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THE PRESENT STATE AND SOME NEW RESULTS OF THE MOLECULAR-BEAM METHOD

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1. INTRODUCTION

THE term "molecular beam" (MB) is defined to mean a spatially-localized flow of non-interacting particles in parallel flight; here we usually do not distinguish between atoms and molecules, but consider them as one.

The molecular-beam method (MBM) is based on making a beam, formed in some manner, the object of study, either directly as obtained, or after being subjected to some influence. While in the former case the particles of the beam "carry" information on the thermodynamic and physicochemical state in the region where the beam is formed, in the latter case we can get information on the reaction of the particles forming the beam to the given influence. The methods of exerting an influence on the particles of the beam can vary: irradiation by light, reflection from the surface of a solid, intersection with a perpendicular beam, passage through a magnetic field, etc.

Since in the limiting case we can detect the individual particles of the beam, obviously, the MBM can make possible an experiment at the level of the individual elementary event. However, this does not exhaust the merits of the method. In most cases in an experiment, an immediate effect unconfused by side phenomena is observed, and this considerably simplifies the interpretation of the obtained data.

A convincing illustration of the rich possibilities of the MBM is found in the far-from-complete list given below of the problems that have been or can be solved by this means.*

1. The first studies involving this method were concerned with problems of substantiating the kinetic theory of gases.

2. The method has been brilliantly applied in fundamental experiments devoted to proving the wave nature of particles.

3. The method has been very widely applied in studies concerned with precise measurements of the electric and magnetic moments of atoms and molecules, the spin and magnetic moments of nuclei, and the study of microwave spectra of molecules and atoms.

4. It has proved fruitful to apply this method to study the effective scattering cross-sections in molecular collisions. Valuable information has been obtained from these measurements on the force fields of molecules and atoms, both in the region of pure repulsion and that of pure attraction.

5. The MBM is perhaps the most suitable means of solving a set of problems involving the interaction of molecules and atoms with the surface of a solid. The importance of these studies with regard to problems of current technology is obvious.

6. The MBM, combined with mass analysis, is an effective means of getting information on the thermodynamic and physicochemical state of matter at high temperatures.

7. In concluding this list, we must mention that molecular beams can be used for analyzing a plasma, as one of the important elements of quantum amplifiers and generators (masers, lasers), and also as ion sources for injection of particles into accelerators and thermonuclear-fusion apparatus.

In practice, the decisive factor in carrying out most of the studies mentioned above is the problem of beam intensity. The more subtle the effect being studied is, the greater the intensity must be. Obviously, we can consider this in a broader sense to involve the signal-to-noise ratio.

Thus we can proceed in two ways in an experiment: on the one hand, by directly increasing the intensity of the beam, and on the other hand, by improving the detection conditions, that is, by using the obtained signal more efficiently. Both methods are equivalent in their results, but we must obviously choose the best method in each concrete case.

It would be inexpedient within the limits of this article to attempt any full description of the numerous designs and individual problems encountered in practical MB work. The original articles can serve this purpose considerably better, while here we shall emphasize only the fundamental principles of the experimental apparatus. We find an analogous situation also in examining the numerous applications of the MBM. We shall also sketch only the fundamental outlines of the applications. The discussion below will take up the methods of obtaining and detecting molecular beams, as well as a number of applications of the MBM to solve concrete problems of molecular and chemical physics. In view of the existence of [1-5], we shall naturally try as much as possible to avoid here the topics taken up in detail in these articles.

2. TECHNIQUE OF THE MBM (METHODS OF OBTAINING, DETECTION, AND VELOCITY-SELECTION OF BEAMS)

1. The "oven" method. The classical "oven" method, which was first used by Dunoyer,[6] has been brought practically to instrumental perfection by

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*A detailed bibliography of studies published up to 1955 is found in [1].

Stern.* Fig. 1a shows a diagram of an oven, or effusion source. This type of source has been applied most widely up to the very present. By this means beams have been obtained of a large number of the elements of the periodic table and of chemical compounds.[4] The merit of this MB source, which has been described in detail in many articles, [1-3] is that one can calculate the intensity of the beam when the geometry of the source is given. Its defect is that one cannot obtain high velocities and intensities in a collimated beam (i.e., one cannot obtain beams with a high current density of particles). Thus, in [8], beams of high intensity of the order of 10^{17} molecules/cm^{2}sec were obtained through a considerable increase in the pumping speed; however, here the cross-section of the beam amounted to 4 mm × 8 mm even at a distance of 4 cm from the exit aperture. Substantial improvements in oven-type sources have involved the use of separate long tubes [9] and a "packet" system, as proposed in [4]. A schematic view of such a multichannel source is shown in Fig. 2a. Also shown here (Fig. 2b) is the experimental angular intensity distribution for this source.[10]

Multichannel sources of various designs have been studied and used by a number of authors.[10-13] A detailed theoretical study of the characteristics (intensity, angular distribution diagram) of such sources has been made in [14-16], though indeed, without taking into account the mutual influence of the separate beams. In particular, Troitskiĭ [16] has developed a general method for calculating the angular distribution diagram and the beam intensity.

Obviously, for multichannel sources the limitation on the energy of the particles of the beam still holds, since the velocities of the particles are determined by the temperature, which cannot be raised greatly.

One of the successful design methods in building them is the method proposed in [11] of electrolytic etching of fine (20 μ) wires collected in a bundle in
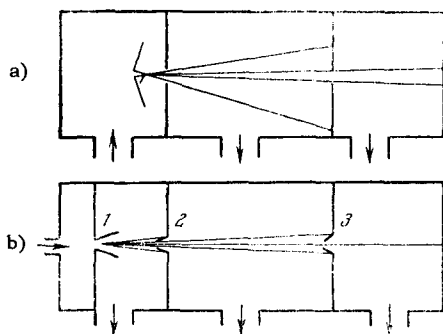

FIG. 1. Schematic diagram of sources of the oven (a) and gas-dynamic (b) types. 1—Nozzle; 2,3—conical apertures.

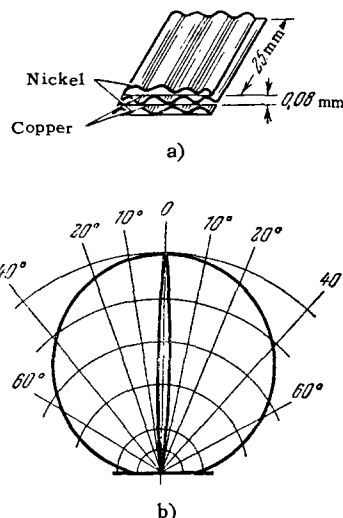*There is a detailed bibliography of Stern's fundamental studies in [7].

FIG. 2. Design of a multichannel source (a) and the angular intensity distribution obtained[19] for this source (b). The intensity diagram corresponding to an ordinary effusion source is shown around the outside.

a plastic formed by polymerization. Here one can attain channel densities up to 530 per mm^2, and "transmissions" up to 65%. The practical advantages of using multichannel sources can be illustrated by the following: in reference [10], it was possible to obtain a beam (N$_2$, H$_2$) at a distance of 40 cm from the source at a pressure of 10^{-5} mm Hg with a current density of 10^{15} molecules/cm^{2}sec, the cited pressure being maintained by a pump of speed 100 liters/sec. The use of an ordinary effusion source to attain the same results would require a pump of speed 10,000 liters/sec. We might remark that, along with their important technical application (masers), multichannel sources have a great methodological value in providing high-density gaseous targets.

2. The gas-dynamic source. This source was proposed by Kantrowitz,[17] has been intensively developed in recent years, and is finding continually wider application. [18-20] In this very ingenious method, the effusion "oven" of the classical source is replaced by a supersonic jet of low-density gas (see Fig. 1b). The stepwise expansion of such a jet results in its being transformed into a flow of molecules, or a beam. The superposition of the bulk movement leads to a narrowing of the diagram, analogous to that shown in Fig. 2b. This permits us to retain a considerably greater number of particles in the beam upon collimation, and to get an intensity gain over the classical oven source.

In the gas-dynamic source, in contrast to the classical source, the formation of the beam is effected in a region where the directional distribution of the velocity vectors differs from that in free space, owing to the superposition of the bulk movement. One should be able to express this effect analytically, and

upon performing the calculations, to compare the intensity of the gas-dynamic (I_{gd}) and effusion (I_{eff}) sources under the same conditions. As one can show, the intensity attainable by a gas-dynamic MB source is expressed as follows (with standard notation):

$$I_{gd} = I_{eff} \frac{\left(1 + \frac{\gamma}{2} M^2\right) \sqrt{\frac{\pi\gamma}{2}} M \left[1 + \mathrm{erf} \sqrt{\frac{\gamma}{2}} M + \exp\left(-\frac{\gamma}{2} M^2\right) + \frac{1}{2} \sqrt{\frac{\pi\gamma}{2}} M\right]}{\sqrt{1 + \frac{\gamma-1}{2} M^2}} .$$

The results of the calculations for different values of the Mach number M are given in Table I.

The data of this table, which are also confirmed by direct experiment, [18,19] clearly characterize the efficiency of the gas-dynamic source. In experimental practice, we can easily attain Mach numbers M within limits of 4—6. Thus the intensity of a gas-dynamic source proves to be approximately two orders of magnitude greater than for an effusion source of the same dimensions. In order to describe the source completely, we must know the nature of the distribution and the values of the velocities in the beam. We can write the distribution function by taking into account the bulk movement and the expansion of the gas jet; Fig. 3 shows the calculated distribution curves corresponding to different values of M. As we see from Fig. 3 (and as confirmed by direct measurements), the value of the most probable velocity is shifted considerably upward in the beam obtained from a gas-dynamic source. The curve M = 0 corresponds to the classical source.

Table I

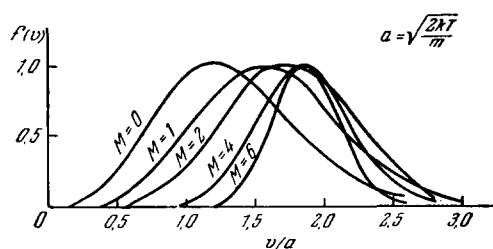| M	1	2	4	6	10
I_{gd}/I_{eff}.	4	18	70	152	475

FIG. 3. Velocity-distribution curves of the molecules for a beam produced by a gas-dynamic source for various values of the Mach number M. The curve M = 0 corresponds to an ordinary effusion source.

