This fact emphasizes that one must apply the inverse-power dependence very cautiously. By using O. B. Firsov's method, one can find $V(r)$ from a known $\sigma(\theta)$; Table I also gives the parameters A and λ obtained for an exponential approximation $V = A \exp(-\lambda r)$ and their regions of applicability. Figure 7 shows for comparison the potential curves of the He-He system obtained from measurements of $I(\alpha)$ and $\bar{Q}(E)$,^[35,40,42] together with the theoretically calculated curves^[38,39] (the heavy line corresponds to the parameters A and λ of Table I; 1 is from^[41], 2 from^[42], 3 from^[39], and 4 from^[38]). As we see, these results agree well. Besides, Fig. 7 shows the agreement of the experimentally found and calculated values of V for $r < 0.5 \text{ \AA}$. The above-mentioned discrepancy for He was explained by a false interpretation of the earlier measurements, and it has been eliminated in a recent study.^[42] The information on the behavior of the potential at interaction energies $V \geq 3-5 \text{ eV}$ provides a good opportunity for testing the accuracy of the calculations based on the Thomas-Fermi-Dirac statistical theory of atoms.^[43]

Comparison shows agreement within a factor ~ 2 ; the experimental values of $V(r)$ lie below the calculated values. The calculations of Gaydaenko and Nikulin,^[38] who used a Hartree-Fock electron-density distribution

in the atoms to calculate the potential, show substantially better agreement.

For asymmetric atom pairs, the experimental data of Table I and^[27] confirm well the combination rule ($V_{ij} = (V_{ii} - V_{jj})^{1/2}$). Thus, we can consider the combination rule to be experimentally justified for the noble-gas atoms over the range of interaction energies $V \lesssim 1 \text{ eV}$. This rule has not been tested in the high-energy range; we can assume that it holds in this region also according to^[38,43].

Determination of $V(r)$ at short approach distances has recently gained in interest in connection with determining absolute excitation cross-sections of optical transitions in atomic collisions.^[44-46] In particular, energy thresholds E_{thr} of excitation have been obtained for the alkali ions (which are isoelectronic with the noble gases), and an attempt was made to interpret the mechanism of excitation, based on ideas of quasi-crossing of the terms corresponding to atoms in the excited and ground states. One can easily estimate the position of the quasi-crossing point r_c , and correspondingly determine the cross sections, from the potential curves for pairs of isoelectronic atoms of the noble gases from the condition $V(r_c) = E_{\text{thr}}$. This is just how one can determine that $r_c = 0.76$ (in contrast to the value 1 \AA found in^[44]) for the system $K^+ - \text{Ar}$ (which is identical to $\text{Ar} - \text{Ar}$) from the fact that $E_{\text{thr}} = 140 \text{ eV}$. By using the combination rule, one can construct the potential curves for the systems $K^+ (\equiv \text{Ar}) - \text{He, Ne, Kr, and Xe}$, and estimate the position of the quasi-crossing points r_c from the experimental values of E_{thr} .^[46]

b) Interaction of H, O, and F atoms with the noble gases. It has been of interest to study pairs of these atoms in connection with detecting existence of compounds of the noble gases^[46] and with the problem of translational relaxation of fast particles in an inert moderator. While in the former case study of the interactions can facilitate solution of the quantum-chemical problem of quantitative description and prediction of the properties of compounds to be synthesized, in the latter case a knowledge of the energy spectra of the particles being decelerated makes it possible to study the nature of reactions of hot atoms (i.e., those with energies above thermal).

The $\bar{Q}(E)$ relations observed for these systems are mostly monotonic,^[47-49] and they were interpreted in these studies in terms of a potential of the type $V = K/r^s$. An inaccuracy in estimating the aperture angle θ_a in^[47,48] led to a certain distortion of the values of the parameter K . Hence the results have been treated again in the exponential approximation of the interatomic potentials, with exact account made of aperture effects. Table II gives the obtained values of the parameters A and λ of a potential $V = A \exp(-\lambda r)$ for H, O, and F atoms and noble-gas atoms (the parameters for the systems involving Kr and Xe atoms were obtained from the values of \bar{Q} ,^[47-49] corrected for the more precise value of the constant of the ionization manometer).