Thus, by using this source, without heating, we can attain an equivalent increase in the initial "temperature" of about 3—4 times. Preliminary heating can provide even greater velocities. Another peculiarity of the distribution is the appreciable narrowing (see Fig. 3) of the curve as M increases, or monokinetiza-

tion of the particles of the beam. This is of great methodological value, since it diminishes the loss of particles when mechanical selectors are used. The design of the source can be shown from Fig. 1b. A supersonic jet of rarefied gas (at supply pressure 20—50 mm Hg) is generated by the convergent-divergent nozzle 1, whose orifice diameter, determined by the pumping speed of the system, is of the order of 0.5 mm. The action of the nozzle under these conditions could hardly be in complete agreement with the calculated situation; in particular, this is indicated by the results of [21]. In the latter study, the nozzle was only convergent, while the divergent section was apparently formed by the boundary layer. As the measurements showed, no appreciable loss of intensity was observed; this result greatly simplifies the problem of preparing nozzles for gas-dynamic sources. The forming aperture 2 having the shape of a truncated cone has very sharp edges to avoid the possibility of appearance of desnity discontinuities at them. The final slit 3 has the same shape. All the chambers are independently evacuated by powerful pumps. A detailed description of the vacuum section and the design particulars of these sources can be found in [18-21]. The intensity and velocity of the beam obtainable with a gas-dynamic source can be considerably increased by using mixtures as the working gases. This effect is discussed in more detail below in the description of the separation of gas mixtures.

A sharp increase in the intensity of the obtained beam has also been found [22,23] upon using strongly cooled gases: the intensity rose by two orders of magnitude, attaining a value of 6×10^{19} molecules/ cm^2 sec for hydrogen. These results will be discussed in somewhat more detail below.

3. <u>Charge-exchange sources.</u> A widespread type of source of beams of high-velocity particles is the so-called charge-exchange source. [24-26] In this source, an ion beam obtained in some manner is subjected to charge exchange by passing it through either a neutral gas [24-26] or an electron cloud. [25] A great merit of such a source is that one can control electrically the ion beam, and hence also the neutral beam obtained after charge exchange (modulation, focusing, acceleration or deceleration).

In building a charge-exchange source, one must solve two fundamental problems, the choice of the type of ion source and the method of subjecting the ions to charge exchange. An analysis of these prob-

lems is outside the limits of our discussion. How-
ever, we shall point out one promising possibility,
as we see it, of building a simple high-intensity ion
source based on a hollow cathode, making possible
densities of the ionizing electron current up to 25
A/cm^2.[27] The designs described in [24] and [25] were
practically the first instances of achievement of
charge-exchange sources. Simonenko [25] has de-
scribed a source having an intensity about one hun-
dred times greater than that of an effusion source of
the same geometric dimensions. An interesting pe-
culiarity of this apparatus is the attempt made in it
to apply charge exchange in an electron cloud. He
was able to establish that for effective neutralization,
the density of the electron current must exceed the
density of the ion beam by approximately 1000 times,
as is quite attainable. Unfortunately, an error ap-
parently crept into this study, which was not con-
tinued. The ion-electron recombination cross-sections
turn out to be unreasonably large for the attained ef-
ficiency of charge exchange. The efficiency of charge
exchange was tested by the weakening of the ion cur-
rent at the collector; however, this weakening can
evidently arise from compensation by a current of
entrained electrons.

In [24], the beam, which was obtained by extraction
of ions from a glow-discharge region, was neutralized
in a special chamber by collisions with the gas and
the walls. A defect of both of these sources is the in-
definiteness of composition, but it can be eliminated
by introduction of a mass spectrometer between the
source and the charge-exchange chamber, as, e.g.,
in [28].

Another defect of these designs is the impossibil-
ity of directly obtaining intense monoenergetic beams
having energies in the range 1—20 eV, which would
be of great practical interest.

As we know, the space-charge effect can prevent
the obtaining of ion beams of high intensity and low
energies. Hence, an apparatus [29] designed for ob-
taining intense (10^{18} molecules/cm^2sec) molecular
beams with velocities from 10 to 30 km/sec is of
especial interest. The basic design of the apparatus
is shown in Fig. 4. The beam is formed as follows:
the supersonic nozzle 1, which feeds into a cylindri-
cal tube, generates a gas flow. During passage, it
becomes ionized by a high-frequency electrodeless
discharge (of frequency 10—150 Mc). Then, the
cylindrically-symmetrical jet of partially (10%)
ionized gas enters the field of the sector magnet 3,
which deflects the charged heavy particles (ions)
through 90°. Besides the deflection, the magnet
monochromatizes the velocities and separates the
particles according to mass. The neutral component
of the jet directly enters the pump orifice, while the
electrons are removed through the grounded poles of
the magnet. The velocity of the deflected ions
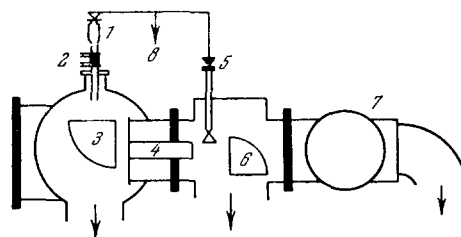amounts to about 2 km/sec, and in order to attain the

FIG. 4. Schematic drawing of a source for obtaining an intense
beam of fast particles.[29] 1—Nozzle feeding into a tube; 2—in-
duction coil of an UHF generator; 3—sector magnet to rotate the
trajectories of the ions through 90°; 4—ion accelerator; 5—nozzle
producing the gaseous target for charge-exchange with the ions;
6—sector magnet to remove the undischarged ions; 7—working
space; 8—supply of working gas.

required velocity they are accelerated in the accel-
erator tube 4. The beam of neutral particles is ob-
tained by charge exchange of the ion beam in the
supersonic jet 5 directed into the vacuum. The ions
and the neutral particles are separated by the sector
magnet 6, after which the intense beam of neutral
particles enters the working section 7. The evacua-
tion is done by powerful diffusion pumps supplemented
by refrigeration.

The source having the construction described here
was designed for use in problems of study of interac-
tion of molecules with the surface of a solid.

Obviously, charge-exchange sources generate in-
tense beams, principally of gases and easily-vapor-
ized substances. However, the relative ease of de-
tecting particles of energies above 100 eV permits
one to work also with low-intensity beams. A source
permitting one to obtain a beam of molecular nitrogen
with an intensity of 10^8—10^{10} molecules/sec in an
energy range 5—1000 eV, respectively, is described
in [26].

4. The sputtering source. A source of intense
beams of metal atoms in an energy range 1—10 eV
can be built on the basis of the relatively recently
discovered phenomenon of directional sputtering of
atoms. Wehner,[30] followed by a group of other
authors,[31] found that the sputtering of single-crystal
specimens by fast ions occurs anisotropically; the
sputtered atoms travel preferentially in directions
coinciding with the close-packing directions in the
crystal. The measurements of the energies of the
ejected atoms performed in [31,33] showed values of
the order of 10 eV and greater.

On the basis of sputtering-efficiency data,
Wehner [30] concluded that one thus could easily ob-
tain beams of density 10^{17} atoms/cm^2sec. A source
of this type permits one to obtain beams of prac-
tically any metal atoms of measureable and regulat-
able density, as is very convenient in the use of these
beams as targets.

A directional ejection of atoms has also been
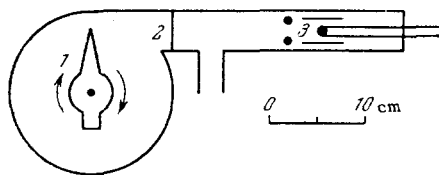found [34] in the bombardment of foil (Au) by fast

FIG. 5. Diagram of a "catapult" source.[35] 1—Vane rotating at high velocity; 2—collimating slit; 3—detector.

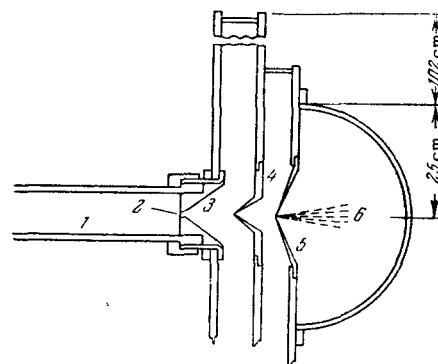

FIG. 6. Schematic diagram of a pulsed MB source using a gas heated by a shock wave.[40] 1—Shock tube; 2—microfilm diaphragm; 3—nozzle; 4,5—forming apertures; 6—beam.

protons. In spite of obvious advantages, this method has not yet been applied. We should note that up to now the degree of velocity homogeneity of atoms in such beams has not been studied enough.

5. The molecular "catapult". A simple and original method of obtaining modulated beams is described in [35]. The principle of the method (Fig. 5) is based on the "catapulting" of particles by a vane rapidly rotating about an axis. This method is, so to speak, a peculiar inversion of the vane radiometer. In order to obtain a beam, one places the vane in a space filled with gas at a pressure of 10^{-4}—10^{-3} mm Hg. When the chaotically-moving particles strike the surface of the rotating vane, they acquire a velocity whose magnitude is related in a definite manner to the linear velocity of the vane. Depending on the nature of the reflection (inelastic or elastic), the velocity will either approximate the linear velocity, or twice the latter. If the working gas is one of high molecular weight, one can effectively increase the energy of the particles of the beam (up to an energy of ~1 eV). Estimates show that at a working pressure of 10^{-3} mm Hg and a linear velocity of the vane of the order of 10^5 cm/sec, each square centimeter of the vane will impart momentum to about one milligram of gas (Hg) per second (i.e., about 10^{19} molecules/sec). Hence, by the ordinary collimation method, we can isolate a beam of intensity no lower than that of a corresponding effusion source. However, in distinction from the latter, the intensity will now be modulated. This is of undoubted value for detection. A source of this type can be modified by coating the surface of the vane with an easily vaporized substance. Such sources have thus far found only limited applications.[36]

6. Pulsed MB sources. A highly suitable means of obtaining beams of metal atoms might be the electrical explosion of fine wires in vacuo.[37] Here the cloud of high-temperature (several tens of thousands of degrees) metal vapor behaves like a peculiar pulsed "oven". This method would seem to permit one to obtain beams of high density; however, one would have to determine the degree of velocity homogeneity of the particles. In a certain modification, this method has been used as a plasma source, the plasma being emitted and accelerated in vacuo.[38,39]

Another powerful pulsed source of fast particles has been built recently on the basis of using a gas heated by a reflected shock wave.[40,41] Here the gas

jet flows out through an orifice (Fig. 6) in the end of the shock tube, and after expansion, can be transformed into a high-intensity molecular beam with effective velocities of the order of 1—10 eV.[40] The merit of this method is a quite thorough knowledge of the thermodynamic and physicochemical state of the gas, although one must remember that in the process of molecular-beam formation, certain deviations from these values can occur, as will be shown below. Using this source, one can construct a convenient instrument for studying the kinetics of chemical reactions occurring in a gas heated to high temperatures.[42] This method was used in [40], which was concerned with studying intermolecular interactions in high-temperature gases by measuring the effective scattering cross-sections and in [43], which was concerned with measuring the electron concentration following a reflected shock wave. An obvious but surmountable difficulty in using these sources is that one has to make the measurements during the single and brief (10—100 μsec) operation of the source. The latter suggests the idea that it would be expedient to construct a periodically-acting source. This type of source apparently can be constructed on the basis of recent advances in the technique of pulsed discharges in tubes, [44] using, for example, an oscillating pulse discharge, in which the charge-discharge cycle of the battery and the injection of the working gas are synchronized. If we remove the charged component from the jet, we can obtain a beam of neutral particles with energies of several (up to 10) eV. The application of an electrodeless discharge can improve considerably the homogeneity of composition of the beam. Thus far, no report has appeared in the literature on the realization of such a possibility.