For systems including H atoms, the question can arise whether analysis of the results on the basis of classical description is valid. A detailed analysis has been performed for the H-H₂ system and is described below. It showed that the smallness of the apparatus function in the angular range that requires a quantum

Table II

System	A, eV	λ , \AA^{-1}	System	A, eV	λ , \AA^{-1}
H—He	87	3.59	O—Kr	14450	5.20
H—Ne	239	4.22	O—Xe	204	3.6
H—Ar	980	4.53	F—He	630	4.91
H—Kr	870	4.31	F—Ne	2720	5.18
H—Xe	3260	4.63	F—Ar	9780	4.82
O—He	1200	5.28	F—Kr	12400	5.23
O—Ne	925	4.25	F—Xe	27200	5.38
O—Ar	2940	4.23			

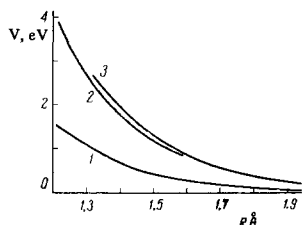


FIG. 8. Comparison of the result of experimental (1) and theoretical (2 and 3) determinations of the interaction potential for the system F—He (2 is from [38], 3 is from [50]).

description strongly suppresses errors involved with using classical mechanics. Although, strictly speaking, one should have gotten correct values of A and λ by using the quantum dependence of the differential cross section, the calculations for the H—H₂ system support the idea that the actual errors of determining $V(r)$ in the region ≤ 1 eV are such that the corresponding deviations from the true values are apparently no greater than $\sim 20\%$. These ideas in particular and the cumbersome calculation by the quantum formulas have compelled us thus far to restrict the treatment to the stated accuracy.

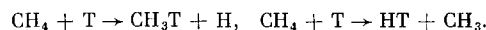
As I have said, systems containing O and F atoms are of interest in connection with the problem of quantum-chemical prediction of the properties of noble-gas compounds.^[46] The calculations of $V(r)$ performed for the systems O—He, Ne, and F—He, Ne (and H—He)^[50] can be compared with the experimental determinations. Such a comparison (Fig. 8) shows poor agreement, and it can serve to indicate the necessity of using more precise approximations in the quantum-chemical calculations. The calculations of Gaydaenko and Nikulin^[38] also show poor agreement: the calculated values of $V(r)$ are systematically higher than the experimental values. We note that the disagreement with the calculations, e.g., in^[51], for the H—He system can be partially due to using the classical description of scattering, and it can be easily eliminated.

The features in the scattering of O and F atoms by Kr and Xe found in the measurements of^[47] (breaks in the $\bar{Q}(E)$ plot) may be of interest from the standpoint of explaining bond formation in the corresponding systems. Although one can draw better-grounded conclusions only from thorough study of the differential cross sections, however, the possibility was noted already in^[47] of explaining these anomalies by the influence of a bound-state term. We have used^[48] data for systems including hydrogen atoms to calculate the size of Δ (the mean logarithmic energy loss), which is used in the kinetic theory of hot-atom reactions. The calculations corresponded to the case of deceleration of tritium (T) atoms (which are equivalent in their electron cloud to H atoms) in different noble gases. One cannot determine the ab-

solute value of Δ directly from the data from studying hot-atom reactions, but only its ratio for different moderators. Comparison of the ratios calculated from our data and the values from^[52] showed that they agree poorly. Apparently this involves the crudity of the approximations of the kinetic theory^[13] of hot-atom reactions. It seems promising to use information on the potentials for computer simulation of passage of fast particles through a reagent-inert moderator mixture. This approach, which uses the Monte Carlo technique, was developed in^[14]. A form of the excitation function of the reaction was assumed:

$$S_{\text{chem}} = S_0 [1 - (E_{\text{thr}}/E)]^p \exp(-\beta/E) \quad (11)$$

($S_0 = \pi b_{\text{chem}}^2$, b_{chem} is the "chemical radius," E_{thr} is the threshold energy, and p and β are parameters that determine the form of dependence of S_{chem} on the energy). With this assumption, the method permitted them to select the values of β and p that give the best agreement of calculated and measured yields of products of the reactions:



Recently obtained results^[14,15] confirm the great potentialities of this approach, which is based on stochastic calculation of the results of collisions in different (elastic and inelastic) channels, for quantitatively describing reactions that occur at superthermal energies.

The data of Table II show that the values of the parameter λ in the successive series of noble-gas atoms do not usually fit the commonly-made assumption that they are directly proportional to the ionization potential.^[53] According to this assumption, λ should have declined in going from He to Xe, but a decline is not observed (Table II).

c) Interaction of noble-gas atoms with molecules. Study of interaction of noble-gas atoms and molecules makes it possible to extend considerably the set of systems under study (including a new factor; spatial anisotropy of the potential), while avoiding complications involved with chemical interaction. The systems He—H₂,^[36] Ar—N₂, O₂,^[54] He—CH₄,^[55] and all combinations of noble-gas atoms with the molecules CO₂^[56] and N₂O^[57] have been studied.

If we consider the structure of the molecules, treatment of the measured relations in terms of a spherically-symmetric potential seems to be a very rough approximation, although it has been used in^[36,54,55]. In this regard, the results for a number of systems have been interpreted afresh. Within the framework of an additive-potential system, this permitted using the above-described method to find the parameters A and λ

Table III

System	A, keV	λ , Å ⁻¹	\bar{A} , keV	$\bar{\lambda}$, Å ⁻¹	System	A, keV	λ , Å ⁻¹	\bar{A} , keV	$\bar{\lambda}$, Å ⁻¹
He-H ₂	0.098	3.65	0.21	3.54	Ne-N ₂ O	0.84	3.93	5.68	3.63
He-CH ₄	0.41	4.82	6.12	4.40	Ar-CO ₂	7.88	4.63	122	4.42
Ar-O ₂	4.07	4.25	14.18	4.17	Ar-N ₂ O	1.47	3.7	11.4	3.53
Ar-N ₂	1.09	3.51	28.76	3.46	Kr-CO ₂	14.4	4.72	269	4.55
He-CO ₂	0.3	3.87	1.41	3.42	Kr-N ₂ O	2.58	3.78	22.5	3.63
He-N ₂ O	0.12	3.19	0.55	2.98	Xe-CO ₂	46.2	5.0	1058	4.82
Ne-CO ₂	2.31	4.63	32.6	4.38	Xe-N ₂ O	6.8	4.02	68.33	3.85

of the interatomic potentials. Table III summarizes the values of the parameters A and λ of the interatomic potentials obtained in this way (the interval of applicability of these values is 0.1–10 eV). Table III also includes the values \bar{A} and $\bar{\lambda}$ of the parameters of the exponential relation $\bar{V}(R) = \bar{A} \exp(-\bar{\lambda}R)$ that approximates the total potential averaged over the orientation: $\bar{V}(R) = \bar{\Sigma} V(r_{ij})$.

It is interesting to note here that the values of the potential energy given by \bar{V} are about twice as large as those obtained by measuring $\bar{Q}(E)$ in the PCR approximation. Hence, we cannot consider the PCR model to be justified for systems of the discussed structure. Such discrepancies indicate the error in the method proposed in^[28] of determining the interatomic potentials by subdividing the effective spherical potentials (e.g., for the N₂-Ar system) into the "atomic" contributions $V(\langle N \rangle - Ar)$. Use of the reduced "atomic" contributions, followed by the combination operations ($V(\langle N \rangle - Ar)$ and $V(Ar - Ar)$), for example, and averaging will lead to underestimating the intermolecular $V(N_2 - N_2)$ potentials.

We should note that underestimating with respect to the true values can be manifested only when the combination rule of interatomic potentials is valid, as was simply postulated in^[25]. However, it will be shown below that this rule is false in the general case of intermolecular interaction. In line with this, the agreement found in a recent study^[58] between the combined potentials and our direct determinations^[6] apparently arises from compensation of errors. There is another indication against this use of an additive system for semi-empirical construction of the intermolecular potentials.^[55] As was shown in^[55], direct combination of the potentials $V(He - CH_4)$ and $V(He - He)$ that correspond to structureless repulsion centers gave considerably better agreement for $V(CH_4 - CH_4)$ than using an additive system and combining the interaction potentials of the atoms $\langle H \rangle$ and He.

For linear molecules, the potential-energy surface obtained from the additive-interaction system can be described by an expression like (5). Only the even terms will exist in the expansion of (5) for homonuclear molecules, and the values of the corresponding parameters can be easily chosen numerically. Here one can effectively overcome the difficulty of determining the asphericity parameter β_1 . Such a compact representation of the potential-energy surface (hereinafter abbreviated PES) will be convenient for use in calculations, e.g., of excitation of internal degrees of freedom.