7. Detection and velocity-selection of molecular beams. The problem of detecting molecular beams is the second part of the two-sided problem of raising the useful signal level. Fast particles (with energies above 100 eV) are detected, as a rule, by secondary-electron emission; detectors for particles having

gas-kinetic velocities will be described below. The literature contains a large number of descriptions of various detectors, which can be classified into the following fundamental types:

1. Universal detectors.
2. Surface-ionization detectors.
3. Manometric and Stern-Pirani detectors.
4. Sensitive balances.
5. Semiconductor and condensation detectors.

These types of detectors have been discussed in considerable detail in [1], and hence we shall take up here only the new developments that have appeared since its publication.

The universal detectors, which are the most promising, are based on the impact ionization of the particles of the beam by electrons and the collection of the ions formed for subsequent detection. The efficiency of the ionization detector increases with increasing electron current density and effective free path of an electron in the ionization space. In designing ionization detectors, one tries to make use of these characteristics. For this purpose, the electron-beam source is often constructed in the form of a Pierce electron gun.[45-48]

In order to increase the ionization efficiency, a magnetic field can be applied, with lines of force parallel to the direction of motion of the electrons. This method makes it possible in certain designs to increase the ion currents by an order of magnitude.[49] It seems promising to use a hollow cathode as the ionizer; this provides an electron current density exceeding the possibilities of ordinary electron guns by an order of magnitude or better.[27]

The positive ions arising from ionization can be used in two ways. First, we can directly collect them at an ion collector connected through a load resistor to the input cascade of an amplifier.[47,50-52] Another possibility is to extract the ions from the ionization region and accelerate them to energies ~ 10 keV, and then direct them onto the first cascade of an electron multiplier.[46,48-49] The use of an electron multiplier requires a preliminary mass analysis of the ions, since the background due to the residual gas would hinder the detection of the signals.

The sensitivity of universal detectors using multipliers is very high, permitting the detection of individual ions. With an ionization efficiency of 0.01, this implies that one can detect beams of thermal velocities at the very low intensity of 10^4—10^6 molecules/sec. A detector of neutral beams of energies 50—500 eV is described in [55].

With direct amplification of the ion current, the detection is considerably simplified if the beam is modulated.[53,54] An effective means of increasing the sensitivity further is to synchronize the detection. Such a detection system is discussed in [47].

Universal detectors are very convenient in relative measurements; they must be calibrated for carrying out absolute measurements.

A very convenient and quite simple means of absolute measurement is the membrane manometer of the capacitance type, developed in [56], and having a sensitivity of 2×10^{-6} mm Hg per scale unit. The instrument is distinguished by its great zero stability, simplicity of taking readings, and independence of the sensitivity of the absolute value of the pressure created by the beam.

Condensation detectors have been applied by a number of authors. However, since there is a detailed analysis of this topic in [57], we shall discuss here only a recently proposed detector,[58] which makes the measurements considerably simpler and briefer. The sensitive (receiving) element of the detector is a quartz crystal plate held at constant temperature, which serves as the resonance element of a 10 megacycle generator. The deposition of molecules from the beam changes the mass of the crystal, causing a change (a decrease) in the resonance frequency. This frequency shift can be measured with high accuracy. The sensitivity of the detector is so great that it permits the detection of changes in mass as small as 10^{-9} gram. Akishin and Zazulin [59] have developed an analogous apparatus.

Detectors based on the sensitive-balance principle permit one to measure the momentum being transferred, under certain assumptions on the nature of the reflection of the particles; they have found very widespread application.[30,32,60-62] However, for absolute measurements one must know precisely the intensity of the molecular beam. The use of these detectors has made it possible to estimate the energies of particles ejected in cathode sputtering,[30-32] by measuring the aerodynamic forces acting in the flow of highly rarefied gas.[60,61] The sensitivity of these instruments is as much as 10^{-6} dynes with an accuracy of 0.2%.[62] However, they show much lag.

In conclusion, we shall discuss an original method, [63] which is the electron-optical analog of the schlieren method known in optics. The method is based on the analogy between the refraction of a light beam and the scattering of an electron beam in gases, and on the fact that the scattering cross-section is independent of the pressure.

The principle of the method is evident from Fig. 7. The deflection of an electron ray upon scattering by the molecules of the beam has the result that the ray by-passes a "Foucault knife-edge" set at the focus of the electron-optical system in the absence of the beam. A requirement limiting the application of this system is that the density of the particles in the beam must be considerably higher than that of the residual gases. If this is so, synchronous modulation of the molecular and electron beams makes it possible to study both the density and pulse formation of the par-
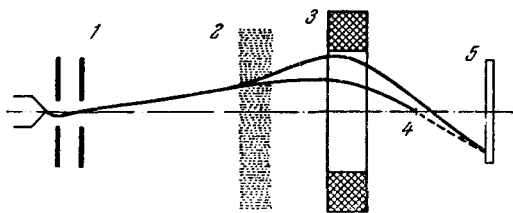
FIG. 7. Diagram of the detection of molecular beams (according to [63]). 1—Electron beam; 2—molecular beam; 3—electron-optical lens; 4—Foucault knife-edge; 5—detector (photographic plate).

ticles, and the velocity of the particles of this pulse (from the time variation of the density).[64]

Finally, we shall discuss briefly the methods of velocity-selection of molecular beams, by which we mean the controlled regulation of the velocity of the beam particles. The use of molecular beams with a Maxwellian velocity distribution complicates the data reduction and blurs valuable details, as will be evident from what is said below. Hence, a MB selector is incorporated, as a rule, in contemporary experimental arrangements. The principle of action of a mechanical velocity selector is well known,[2,65,66] and the selectors in recent use are distinguished by high accuracy and low attenuation of the beam (high "transmission"). An original design solution is the use [66] of two independent low-power synchronous motors (800 rev/min) to turn the selector disks. The use of the synchronous motors permits one very accurately to vary the angle of relative displacement of the slits in the disks (with a velocity deviation less than 1%) practically within any limits by a simple phase shift in the supply voltages. In recent years, the so-called multidisk selectors [67-69] have been widely applied. Refernce [67] describes a six-disk selector which makes possible a high accuracy (~ 5%) of selection with a high "transmission". This is achieved by making the number of slots per disk as great as 278; an eight-disk selector with 360 slits is described in [68].

The problem of calculation for a multidisk selector has been discussed analytically in [70]. This article gives rational criteria for choice of the optimum parameters of a selector, and also gives a bibliography of almost all the published studies on mechanical selectors.

A simple method of measuring velocities and isolating particles of a given velocity is afforded by "time-of-flight" selection. The principle of this method is based on the spatial spreading of a pulse of particles generated by the rotation of a disk with narrow slits. The difference in velocities of the particles of the initial (square) pulse results in its spreading during the time of flight to the detector. If we record the course in time of the variation of the ion current at the detector, we can directly reconstruct the velocity-distribution curve of the particles

from the oscillogram. One can easily show [71] that when the open time τ (pulse duration) is short in comparison with the time of flight T for the distance L from the disk to the detector, the number of particles having a velocity $v (v = L/T)$ will be related to the instantaneous value $i(T)$ of the ion current as as follows:

$$f(v) \sim i(T) T.$$

Figure 8 shows some oscillograms as calculated with this equation for the ion currents for beams of argon (1), hydrogen (5), and mixtures of them (2—4). The accuracy and simplicity of this method favorably distinguish it from that ordinarily used. With use of a stroboscopic electronic apparatus, this method can make possible the selective detection of particles of a given velocity.
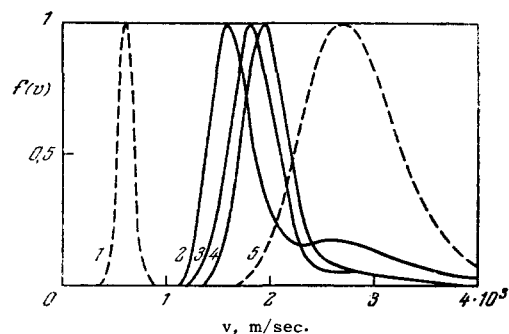

FIG. 8. Processed oscillograms of the time-of-flight analysis of a modulated beam at various pressures of the initial mixture (2% Ar-98% H_2). The ordinates of the curves correspond to the instantaneous values of the ion current. The time separation (and thus also the linear separation) of the components of the mixture and the sharp increase in the relative Ar content in the beam are clearly marked.[71]

3. APPLICATIONS OF THE MOLECULAR-BEAM METHOD

1. Elastic scattering of molecular beams and the study of intermolecular forces. The study of elastic scattering in gases is one of the most fruitful applications of the MBM, and is a direct source of information on the forces acting between atoms and molecules. As is known,[72] we can get information of this sort by other methods too, such as: direct quantum-mechanical calculation, which, in fact, can be performed only for the simplest systems; study of the thermodynamic and kinetic properties of gases; measurement of pressure broadening of lines in the microwave region; study of the thermodynamic properties of the noble gases in the crystalline state, etc. In the energy region corresponding to low and room temperatures, the MBM supplements these methods. However, it is the only way that is sufficiently substantiated theoretically for studying intermolecular interactions in the energy range corre-

sponding to temperatures above 1000°K. Besides, the MBM is practically the only method permitting us to study this interaction for dissociated atoms.