The studies^[59,60] give values of the parameters A_0 , λ_0 , and β_1 for the PES of the He-H₂ system that were obtained by quantum-mechanical calculation of the energy of this system. It is interesting to note that the potential^[59] averaged over the orientation is described

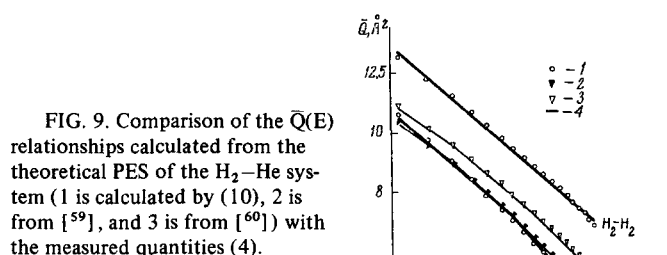


FIG. 9. Comparison of the $\bar{Q}(E)$ relationships calculated from the theoretical PES of the H₂-He system (1 is calculated by (10), 2 is from^[59], and 3 is from^[60]) with the measured quantities (4).

by an exponential function having parameter values $\bar{A} = 220$ eV, $\bar{\lambda} = 3.53$ Å⁻¹ that practically coincide with those in Table III. If one uses Eq. (6) and includes the function $f_0(\theta)$ in it, one can calculate the measured cross-sections and compare the theoretical and experimental $\bar{Q}(E)$ relationships. Figure 9 compares the experimental $\bar{Q}(E)$ relation (heavy line, while the circles are the calculated relationship with the parameters A and λ of Table III) and that calculated for the PES of^[59,60]. This comparison indicates rather clearly that the PES of^[59] is preferable to that of^[60]. Figure 9 also shows examples of comparison of measured $\bar{Q}(E)$ relations (heavy lines) with those calculated (1) with the parameters A and λ of Tables IV and V.

The data included in Table III for noble gas-CO₂ or N₂O systems permit us to judge on possible correlation with atomic properties of the values of the potential parameters (chiefly λ). The idea is widespread, but strictly valid only for interaction at relatively great distances, that λ is directly proportional to the ionization potential of the interacting atoms. Thus, as one goes in the noble-gas series from light to heavy, λ should correspondingly decline (see, e.g.^[61]). The data of Table III indicate the opposite trend. This fact renders problematical the establishment of simple correlations of this type. Apparently, further expansion of the set of studied systems will be required in order to reveal them. It is interesting here also to note that the values of the parameters A and λ are not the same for the isoelectronic molecules CO₂ and N₂O. I shall give below analogous data on some other isoelectronic molecules (N₂ and CO). Thus, we cannot consider the isoelectronicity approximation, which is convenient in practice, to be valid for short-range intermolecular forces. The data of Table III present a good opportunity for testing the predictions of the theory of collisional excitation of molecular degrees of freedom, and correspondingly, of calculating the relaxation characteristics of various gas mixtures. The interaction model used in the different theories is the additive-potential model.^[7] Hence, the reliable parameter values for them make it possible

Table IV

System	A, keV	$\lambda, \text{\AA}^{-1}$	\bar{A}, keV	$\bar{\lambda}, \text{\AA}^{-1}$	System	A, keV	$\lambda, \text{\AA}^{-1}$	\bar{A}, keV	$\bar{\lambda}, \text{\AA}^{-1}$
O-H ₂	0.087	3.64	0.186	3.56	N-N ₂	0.25	3.4	0.62	3.31
O-N ₂	2.88	5.23	11.35	5.12	N-CO	0.6	3.81	1.57	3.72
O-O ₂	2.56	5	10.25	4.85	N-NO	1.74	4.35	5.33	4.21
O-CO	0.87	4.06	1.22	3.56	N-CH ₄	0.25	4.2	3.7	3.95
O-NO	1.1	4.06	3.14	3.95	H-O ₂	0.33	4.73	1.24	4.6
O-CO ₂	1	4.06	7	3.89	H-N ₂	0.54	4.62	1.74	4.52
N-O ₂	1.17	4.25	3.87	4.13					

Table V

System	A, keV	$\lambda, \text{\AA}^{-1}$	\bar{A}, keV	$\bar{\lambda}, \text{\AA}^{-1}$	System	A, keV	$\lambda, \text{\AA}^{-1}$	\bar{A}, keV	$\bar{\lambda}, \text{\AA}^{-1}$
H ₂ -H ₂	0.059	3.37	0.246	3.22	O ₂ -CO ₂	0.49	3.58	8.72	3.33
N ₂ -N ₂	0.367	3.27	2.29	3.16	NO-NO	0.33	3.4	2.16	3.26
N ₂ -O ₂	0.245	3.16	1.43	3.02	NO-CO	0.57	3.63	4.28	3.49
N ₂ -CO	0.9	3.79	7.06	3.66	CO-CO	0.65	3.6	4.74	3.47
N ₂ -NO	0.73	3.78	5.78	3.64	CO-CO ₂	0.897	3.81	19.2	3.55
N ₂ -CO ₂	1.17	4.06	30	3.78	CO ₂ -CO ₂	1.09	3.96	44.9	3.43
N ₂ -N ₂ O	0.44	3.5	6.77	3.25	N ₂ O-N ₂ O	0.407	3.54	10.76	3.07
O ₂ -O ₂	0.15	3.0	0.82	2.85	CH ₄ -CH ₄ [†]	—	—	23.9	4.35
O ₂ -CO	0.41	3.27	2.7	3.15	NH ₃ -NH ₃ [†]	—	—	0.12	2.65
O ₂ -NO	0.83	3.94	7.62	3.78					

to ascribe the reason for discrepancies between calculated and measured cross sections (probabilities) of translational-vibrational transitions or relaxation times to defective approximations used in the theory. Detailed calculations have been made in^[62] of vibrational relaxation times over a broad temperature range for the mixture O₂-Ar. They used in the calculations the potential "splitting" of^[54], which corresponds to point centers, while the value that they used for the parameter A (A = 32,250 eV) differed appreciably from that given in Table III. We might expect that repetition of these calculations with new data will make it possible to draw more reliable conclusions on the validity of the classical description of translation-vibration transitions, and correspondingly, to extend the practical applications of the computational programs.

d) Interaction of H, N, and O atoms with molecules.

In the group of systems to be discussed here, we shall find it necessary to take account of the possible manifestation of "chemical interaction." One of the stimuli to studying systems involving H, N, and O atoms and the molecules H₂, N₂, O₂,^[63] CO, NO,^[64] CO₂, N₂O, and CH₄^[57,65] has been the need of getting data for calculating the kinetic properties of dissociated gas mixtures. The possibility of studying manifestation of chemical interaction at approach distances of the order of the characteristic bond lengths in molecules also provides a strong stimulus for studying such systems.

For a large number of the systems listed above, the measured $\bar{Q}(E)$ relations show an anomalous behavior as compared with the trend for the systems discussed above. Figures 10 and 11 show these relations for the systems H-CH₄, O-N₂, O-CH₄, H-H₂, etc. (in Fig. 11, the three curves correspond to measurements with detectors of different widths). Table IV gives values of the parameters of the interatomic (A, λ) and averaged (\bar{A} , $\bar{\lambda}$) atomic-molecular interaction potentials for several of the studied systems.

Roughly speaking, the anomaly in the $\bar{Q}(E)$ relations is manifested in breaks that are so pronounced that they cannot be fitted by monotonic interatomic interaction potentials. Moreover, for breaks like that occurring in

FIG. 10. Typical examples of anomalous experimental $\bar{Q}(E)$ relationships (showing breaks).

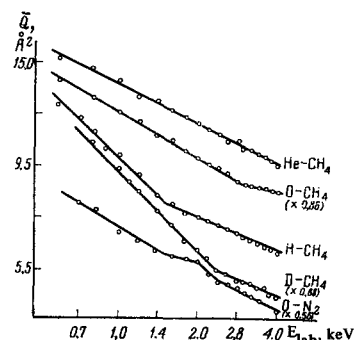
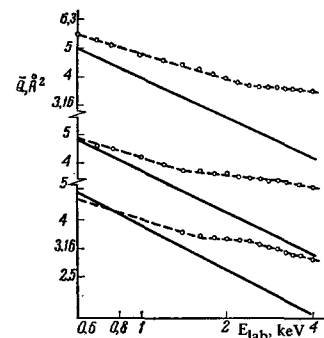