At first, without going into a detailed presentation of the theory of elastic scattering,[73-76] we shall write down some expressions necessary to illustrate the technique of determining the potential energy from elastic-scattering data, and then we shall discuss some concrete results. In the classical scattering theory, an unequivocal relation is established between the angle χ of deflection from the initial trajectory of a particle and the parameters of the force field of a stationary scattering center:

$$\chi = \pi - 2\theta_m = \pi - 2b \int_{r_{min}}^{\infty} \frac{dr}{r^2 \sqrt{1 - \frac{V}{E} - \frac{b^2}{r^2}}}. \qquad (1)$$

The notation is evident from Fig. 9; E is the initial kinetic energy of the particle, and V is the potential energy of interaction.
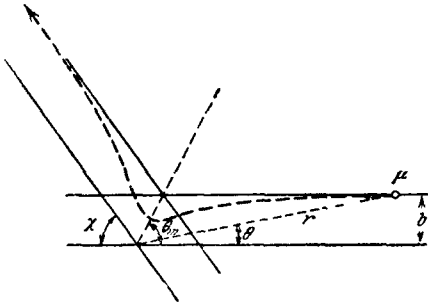

FIG. 9. Schematic diagram of the scattering of an atom by a center of force.

The differential scattering cross-section determines the relative number of particles in an axially-symmetric beam scattered at angles in the interval from χ to $\chi + d\chi$, and is equal to the number of particles passing by at an impact parameter within the range from b to b + db; it can be expressed as follows:

$$dQ(\chi, E) = \frac{1}{2\pi \sin \chi} \, b \left| \frac{db}{d\chi} \right|. \qquad (2)$$

With the aid of (1) and (2), we can show that for a potential having the very simple form $V = K/r^s$ (which is all that we shall discuss)

$$dQ(\chi, E) = \left(\frac{K}{E}\right)^{2/s} \Phi(s, \chi), \qquad (3)$$

where $\Phi(s, \chi)$ has the following form [73] for scattering at small angles:

$$\Phi(s, \chi) = \frac{1}{s} f(s)^{2/s} \chi^{-\frac{2s+2}{s}},$$

$$f(s) = \sqrt{\pi} \, \frac{\Gamma\left(s + \frac{1}{2}\right)}{\Gamma(s/2)}$$

(where Γ is the gamma function). For scattering at

large angles, numerical calculations have been made in [77] of $\Phi(s, \chi)$ for $6 \leq s \leq 14$. If the potential functions are of more complex form (having a minimum), numerical calculations can be performed, and results are found in [78-80].

The total cross-section characterizing the scattering at angles from zero to π is defined as follows:

$$Q(E) = 2\pi \int_0^{\pi} dQ(\chi, E) \sin \chi \, d\chi. \qquad (4)$$

This expression diverges for a potential of any form not vanishing identically at infinity. Hence, in the classical scattering theory, the concept is introduced of an effective scattering cross-section at angles greater than a certain minimum angle determined by the actual resolving power of the apparatus. Then, in the small-angle approximation,

$$Q(E, \alpha) = 2\pi \int_{\alpha}^{\pi} dQ(\chi, E) \sin \chi \, d\chi = \pi f(s)^{\frac{2}{s}} \left(\frac{K}{E}\right)^{\frac{2}{s}} \alpha^{-\frac{2}{s}}. \qquad (5)$$

What is a reasonable value for the minimum deflection angle? The order of magnitude of α can be determined, for example, from the condition that classical mechanics should be applicable. Using the uncertainty principle, α can be represented in the form

$$\alpha > \frac{h}{2\pi\mu v \cdot 2b} = \theta^*, \qquad (6)$$

where μ is the reduced mass, and v is the relative velocity.

For deflection angles much larger than θ^*, we can neglect quantum effects. Thus, $\alpha = k\theta^*$, where k is a numerical factor whose value we wish to determine.

In the quantum theory of scattering, the total cross-section does not diverge (for s > 2), and the corresponding expression has the form [75]

$$Q_q(E) = \pi \frac{2s-3}{s-2} f(s)^{\frac{2}{s-1}} \left(\frac{4\pi K}{hv}\right)^{\frac{2}{s-1}}. \qquad (7)$$

If we substitute $\alpha = \theta^*$ in (5), we get an expression differing from Eq. (7) at s = 6 only by a factor near unity.

Experimentally, the effective cross-section is determined by the attenuation of a collimated mono-kinetic beam passing through a homogeneous layer of scattering gas,

$$Q(\alpha, E) = \frac{1}{nl} \ln \frac{I_0}{I}, \qquad (8)$$

where I and I_0 are the intensities of the beams after and before scattering, respectively, n is the density of stationary scattering particles, and l is the path length of scattering. In an actual experiment, not nearly always can one attain stationary or mono-kinetic conditions of the interacting particles. Hence we must include corrections in Eq. (8) to take into account the deviations from an ideal experiment. Useful calculations for experimentalists have been

performed in [81] of the numerical values of these correction terms. Since the measured value of the effective cross-section $Q(\alpha, E)$ will depend on the resolving power of the apparatus, the problem arises of a rational choice of resolving power to ensure an objective measurement of the total cross-section.

We shall return somewhat later to the problem of choice of the resolving power, and shall point out now some methods of determining the potential parameters from the measured values of the cross-sections. Using Eqs. (5), (7), and (8), we can write

$$\frac{1}{nl}\ln\frac{I_0}{I} = \pi\left(\frac{K}{E}\right)^{\frac{2}{s}} f(s)^{\frac{2}{s}} \alpha^{-\frac{2}{s}}, \tag{9a}$$

$$\frac{1}{nl}\ln\frac{I_0}{I} = \pi\frac{2s-3}{s-2} f(s)^{\frac{2}{s-1}} \left(\frac{4\pi K}{hv}\right)^{\frac{2}{s-1}}, \tag{9b}$$

$$d\theta(\chi, E) = \frac{1}{s}\left(\frac{K}{E}\right)^{\frac{2}{s}} f(s)^{\frac{2}{s}} \chi^{-\frac{2s+2}{s}}. \tag{9c}$$

These relations, along with the quantum formula for the differential cross-section, are the fundamental ones for determining the parameters. Here, the quantum relations are used as a rule for beams of thermal velocity, and the classical relations for fast beams. We see from (9), where K and s are the unknowns, and $Q(\alpha, E)$ and $dQ(\chi, E)$ are the measured quantities, that if we vary n with E constant, or vary E with n constant, in the former case we can determine K for a given s, and in the latter case, s for a given K. We can easily see that variation of the resolving power α at constant n and E can provide another suitable possibility for determining the parameters K and s.

In line with what we have said, studies on the elastic scattering of molecular beams can be provisionally divided into two groups: 1) determining the resolving power of the apparatus that will make it possible to measure objectively the total cross-section and to find the limits of the range of deflections describable by classical mechanics; 2) determining the potential parameters and the nature of the interaction forces from the data of the cross-section measurements.

The problem of the resolving power has been discussed in [82-84], while the related problem of the limits of applicability of the classical description has been discussed in [82]. The crux of the matter amounts to the fact that at a given resolving power of the apparatus, first, the experimenter must be able to estimate how far the measured value deviates from that of the total cross-section, and second, he must know in which region, quantum or classical, the deviations being measured fall. An illustration of the grounds for such an analysis is given in Figs. 10 and 11. As we see from Fig. 10, the value of the measured cross-section can vary considerably with varying resolving power. We see from Fig. 11, in addition, that the classical description of the scattering
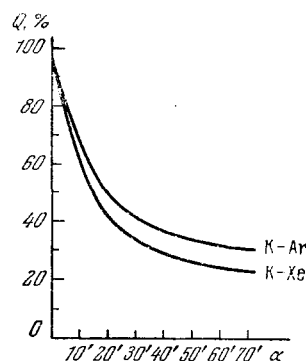

FIG. 10. The relation of the measured value of the effective scattering cross-section to the resolving power of the apparatus.[84]
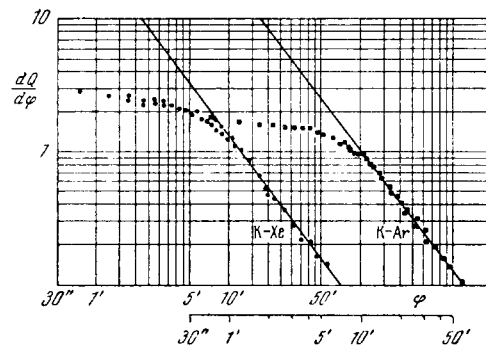

FIG. 11. The relation of the differential scattering cross-section to the angle of deflection.[84] The straight line corresponding to Eq. (9) ceases to describe the experiment at deflection angles of the order of 10'–20'. The relation in this region can be described by quantum relations using the same potential parameters;[72] ϕ is the deflection angle in the laboratory system.

in the small-angle region ceases to be valid at a certain angle, beyond which the experimental points are in good fit with a curve calculated by the quantum formulas.[82] Hence, before we proceed to find, e.g., the potential parameters, we must evidently determine both the resolving power and the angular region to be studied.

Experimentally, the transition from the region of classical scattering to that of quantum scattering (see Fig. 11) has been observed in a study of the angular distribution of scattered particles in an apparatus of high resolution (several seconds of arc in the laboratory system).[81,82,84] It turned out here that, e.g., for the Na-Hg and K-Hg systems, k is ~4 in the expression $\alpha = k\theta^*$ (and analogously in other systems). This permits us to fix rather definitely the limits of the classical-description region.

Massey and Burhop's monograph[85] gives a method of estimating the necessary resolving power, based on approximating the interacting particles by hard spheres. According to [85], the error in determination of the cross-section will not exceed 10% if the resolving power $\alpha = \theta_0$ ($\theta_0 = h/2\pi\mu va$, where a is the

sum of the gas-kinetic radii). However, it seems obvious that the gas-kinetic radius, which is determined by the momentum-transfer cross-section, cannot provide any satisfactory characterization for small-angle scattering when attractive forces are present.

In [82] there is proposed another, more rational criterion: the quantity a is replaced by twice the maximum impact parameter

$$\alpha = \theta^* \qquad \left(\theta^* = \frac{h}{2\mu v \cdot 2b} \right).$$

As we should expect, the quantities θ_0 and θ^* differ greatly in value; thus, for the Na-Hg system, θ^* = 2.3 minutes, while θ_0 = 78.9 minutes. The experimental study of the angular distribution of particles scattered at small angles has shown that the particles scattered at angles less than θ^* make practically no further contribution to the value of the cross-section (see Fig. 11). Fig. 12 shows the relation obtained in these experiments [79] between the relative error of measurement of the total cross-section and the resolving power expressed in units of the critical angle θ^*. Comparing these and the results given by Massey and Burhop, we may note a large discrepancy (which increases as the long-range attraction forces become more marked).

Apparently, the results discussed above answer the doubts expressed in[83] as to the possibility of objective measurement of the total scattering cross-section, and permit us to conclude that the data presented in Table II correspond with high precision with the total scattering cross-sections.

In working with fast particles (of energies above 100 eV), the problem of the resolving power becomes less crucial. The point is that, as the velocity increases, the value of the limiting angle θ^* declines, and it can happen that the resolution permitting a
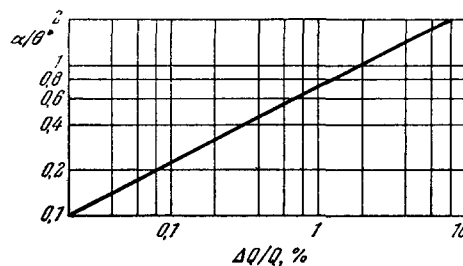

FIG. 12. The relation of the relative error of measurement of the total cross-section to the resolving power expressed in units of the critical angle.[82]

measurement of the total cross-section will be practically unattainable. Hence, one must use here the effective cross-section described by Eq. (5). To do this, we must choose the aperture angle large enough that quantum effects cannot be manifested. For example, for a beam of energy 1000 eV, quantum effects can occur at angles of 10″ for Ar and 1.5′ for He. If we know exactly the resolving power of the apparatus, we can find the potential parameters by use of (9a).

We shall now discuss some concrete data (obtained in recent years) on the scattering of both slow and fast beams, excluding from discussion inelastic collisions.[86,87] The fundamental results of the measurements of total cross-sections of thermal-velocity beams are given in Table II. Here we can see that the data of different authors agree quite satisfactorily (we must bear in mind possible differences in beam velocities and the velocity-dependence of the cross-section and the imprecision of the measurements of the density of the scattering gas). Furthermore, the unified treatment performed in [94]

Table II. Total elastic-scattering cross-sections ($\overset{\circ}{A}{}^2$) measured for thermal-velocity beams

Beam	Scattering gas								Literature
	H_2	D_2	He	Ne	Ar	N_2	O_2	Hg	
Li	120	124	106 113		301 365				88 89
Na	154	182	132 247	211	403 430 480	556 606 689	386 510	1995	88 82 84 107
K	176 196	227 254	167 171	261	580 592	615 680 490 470 755		2190 1820	88 89 82 90 83 91 13
Rb	173	211	154	266	572	774		2552	88 92
Cs	176	216	163 470	289	572 860	908 926		3019	88 92 82 93

of the data from measurements for the K-Ar sys-
tem [88-90,92] using the numerical results of [81] has
shown that the deviations of the cross-section values
given by different authors from the arithmetic mean
does not exceed 2%. Such a good agreement allows us
to accept this value as a standard, and thus to reduce
the uncertainty in the measurement of the density of
the scattering gas in subsequent measurements by
making test measurements of it. The only exceptions
in Table II are the results of [93]; the discrepancies
here are so great that Massey and Burhop [85] remark
thereupon in their monograph, "Until this situation is
clarified the results of the analysis of all cross-sec-
tions obtained from molecular ray experiments can
only be accepted with caution."

This "compromising" discrepancy seems now to
have been eliminated. Precision measurements of
the differential cross-sections recently performed
with an apparatus with a resolution of the order of
3.5" in an angular range up to 1° (in which 16" de-
flections detected as scattering) have not confirmed
the results of [93] for the Cs-He system; the K-Ar,
K-Xe, K-Br, and K-HCBr₃ systems also did not
show cross-section increases. [84]

The experimental values of the total cross-sec-
tions can be used to find van der Waals constants, if
we assume that the interaction is due to dispersion
forces (i.e., we assume that s = 6). The values thus
obtained can be compared with those calculated from
theory. [72] For the systems given in Table II, the
agreement proves to be good. Such a comparison has
been made in [92] for about 100 different systems, and
it turned out that 57% of the total number of systems
showed discrepancies between the theoretical and ex-
perimental values of less than 1—3%; 18% of them
showed from ±3% to ±6%; 12% showed ±6% to ±10%;
and 13% showed greater than ±10%. They noted that
the greatest deviations correspond to scattering of
particles of relatively low molecular weight.

A comparison of the measured cross-sections and
the van der Waals constants calculated from them
with the theoretically calculated values for scattering
of He, Ne, Ar, Kr, and Xe in argon has been made
in [95]. They noted that the experimental values were
systematically higher than the theoretical, but the
reason for this is not clear. A further source of in-
formation on long-range interaction forces could be
to measure the relation of the scattering cross-sec-
tion to the relative velocity of the colliding particles.
As follows from Eq. (7),

$$Q \sim v^{-\frac{2}{s-1}},$$

and if K is independent of v, then by varying the
velocity we can obviously find the value of s (which
is 6 for van der Waals interaction, and differs from
6 for other types of interaction). In practice, v is
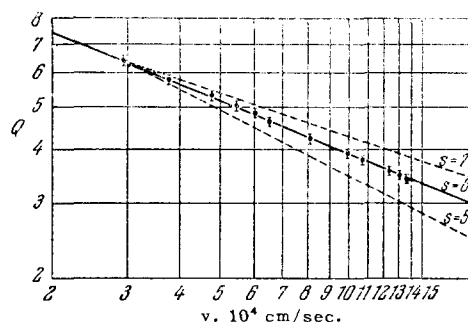varied by the mechanical-selection method, [96,99] or

FIG. 13. The relation of the effective cross-section to the
velocity of the particles being scattered. The straight lines cor-
respond to Eq. (5) for s = 5, 6, 7.[96]

by regulated variation of the oven temperature.[97]
In [96] the velocity-dependence of Q for the K-N₂
system was compared with the theoretical depend-
ence for s = 5, 6, or 7. As we see from Fig. 13, the
agreement of the theoretical and experimental values
permits us to select unequivocally the value s = 6.
A study has been made in [97] of the velocity-depend-
ence of the total cross-section in the scattering of a
beam of the polar CsCl molecules by polar and non-
polar gases. For scattering in a nonpolar gas, the
experimental results can be described well by the
relation $Q \sim v^{-2/5}$ (if we use the theoretical values
of K, the experimental points fit a straight line of
the type of Fig. 13). However, the situation changes
markedly in scattering by polar gases. The experi-
mental relation of Q to v (Fig. 14) is characterized
by an appreciable change in slope, the numerical
cross-section values are greater in size, and they
vary more strongly with the temperature. We can
explain this effect by taking into account the dipole-
dipole interaction, for which the potential energy of
interaction can differ under certain conditions from
the given effective spherically-symmetric poten-
tial.[72] These conditions are determined by the re-
lation of the period of rotation (τ_{rot}) and the time
of interaction (τ_{int}). When $\tau_{rot} \gg \tau_{int}$, the poten-
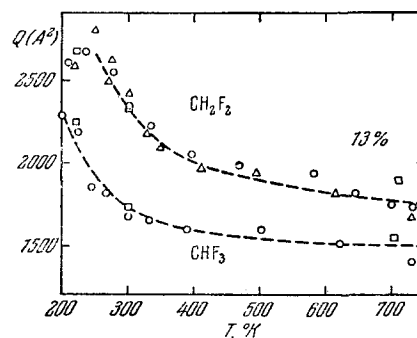tial has the form

FIG. 14. The relation of the effective scattering cross-section
of the polar molecule CsCl in polar gases to the velocity as ex-
pressed in terms of the oven temperature.[97]

$$V = -\frac{\mu_1 \mu_2}{r^3} g$$

(where μ_1 and μ_2 are the dipole moments, and g is a coefficient taking the orientation into account). We can ensure that these conditions are satisfied by varying the temperature. However, in the study under discussion, the range of temperature variation was insufficient, and the results obtained only permitted them to state qualitatively that an effect of the dipole-dipole interaction was manifested. A study of the interaction of polar molecules in NH_3 and H_2O systems has been made in [98].

The theoretical and experimental data indicate that the relation $Q \sim v^{-2/5}$ is poorly satisfied in the interaction of light particles. A special experiment has been conducted [99] on the scattering of atomic and molecular hydrogen and helium in hydrogen and helium. It showed that the velocity-dependence differs very strongly from that predicted by the theory of Massey and Mohr.

A deviation of the velocity-dependence of the total cross-section from the theoretical dependence was found in [100] in a study of the scattering of a mono-kinetic Li beam by mercury. As the velocity of the Li atoms was decreased, the cross-section decreased sharply at a certain velocity (this effect did not occur for K). Somewhat later in a study of the scattering of a Li beam in the noble gases, [101] deviations from the $Q \sim v^{-2/5}$ relation were also observed. For a number of systems (Li—Xe, Kr, Ar), the velocity-dependence was characterized by the appearance of relative maxima and minima. Signs of quantum effects were also found in [100] in small-angle scattering; a periodicity was rather clearly manifested on the scattering curve in the angular region up to 15°, as predicted by quantum-mechanical calculation.

Valuable information on intermolecular forces can also be obtained by studying the angular distribution of particles scattered at large angles. In this case the measurements of the differential cross-sections permit us to reconstruct the form of the interaction potential, and to find the numerical values of the parameters for a chosen functional form of the potential. Monotonic potential functions of the form $V = K/r^s$ are the limiting possibilities for describing the interaction for relatively large and relatively small impact parameters. The real interaction potentials describing the interaction throughout the region of reasonable mutual distances are not monotonic, but show a minimum. These peculiarities of the potential function are reflected in the relation of the deflection involved in scattering to the impact parameter. Consequently, this relation is non-monotonic and multiple-valued. The peculiarities of scattering under these conditions were first discussed in general form by Firsov, [102] from whose article Fig. 15 has been taken. Fig. 15a shows a
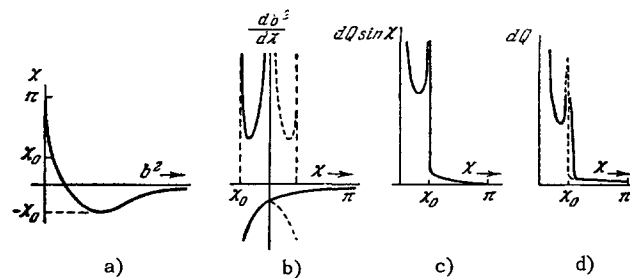

FIG. 15. A qualitative representation of the pecularities of scattering in the case of a non-monotonic interaction potential function.[102]

typical non-monotonic variation in the relation of χ to b^2 (deflections due to repulsion forces are taken as positive, and due to attraction forces, negative). Fig. 15b shows the relation of $d(b^2)/d\chi$ to $\chi(d(b^2)) = 2 dQ (\chi, E) \sin \chi d\chi$). Since in an actual experiment positive and negative deflections are absolutely indistinguishable, the experimental relation will obviously be represented by a curve of the type of 15c, which is the result of adding the branches of Fig. 15b. If we take into account the finite resolving power of the apparatus, then the relation of dQ to χ will be represented by the curve of Fig. 15d. We can see in Fig. 15d the fundamental peculiarities involved in scattering at large angles; these have been examined in later studies.[78,80] The singularity corresponding to the angle χ_0, following [80], is currently called the rainbow scattering (χ_0 is the rainbow angle; for particles of fixed energy, its value is unequivocally related to the depth of the potential well of Fig. 15a; a number of peculiarities of the scattering curve have been analyzed in [104,80]. We must note that the treatments that have been carried out are strictly valid only for monokinetic beams. Otherwise, these peculiarities can be smeared out and totally disappear. This effect can be seen distinctly in Fig. 16, which gives experimental data taken from [103,13,104]. However, even for non-monokinetic beams, a study of the large-angle scattering permits one to find the values of the potential parameters. Thus, in [13], the values of the parameters ϵ and r_m for a Buckingham "exp-6" potential were found from the data of a study of the scattering of K by Hg, $C_{16}H_{10}$, and $C_{14}H_{10}$ in an angular range from 2° to 140°.