FIG. 11. Comparison of the $\bar{Q}(E)$ relationships calculated for the theoretical PES^[66] of the H-H₂ system with the measured values (circles).



the H-CH₄ system, the $\bar{Q}(E)$ relation cannot at all be described by any reasonable combination of repulsion potentials. One can illustrate these qualitative ideas by using the results of^[11] for the H-H₂ system. The H-H₂ system as a classical object of theoretical chemical kinetics has been subjected to the most detailed analysis, and rather reliable theoretical determinations of the potential energy surface exist for it (see the bibliography in the article^[67]). Tang and Karplus^[66] have given one of the most exact representations of the PES, which was used for studying the dynamics of the reaction of isotopic substitution.^[10] The adiabatic PES (in the sense of an invariant equilibrium distance in H₂) has the following form according to^[66]:

$$V(R, \gamma) = V_0(R) + V_2(R) P_2(\cos \gamma) + V_4(R) P_4(\cos \gamma)$$

It can be used for calculating the variation in \bar{Q} measured in^[63].

As I mentioned above, if we know $V(R)$, we can calculate the differential scattering cross sections by classical or quantum mechanics. The classical description is quite natural for scattering of heavy atoms, but we must either justify it for the H-H₂ system or use the quantum relations. The use of classical mechanics in^[11], which made it possible to decrease the bulk of the calculations considerably, was justified as follows. For the two extreme energy values ($E_{\text{lim}} = 600$ and 4000 eV), Fig. 1 shows the course $\sigma_{\text{cl}}(\theta)$ of the classical (straight lines) and $\sigma_{\text{qu}}(\theta)$ of the quantum differential cross-sections as calculated for the potential $V = K/r^s$ ($K = 1.12$ eV, $s = 3.7$), which approximates the course of the PES in the low-energy region.^[66] We see from Fig. 1 that the transition boundary from the classical to the quantum relationship is diffuse, since the differences between σ_{cl} and σ_{qu} are small even at angles below θ_c . In this situation, if we take account of the cutoff action of the apparatus function ($f_0 \rightarrow 1$ when $\theta \ll 10^{-3}$; Fig. 4), we can calculate $\bar{Q}(E)$ by the formula for the truncated integral cross-section (with $\theta_{\text{min}} = \theta_c/2\pi$). The dotted line indicates the values of the cutoff angles in Fig. 1. Control calculations of the integral cross-sections using σ_{qu} showed that the difference between \bar{Q}_{trunc} and \bar{Q}_{qu} $< 5\%$, and it is invariant in sign ($\bar{Q}_{\text{qu}} > \bar{Q}_{\text{trunc}}$). These results are a well-known justification for using the classical description of scattering, and they guarantee correct fitting of the $\bar{Q}(E)$ relation for the chosen potential. Since the PES from^[66] is characterized by an angular dependence, a relation like (6) was used to calculate $\bar{Q}(E)$.

Figure 11 compares the $\bar{Q}(E)$ relationships calculated for three detectors with the measured values. We see that their unsatisfactory agreement is manifested not only in the discrepancy of the absolute values of $\bar{Q}(E)$, but also (as is more important) in irreproducibility of the characteristic breaks in the measured $\bar{Q}(E)$ relationships. We can explain the discrepancy between the calculated and measured relations in two ways. First, an additional scattering channel (inelastic) not accounted for in the calculation might be manifested; second, we might expect that the PES from^[66] is not accurate enough.

We tried in^[11] to take phenomenological account of the effect of an additional inelastic channel. We can assume here that the most probable inelastic process is a substitution reaction that occurs when the partners approach to some characteristic distance. Owing to the large relative velocity and the smallness of the impulse imparted to the atoms of the molecule, this point evidently involves a virtual reaction that forms a new bond only for a time of the order of the time of flight. From the standpoint of interaction, occurrence of a virtual reaction implies that the fast atom on the departing branch of the trajectory will undergo attraction instead of repulsion. However, the attempt in^[11] to take account of the possibility that a certain fraction of the scattered atoms will have "composite" trajectories did not permit us to improve the agreement with the experimental data. As it seems to us a subsequent, more

rigorous analysis (rejecting a purely classical description of scattering for this system) will make it possible to solve the contradiction that has arisen. We also cannot rule out the possibility of making the refinement used in the calculations of the PES in^[66]. We note that it will be more indicative to compare not the integral $\bar{Q}(E)$ values, but the differential scattering cross-sections $\sigma(\theta, E)$.