In [104], the parameters r_m, ϵ, and α of the Buckingham potential were determined for the K-Kr and K-HBr systems (in the elastic-interaction region for the latter) from data on scattering in the rainbow-angle region. A painstaking investigation led the author [104] to conclude that one must take into account the quantum effects predicted in [80] in handling the rainbow-scattering data. The potential parameters can also be determined from the relation of the differential scattering cross-section to the relative kinetic energy, and such a study has been
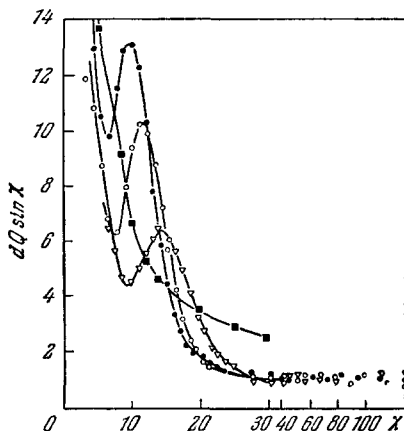
FIG. 16. The experimental scattering curves of monokinetic (K − Kr − ▽, o, ●)[104] and Maxwellian (K − Hg − ■)[103] beams in the high-angle region; the influence of the monokinetization is clearly visible. The curves ▽, o, ● correspond to different temperatures of the atom source.

carried out in [105,106] for the Cs-Hg and K-Hg systems.

The examination made here has shown that the advances in the technique of the MBM and in the theoretical analysis of scattering phenomena have now equipped experimentalists with effective means of studying intermolecular forces in the thermal-energy region.

In concluding the discussion of the scattering of thermal-velocity beams, we must point out a study [107] unique in nature, which affords an illustration of the substantial progress in experimental technique, besides being of physical interest.

As is well known, if only one of the partners is in an S-state, the long-range forces are sensitive to the relative orientation of the interacting atoms. In [107], the problem has been posed of experimentally detecting and quantitatively measuring this orientation effect. The problem consisted in, first, obtaining monokinetic beams of polarized atoms, i.e., beams having a given angle between the spin directions and the velocity vector of the particles; and second, they had to detect the difference in the measured values of the total cross-sections, which did not exceed 1% of the mean cross-section according to preliminary estimates.

In order to obtain polarized beams of Ga atoms, as in the Stern-Gerlach experiment, they used the effect of spatial separation of the trajectories of polarized particles in an inhomogeneous magnetic field. By stepwise variation of the magnetic-field intensity, beams of atoms of the differing polarizations were alternately transmitted through the exit slit of this unique source. Some useful information on polarized-beam sources is found in [108].

After monokinetization by a selector, the obtained beam was passed through the scattering chamber, and the scattering cross-section was measured in the standard way from the attenuation of the beam intensity. The scattering chamber was placed in the field of a permanent magnet to reduce "depolarization" effects. In solving the second problem, that of comparing two cross-section values differing by about 1%, they used an ingenious automatic system. This permitted them to make this comparison under conditions in which, while the accuracy of intensity measurements was 10^{-4}, the fluctuations due to instability exceeded this value by a factor of 100 or even 1000. The possibility of measurements under these conditions involved repetitive determination of the attenuation of the two beams for sufficiently short periods of time, and the averaging of the results [using a counting apparatus (scalers)] over a long time interval to eliminate random fluctuations. Using a control apparatus that switched the magnetic field and the receiving channels automatically, they could reliably detect and measure the difference in the scattering cross-sections for the beams of particles of differing polarizations with an accuracy as good as 3—5%. The technique used by the authors of detecting weak effects on a background of strong interference can be considered classical in many respects, and is undoubtedly worthy of the attention of experimentalists.

We shall discuss now the fundamental results of studying the elastic scattering of fast particles (with energies greater than 100 eV) and the possibilities of using these results in practice.

The vigorous growth of nuclear energy and rocket technology that has occurred in recent years has sharply heightened interest in studying the properties of high-temperature gases (in particular, the kinetic properties). At the temperatures of interest, from thousands to tens of thousands of degrees, a direct measurement of, e.g., the transfer coefficients is impossible. Thus one must obviously develop new methods of obtaining the necessary data. The single quantity characterizing the collision and entering into the expression for calculating the transfer coefficients is the deflection angle of the trajectories of the particles. However, the study of elastic scattering permits direct measurement, in particular, of the deflection angles, or more exactly, the probability of deflection at a given angle in an interaction at the given energies. When we possess these data and use rapid computers, the problem of finding the transfer coefficients becomes relatively simple. Hence, the practical value of this type of experiment is evident. In line with the relative simplicity of obtaining and detecting particles of energies above 100 eV, monokinetic beams of particles of these energies are used in the experiments, and the effects are detected of grazing collisions at impact parameters of 1—3 Å. This corresponds to the distances of closest approach of the particles at temperatures of the order of 1000—10,000°K.

A necessary condition for the interpretation of the

Table III. The interaction potential of various systems in the region of repulsive forces

System	Potential $V(r) \times 10^{12}$, ergs; r in Å	Range of distances, Å	Litera-ture
He—He	$0,201/r^{4,95}$	0.5—1	109
He—He	$4,62/r^{1,79}$ and $314 \exp(-4,12r^{1/2})$	0.52—1.02	110
He—He	$7,55/r^{5,94}$	1.27—1.59	111
He—He	$5,56/r^{5,03}$	0.97—1.48	112
Ne—Ne	$500/r^{9,99}$	1.76—2.13	113
Ar—Ar	$46,1/r^{4,33}$ and $3.66 \cdot 10^4 \exp(-6.82r^{1/2})$	1.37—1.84	114
Ar—Ar	$1360/r^{8,33}$	2.18—2.69	115
Kr—Kr	$255/r^{5,42}$	2.42—3.14	116
Xe—Xe	$1,1310/r^{7,97}$	3.01—3.60	117
He—Ar	$99,5/r^{7,25}$	1.64—2.27	118
Ne—Ar	$1010/r^{9,18}$	1.91—2.44	119
H—He	$3,75/r^{3,29}$	1.16—1.71	120
H—H$_2$	$70,8 \exp(-2.99r^2) + 6.07 \exp(-0.942r^2)$	0.27—0.68	121
D—D$_2$	$45,9 \exp(-5.17r^2)$	0.29—0.56	121
He—N$_2$	$119/r^{7,06}$	1.79—2.29	122
Ar—N$_2$	$1210/r^{7,78}$	2.28—2.83	122
N$_2$—N$_2$	$954/r^{7,27}$	2.43—3.07	122
He—CH$_4$	$965/r^{9,43}$	1.92—2.37	123
He—CF$_4$	$9,9 \cdot 10^6/r^{17,51}$	2.43—2.74	123
CH$_4$—CH$_4$	$9,63 \cdot 10^6/r^{15,47}$	2.47—3.06	123
CF$_4$—CF$_4$	$1,87 \cdot 10^{22}/r^{39,27}$	3.43—3.77	123

experimental results is that the total elastic-scattering cross-section should be considerably greater than the inelastic-scattering cross-sections, a condition that is usually satisfied in the chosen energy range (100—3000 eV).[85] As was stated above, the scattering of fast particles can be rigorously described within the framework of classical mechanics, and hence, the parameters K and s of a spherically-symmetric potential of the form $V = K/r^s$ can be found by using Eq. (9a).

Table III gives practically all the experimental results obtained from measurements of the energy-dependence of the effective scattering cross-section. The table does not include the results of [124], which deviate appreciably from those given in the table for the Ar-Ar and Ne-Ne systems, and which were obtained from measurements of the differential scattering cross-sections. As we see from Table III, data have been obtained at present on repulsion potentials for atom-atom, atom-molecule, and intermolecular interactions. The treatment of the experimental data for atom-atom systems is simple, and is briefly described above. When one or both of the two collision partners are molecules, the treatment becomes more complicated. A procedure is proposed in [122,123] for calculating the intermolecular potentials on the basis of scattering of atoms (of the noble gases) by the molecules. Since this method permits us to simplify considerably the obtaining of information on inter-molecular interaction at small distances, we shall discuss it in more detail. We shall make use of Fig. 17, which represents schematically the passage of the particle being scattered past a molecule whose force field is evidently not spherically symmetric. In terms
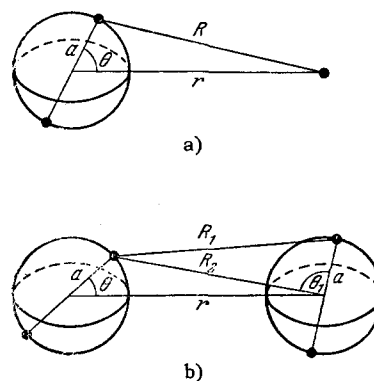
a)

b)

FIG. 17. Configuration of particles used in calculating the atom-molecule and intermolecular repulsion potentials.

of the phenomenon, it is convenient to consider the problem as being that of the deflection of the particle by two spherically-symmetric centers of force; in the course of the experiment we measure some effect of this scattering averaged over the orientation (angles θ, θ_1 in Fig. 17). The problem of treating the phenomenon theoretically consists in developing a method of determining from the experimental data the effective interaction potential of a free atom with atoms belonging to a molecule. This can then be used to construct the intermolecular potential. In what follows, we shall require the following sufficiently justified assumptions: a) we shall consider the molecule to be a rigid stationary structure during the time of interaction, so that neither rotation nor vibration will occur during this time; b) the atoms forming the molecule are independent (additive) spherically-symmetric point centers of force (with a potential of the form

$V = K/r^s$) c) all mutual orientations are equally probable. As we see from Fig. 17a, the distance R between the atom being scattered and the center of force is

$$R = r(1 \pm 2\alpha \cos \theta + \alpha^2)^{1/2}, \quad \alpha = \frac{a}{r} .$$

Hence, the total potential for a certain orientation θ has the form

$$V_{AM} = \frac{K}{r^s(1+2\alpha \cos \theta+\alpha^2)^{s/2}} + \frac{K}{r^s(1-2\alpha \cos \theta+\alpha^2)^{s/2}} .$$

When we average over all (equally-probable) orientations, we obtain

$$\overline{V}_{AM} = \frac{2K}{r^s} \frac{(1+\alpha)^{s-2}-(1-\alpha)^{s-2}}{2\alpha(s-2)(1-\alpha^2)^{s-2}} . \tag{10}$$

We see from the structure of this expression that the average total potential is equal to twice the interatomic potential, with a correction factor taking into account the lack of spherical symmetry. The second factor approaches unity as r increases. In principle, we should now substitute the obtained expression into Eq. (1) and find the functional relation of the cross-section to the potential parameters and the energy. Thereupon, we could reconstruct the form of the potential function from the experimental relation of the cross-section to the energy, or find the parameters K and s. However, in this case we cannot get an analytical expression such as (5), and another method has been suggested in [122]. We note that the use of mechanical computation can resolve this difficulty, while the method to be discussed below does not have enough physical clarity.

Thus, we assume, as is done in [122], that within the accuracy of the experimental errors the scattering of the atoms by the molecules can be described by some effective spherically-symmetric potential function $V' = K'/r^{s'}$. Then the numerical values of K' and s' can be easily obtained from the experimental relation of $Q(\alpha)$ to E. Further, we can obviously choose values of K and s such that Eq. (10) will describe the variation of $V'(r)$ within the given energy range with sufficient accuracy. In short, this is the way of determining the parameters of the effective interatomic potential. These parameters are obtained for systems of non-identical atoms (He-(N)$_2$, Ar-(N)$_2$, etc.). To find the effective interatomic potentials for homonuclear molecules, one can use the empirical combining law, which has been experimentally tested in atomic systems. The combining law [72] permits us to find the potential parameters of the interaction of like atoms (K_{ii}, s_{ii}) from their values for unlike atoms (K_{ij}, s_{ij}), and has the form

$$K_{ij} = \sqrt{K_{ii} K_{jj}}, \quad s_{ij} = \frac{1}{2}(s_{ii}+s_{jj}).$$

It is just in this way that the parameters of the effective interatomic interaction potential of identical atoms are found from the obtained values. The in-

termolecular interaction potentials are constructed from the obtained effective interatomic potentials as follows. As is implied by Fig. 17b,

$$R_1 = r(1 \pm 2\alpha \cos \theta + \alpha^2)^{1/2},$$
$$R_2 = (R_1^2 \pm 2\alpha \cos \theta_1 + \alpha^2)^{1/2}.$$

Here, in distinction from the atom-molecule systems, another angle has been introduced (θ_1), which characterizes the mutual orientation. If we know the effective interatomic potential and use the assumption of additivity, we can write the total interaction potential of the four atoms, and upon averaging over the angles θ, θ_1, we obtain

$$\overline{V}_{MM} = \frac{4K}{r^s} \frac{(1+2\alpha)^{s-3}-(1-2\alpha)^{s-3}-2(1-4\alpha^2)^{s-3}}{4\alpha^2(s-2)(s-3)(1-4\alpha^2)^{s-3}} .$$

If we construct the relation of $\overline{V}_{MM}$ to r using the known parameters K and s of the effective interatomic potential, we can then choose values K* and s* such that this relation will be described by a potential function of the form $V^* = K^*/r^{s^*}$ with sufficient accuracy in the given energy range. It is precisely these parameters, K* and s*, that are given in Table III for the systems N_2-N_2, CH_4-CH_4, and CF_4-CF_4.

One can hardly overestimate the effectiveness of the method of fast-particle scattering as a means of studying repulsion forces. However, the existence of the material given in Table III apparently does not give us reasons to think that the afforded possibilities have been fully realized. It is expedient here to discuss briefly the possible inaccuracies in the results shown.

The results could be tested by comparing them with analogous results of other authors. Unfortunately, this is not yet possible; the old results obtained in [124] differ greatly from those given in the table, as was stated above. An indirect method of test is the "joining" of the potential curves extrapolated to great distances with those obtained at normal temperatures. However, according to [125], this method cannot be considered to be unambiguous and sufficiently validated. Another method of test consists in comparison with the theoretical variation of the potential curves calculated for the simplest systems; here [126] one finds that the experimental values are much lower than the theoretical values for small distances.

We should point out the basic sources of the possible experimental errors of these measurements. One of them is that the value of the resolving power of the apparatus is not well enough defined.

Owing to insufficient localization of the scattering region, the geometric aperture in these experiments was not equal to the resolving power, and the effective resolving power was determined by a complex calculation, in which one must use the values of the parameters K and s [110] being determined. It is

precisely to attempts to eliminate this defect that a new series of studies has been devoted,[109] involving the redetermination of the potential parameters.

Obviously, this defect fundamentally explains the difference between the results obtained with narrow and wide detectors. Another source of error in the experiments being discussed (indeed, inherent in many studies on scattering) is the uncertainty in the density of the scattering particles in the scattering chamber. There is also some uncertainty in the composition of the beam and a number of other, less essential defects. All this permits us to consider the results obtained as being only approximate. Of course, this does not diminish their value.

If we take into account these defects, and perfect the experimental technique, we can make the existing data more precise and obtain highly interesting new data, in particular, on the interactions of dissociated, electronically-excited atoms with atoms and molecules.

2. Use of the MBM to solve certain chemical problems. We shall discuss a set of studies concerned with investigation of chemical or phase transformations using the MBM. In these studies, the MBM can be used, first, for practically lag-free taking of samples, which are then analyzed by some method, and second, to study the effects of inelastic interaction of chemically-active atoms and molecules.

As has been stated, the fundamental peculiarity of a molecular beam is the lack of interaction between the particles in it. Hence, the beam taken from the source bears information on the thermodynamic and physicochemical state of the matter contained therein. If here the outflow of particles from the source does not disturb the state in the latter (and this is almost always true), then evidently such a probe will be a highly effective means of studying, e.g., the relative composition, the energy distribution of the particles in chemically-inert and active mixtures, etc. The problem of distortion of the composition of the beam with regard to that in the source has been subjected to painstaking study in a series of papers.[127]

An analysis of the early studies using the MBM is given in [128]; the possibilities of such studies have grown greatly in recent years, and we shall discuss concretely the most interesting results.

Information on the molecular composition of the vapor above the surface of solid and liquid substances and compounds is of great interest in studying the properties of the condensed phase. One can study either the equilibrium vapor or the composition of the vapor produced by evaporation from an exposed surface.[129]

In a number of cases, mass-spectroscopic analysis of the composition does not permit unequivocal conclusions on the composition of the vapor, i.e., on the partial pressures of the various components in equilibrium with the condensed phase; the heats of

evaporation also remain indeterminate. Using the MBM, we can eliminate the cited difficulties by an analysis based on precise measurements of the velocity distribution of the molecules in a beam formed by effusion from the oven at a known temperature.[130-132] Here, since the experimentally obtained distribution is a superposition of partial distributions, we can determine the composition by choosing them in such a way as to make the theoretically-calculated distribution agree with the experimental. Along with determining the molecular composition in these experiments, we can measure the evaporation coefficients and energy of dissociation of polymeric molecules in vapors (e.g., of the alkali metals).[130] Analogous measurements have been performed in [131], but indeed, with less success. At present this method of analysis is being widely applied.[129,132]

A promising possibility is to use a MB as a pulsed probe in studying the kinetics of high-temperature physicochemical transformations. In this case, by taking a beam from a region where the gas is strongly heated (to several thousand degrees) and analyzing the composition of the beam, we can directly study both the equilibrium composition and the kinetics of reactions that take place.[42] We have discussed above the particulars of construction of pulsed sources based on shock tubes; combined with a time-of-flight mass-analyzer (with a time resolution of 10—100 μsec), such an apparatus makes it possible to follow the time course of the reactions taking place. It is difficult to overestimate the merit and possibilities of this method. In using it to study the thermal decomposition of N_2O, and the polymerization and oxidation of acetylene, it has been possible to identify the intermediate reaction products and measure the rates of the individual stages of the reactions at high temperatures.[41]

Thermal ionization following a shock-wave front has been studied using a similar method.[43] The degree of ionization could be determined from the size of the current of the charged component extracted from the beam.

If we know the composition of a high-temperature gas or plasma, we can study with the MBM the energy distribution of the particles, and thus find the temperature of the gas being studied.[21,133] A method involving such an analysis of fast flows of neutral atoms from a discharge region has been developed and applied successfully in [134]. Apparently, such a method would be useful in application to shock-tube studies.

One of the most promising applications of the MB is to study the mechanism of homogeneous chemical reactions occurring upon collision of the particles of crossed beams. At present, much experimental and theoretical work is being carried out along this line, and we shall discuss some interesting results.

There is a difficulty in using the MB to study the

mechanism of chemical reactions, involving the fact that the activation energy of most reactions is ordinarily greater than the mean kinetic energy of beams of thermal velocities. Hence, in setting up an experiment, we must choose reactions having low activation energies or in some way increase the relative kinetic energies of the interacting particles. Up to now, the fundamental objects of study have been alkali and halogen atoms and their compounds, for which one can overcome the activation barrier and develop simple detectors having sufficient sensitivity.

The first study concerned with chemical interaction in crossed beams is apparently [135]. One of its basic results consists in the development of a simple selective surface-ionization detector, which made possible the separate detection of elastically and inelastically scattered particles. The activation energy of the reaction studied, $K + HBr \rightarrow KBr + H$, was calculated from the value of the yield of products at different temperatures of the K atom source, and turned out to be 3.4 ± 0.12 kcal/mole. They also found the value of the steric factor. A comparison of the measured angular distributions of the products with those calculated under various assumptions as to the reaction mechanism (complex formation) and the value of the activation energy permitted them to decide on the validity of these assumptions. This possibility is of great importance in principle, and has been a stimulus for design of further experiments.