Qualitatively analogous anomalies in the $\bar{Q}(E)$ relation have been found for the systems D, H, O-CH₄ (see Fig. 10). Of interest are the difference in $\bar{Q}(E)$ values and the shift in the breakpoint in the $\bar{Q}(E)$ relation for D-CH₄ as compared with H-CH₄.

Along with the features of the discussed type, the measurements showed also breaks "directed" in the opposite sense. Typical examples here might be the $\bar{Q}(E)$ relations for O-CO and O-N₂.^[64] It is an important circumstance that the calculation of $\bar{Q}(E)$ for such systems based on a system of summing interatomic repulsions does not permit full agreement with the measured relationships (the data of Table IV correspond to approximate agreement). Hence, it is quite justified to expect that these cases also possess a chemical channel that perturbs the elastic scattering. In comparing the measured and calculated $\bar{Q}(E)$ relationships, the parameters A and λ were taken from the curves. This ensured fitting with a smoothed course (with respect to the breaks). Hence, apart from the systems (N-N₂, N-O₂, and O-H₂) (Table IV), the statistical accuracy of calculating $\bar{Q}(E)$ was assumed to be 3%, instead of the usual 1%.

The features found in the course of the $\bar{Q}(E)$ relationship for chemically active systems and the impossibility of explaining them on the basis of a potential surface of purely repulsive type gives us grounds for assuming that use of the technique of fast-beam scattering opens up perspectives of empirically finding potential energy surfaces describing chemical reactions. Naturally, the most reliable information will be obtained in measurements of differential cross-sections.

If we use the representation of the PES of a reaction adopted in quantum chemistry (see, e.g., the book^[9]) in the form of a combination of attractive and repulsive pair potentials, we can solve the inverse problem of determining the corresponding parameters from scattering data.

Thus, if we adopt a trend of the interatomic potentials that is reasonable from the standpoint of existing information (spectroscopic, kinetic, etc.), it seems quite attainable by using Eqs. (3), (7), and (11) to fit measured and calculated differential cross sections by varying the parameters of the potentials. The empirical surface thus obtained will correspond to a "frozen" value of the bond length r_e in the molecule, i.e., it will describe only the entrance valley in the PES of the reaction. However, we can expect that this is a quite sufficient basis for constructing purely empirical surfaces that will permit us to describe very simple chemical reactions of substitution or decomposition types. Evidently, this opportunity presents one of the most attractive perspectives of applying the fast-beam scattering method.

e) Interaction of molecules. A large set of studies of interaction of molecular systems has been conducted in

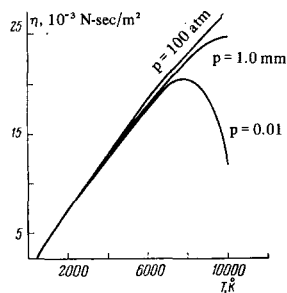


FIG. 12

FIG. 12. Viscosity of air at high temperature, as calculated from experimental data on the interaction potentials of the corresponding components of dissociated air.

FIG. 13. Comparison of the anisotropic interaction potentials of H_2 molecules (Table V) for three relative orientations of the molecules with the results of quantum-mechanical calculation. [70]

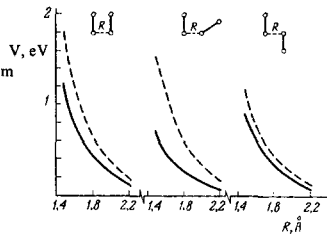


FIG. 13

connection with practical needs of calculating transport coefficients in gas mixtures such as planetary atmospheres at various temperatures. Moreover, the problem has been posed here of experimentally testing a number of models and methods of determining intermolecular forces known in the literature.^[27] Table V gives a list of systems studied in^[6,54], together with the parameters A and λ of the exponential interatomic potentials $V = A \exp(-\lambda r)$. Table V includes the parameters \bar{A} and $\bar{\lambda}$ of the overall potentials averaged over the orientation, as approximated by the exponential function $\bar{V} = \bar{A} \exp(-\bar{\lambda} R)$ (the systems marked by asterisks were treated in the PCR approximation).

For homonuclear molecules, using the additive system described above causes no difficulties, but the problem arises upon going to non-homonuclear molecules of whether the potentials for different atom pairs are identical. Existence of a single electron cloud in the molecule justifies the approximation of identical potentials, and one can rule it out only for experiments with polarized particles. At the current level of experimentation, which does not permit making such measurements, it proves to be practically the only possible way.

From the data of Table V (and Table IV), one can calculate values of the so-called reduced collision integrals $\bar{\Omega}^l, s$ (see^[1]), and correspondingly find the transport coefficients for gas mixtures containing the stated components in arbitrary concentrations over the temperature range 1000–15,000°K. Such calculations of viscosity (and heat conductivity) for air are described in^[5] and the results are given in Fig. 12. We should note that the calculations in^[5] were based on potentials corresponding to the PCR model. Hence we can expect that the data of Tables IV and V will correspond to values of $\eta(\lambda)$ that are about 10% greater than those given in Fig. 12.

The data of Tables IV and V permit one to make a quantitative test of the variant proposed in^[68] of the semiempirical method of determining interatomic and intermolecular potentials. In^[68], they used the spectroscopic information by this method, and found the parameters A and λ of the exponential interaction potential, e.g., for the O and N atoms occurring in O_2 and N_2 molecules. In particular, the values found in^[68,69] $\lambda = 2.7$ and 2.8 (for $\langle N \rangle = \langle N \rangle$), $\lambda = 3.56$ and 2.08

($\langle O \rangle - \langle O \rangle$), and $\lambda = 2.64$ and 2.56 ($\langle N \rangle - \langle O \rangle$) diverge considerably from the data obtained in the same approximation from direct measurements. In this variant of the semiempirical method, the interatomic potentials should be the same in the cases, e.g., of N– N_2 or N_2 – N_2 (or other homonuclear molecules). We see from Tables IV and V that this is not the case. Such discrepancies indicate that direct extension to intermolecular potentials of the semiempirical method that was developed for intramolecular potentials is not exact. Evidently, the defects must be eliminated in further application of this potentially useful method.

The data given in Table V make it possible to test directly the combination rule of interatomic potentials postulated in^[39]. This rule, which is expressed by the relations (i and j being the types of atoms) $V_{ij} = (V_{ii} \cdot V_{jj})^{1/2}$, $A_{ij} = (A_{ii} A_{jj})^{1/2}$, and $\lambda_{ij} = (\lambda_{ii} + \lambda_{jj})/2$, was tested with the results of studies of scattering of noble gases, and it justified itself well. It seemed that one could extrapolate it to interatomic potentials of molecules. The attractiveness of using such a rule in molecular systems involves the opportunity of substantially shortening (whenever it is valid) the experimental program of studying interaction for the practically unbounded number of pair combinations of atoms and molecules. Such a test on the large set of systems included in Tables IV and V shows that the combination rule for the parameters A and λ does not hold, apart from the N_2 – O_2 system. The exceptional nature of this system allows us to conclude that the combination rule of parameters of interatomic potentials and its use in the peripheral model of intermolecular forces^[32] cannot be considered to be justified. However, it turns out here that the values of V_{ij} themselves can be obtained by calculation using the combined parameters, since as a rule an elevated value of A_{ij} corresponds to an elevated λ_{ij} , and the errors compensate.

Apparently, the H_2 – H_2 system is the only one for which one can make reliable enough theoretical calculations of interaction energies corresponding to different relative positions of the molecules. In this sense, it is very interesting to compare the experimental data with the calculations.^[70] The comparison shows a small systematic increase in the calculated with respect to the experimental values (for a comparison for three configurations, see Fig. 13). Partially (within ~20%), we can explain this by the inadequacy of the classical treatment of scattering in this case, and on the other hand, by the approximations used in the calculations.^[70]

6. CONCLUSION

The data presented in this review, which have mainly been obtained in recent years, show pictorially the broad potentialities for detailed study of interatomic and intermolecular short-range forces using the method of elastic scattering of fast beams. Further use and development of this method can give valuable information on the nature of the variation in the interaction energy of atomic systems in a distance range that had formerly been accessible only by the methods of molecular spectroscopy. Studies of intermolecular forces for pairs that include metastable particles may be of considerable

interest. We should consider one of the promising applications of this method to be the study of collisions involving a change in the electronic (or charge) state of the particles.

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