An attempt has been made to determine directly the activation energy of the same reaction, using a monoenergetic K beam. [136] The yield of products observed at an angle of 35° in the laboratory system of coordinates showed a sharp increase with increasing relative initial kinetic energy of the colliding particles, beginning at a relative energy of 1.4 kcal/mole. It attained a maximum at 3.3 kcal/mole, and gradually declined beyond. It was possible to explain this result, incomprehensible at first glance, by the effect of kinematic collisions. [137] The point is that in analyzing experiments of this type, we must take into account the dependence of the reaction probability, as expressed by the differential reaction cross-section, both on the magnitudes of the initial and final relative velocity vectors, and on the angle between them. Hence, in measuring the effect of the reaction at a fixed angle in the laboratory system, when we change the absolute value of the initial velocity, we must take into account the change in the direction of the vector of the relative initial velocity. Neglect of this effect can result in the appearance of an observed false velocity-dependence. The calculations made in [137] permitted the interpretation of the data of [136] with the kinematic effects taken into account. Kinematically, the most suitable systems prove to be $K-CH_3I$ and $K-C_2H_5I$. For these systems, along with the reaction cross-sections, it was possible to show that the distribution of the final relative-velocity vectors is sharply anisotropic (with preferential separation of the products in a forward direction in the center-of-mass system), and that more than 80% of the reaction energy (25 kcal/mole) goes into rotational and vibrational excitation of the product molecules. The reaction yield (the total number of KI molecules divided by the total number of scattered K atoms) is of the order of 10^{-4}. This corresponds to a cross-section of about 10 Å^2. The activation energy proved to be negligibly small, being less than 0.3 kcal/mole. [138] An analogous result has also been obtained for the $Rb-CH_3I$ system. [139] The chemical reaction of a monokinetic beam of K atoms with an HBr beam has been recently studied in [140]. Measurements of the reaction cross-section for various velocities of the K beam gave a value of the energy threshold of the reaction of 0.4 kcal/mole, and showed a weak velocity-dependence of this cross-section up to relative energies of the order of 4.5 kcal/mole. The reaction probability was estimated in relation to the impact parameter b, and it turned out that when b is less than 3.5 Å, 90% of the collisions lead to reaction. The reaction cross-section beyond the threshold amounts to 34 Å^2 according to the estimate. The authors explained the difference of the measured activation energy from that in [136] by the more refined method of varying the relative energies of collision. We might point out that it is very close in magnitude to that measured in the $K-CH_3I$ and $K-C_2H_5I$ systems. [138] The possibility of chemical reaction in the $K-Cl_2$ system was noted in [141]. A reaction of the atoms of a K beam was found in [13] upon intersection with beams of $HgCl_2$, $HgBr_2$, HgI_2, and SnI_4, but the reaction cross-sections could not be determined.

The fundamental information obtained in experiments with crossed beams consists in the angular distribution of the elastically and inelastically scattered particles and the relation of the yield (total and "differential") of the reaction products to the velocity of the colliding partners. These data can be used to ascertain the details of the reaction mechanism whenever, on the basis of a concrete model, we can theoretically calculate the angular dependence of the products and select the model-dependent parameters in such a way as to obtain the necessary agreement with the experimental curve. Such calculations, based on the laws of conservation of momentum and energy, have been carried out for the reaction $K + HBr \rightarrow KBr + H$ in crossed beams having a Maxwellian velocity distribution under various assumptions as to the relation of the reaction cross-section to the relative energy of collision. [142] The use of monokinetic beams and of heavy particles in the perpendicular beam greatly simplify the treatment. However, a difficulty remains even in this case, due to a certain indeterminacy of the impact parameters of collision and to internal excitation

of the reaction products. Obviously, the complexity of the interpretation of the experimental data in no way diminishes the value of this method of studying elementary chemical reactions.

We should pay some attention to a recently [143] proposed modification of the crossed-beam method. Here a beam of chemically-active particles is passed through a chamber filled with a gas that can react with it. Owing to the "pumping action" of the molecular beam, as manifested in the entrainment of gas molecules out of the chamber, the reaction products pass into the ionizer of a mass spectrograph. Using this method, [143] a preliminary study has been made of the reaction of electronically-excited oxygen atoms (the beam) with nitrogen dioxide (the target). The oxygen-atom source was a tube through which a high-frequency electrodeless discharge was passed.

The method under discussion is highly promising, but it will require further refinement and elimination of some uncertainties still inherent in it for obtaining of reliable quantitative data.

The experiments carried out thus far with crossed beams have been seriously limited in their possibilities by the method of detection used (surface ionization). The use of sensitive universal detectors in combination with mass-analyzers will widen considerably the range of deflection angles in which the products can be observed, since the background of elastically-scattered particles will have no effect. The molecular-beam ionization detector described in [144], in combination with a quadrupole mass-analyzer, shows great possibilities. Its high sensitivity and small dimensions make it very convenient in these experiments.

It may prove effective to use the above-described methods of modulation and time-of-flight selection. In the latter case, the time variation of the ion current of the products, with synchronous measurement of the elastically-scattered particles, will permit us to determine the velocity of the reaction products. Thus, another quantity in the energy balance will become known, and naturally, this will simplify the interpretation of the data.

Considering the progress in the technique of obtaining and detecting beams, we can assume that a considerable expansion of studies along this line will occur very soon. In conclusion, we should mention the great possibilities, thus far unused, of studying the reactions of photoexcited atoms. The realization of these experiments is becoming possible in connection with the recent development of powerful pulsed light sources.

3. **Use of molecular beams to study the phenomena accompanying effusion into a vacuum.** The development of the gas-dynamic source described above has made it possible to study experimentally the gas-dynamic and physical processes that accompany the abrupt expansion of a gas into a vacuum.

Thus, in [21] a MB generated by a gas-dynamic source was used to study the deactivation of the internal (rotational and vibrational) degrees of freedom of the molecules upon expansion of a jet into a vacuum.

The first experiments of this sort were performed as early as 1950, [145] but in [21], the effect was detected in a more indirect fashion by comparing the measured velocities of the beam particles with those calculated under the assumptions of total or partial deactivation. They showed that the deactivation is not complete at low supply pressures with heavy molecular gases (UF_6), in distinction from CO_2.

The fact is well known that the composition of the gas in the beam differs somewhat from that in an effusion source, and can be explained by the dependence of the probability of passage through the aperture on the absolute value of the thermal velocity of the particle. However, in studying the characteristics of a gas-dynamic source, Becker[146] found a sharp increase in the intensity of the obtained beam, incomprehensible at first glance, when a gas mixture was passed through a nozzle. We can see the enhancement effect distinctly in Fig. 18a, where the ordinate is the ratio of the beam intensities produced at the same pressure with the gas mixture and with the pure component, respectively. This effect, which is essentially equivalent to an increase in the mass passing through the collimating aperture, can be explained by the separation of the gas components in the supersonic jet, and the increase in the relative amount of the additive component. In other words, it can be explained by the fact that, owing to the spatial separation basically caused by the difference in thermal velocities, the core of the supersonic flow (from which the MB is formed) proves to be enriched in the heavy component, and the peripheral part in the light component of the mixture.

According to [147], Dirac was the first to point out the possibility of separation of gas mixtures in supersonic flows. His idea amounted to the fact that one
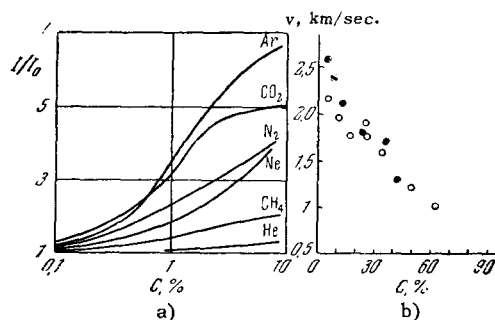

FIG. 18. The increase in the intensity when a mixture of hydrogen with other gases is used in a gas-dynamic source[146] (a); and the relation of the most probable velocity of the molecules in the beam to the initial concentration of the N_2-H_2 mixture at two pressures (b).[133]

can bring about the separating action of a gas centrifuge without any rotating parts in a jet whose lines of flow are curved. The forces that arise here can spatially separate particles of varying masses, just as occurs in a centrifuge.

The separation effect has been studied in great detail [146,148,149] in connection with attempts to develop industrial equipment for enrichment of uranium. Omitting the technical aspects of these studies, we shall briefly mention here the results of physical interest.

In studying the separation effect, it was possible to show an effect of the geometric factors on the efficiency of separation. This permitted them to a certain extent to localize the region of most intensive separation. In a study along a similar line, [147] it was possible to show the possibility of "reversing" the effect, i.e., reducing the separation as the supply pressure was increased. They found it possible in the same study to separate a mixture of particles of identical mass, but having different gas-kinetic cross-sections. The authors termed this effect "size" diffusion. In order to increase the efficiency of the separation apparatus, they studied the phenomena in additionally deflected jets. [149] Besides the enrichment of the core with the heavy component, the separation phenomenon involves another interesting effect, the acceleration of the heavy component. [150] Figure 8 shows (normalized to unity) the oscillograms obtained by the above-described time-of-flight method for a beam consisting of a mixture of 2% Ar + 98% H_2 at various pressures. The dotted lines show the oscillograms of the velocity-distribution curves for pure Ar and H_2. We see from Fig. 8 that the weak maximum for the mixture corresponds to the most probable velocity for hydrogen, and the other maximum to some velocity appreciably greater than the most probable velocity for Ar. Obviously, it can be explained only by the appearance in the beam of fast Ar atoms (accelerated somehow). Interestingly, in spite of the low Ar content in the original mixture, the major part of the ion-current pulse as a function of time (see Fig. 8) corresponds to argon atoms. The author [133] has obtained an analogous result; Fig. 18b shows the relation of the most probable velocity in the beam to the initial concentration in an N_2-H_2 mixture. Evidently, the acceleration of the heavy component even facilitates the abovementioned increase in its passage through the collimating aperture. Qualitatively, the acceleration can be explained by the fact that the particles of the heavy component are "dragged" by the jet, which moves with the mean velocity of its bulk movement.

The separation effect and its concomitant acceleration of the heavy component can considerably extend the possibilities of the gas-dynamic MB source. Thus, the author has been able to obtain with these effects fast (up to 2 km/sec) beams of Ar, CO, N_2,

O_2, etc., with intensities about three orders of magnitude greater than that from an effusion source under analogous conditions. It is pertinent to note here that a velocity of about 2 km/sec corresponds, e.g., for Ar, to the mean velocity at a temperature of the order of 10^4 °K, i.e., to an energy of the order of 1 eV. Preliminary heating of the mixture to temperatures of the order of 2000°K can make it possible to obtain intense beams with energies of 3—5 eV; the use of a high-frequency electrodeless discharge is promising here. The acceleration effect can be successfully used in studying chemical reactions, since by acceleration we can attain the energy necessary to surmount the activation barrier.

Of undoubted interest is the possibility of using the MBM to study the process of condensation. [22,23,146] Here a gas that has been previously cooled (using liquid helium or nitrogen) is expanded in a nozzle serving as the first stage in a gas-dynamic source. The composition of the beam produced was mass-analyzed, and the presence was shown in the mass spectrum of "aggregates" consisting of 2—7 molecules, in addition to individual molecules. [151] Prior to this mass analysis, conclusions had been made on this "adhesion" effect from the sharp increase in the intensity of the beam and the changes in the velocity distribution. [22,146] The measured flow density for a beam of chilled hydrogen exceeded 10^{19} molecules/cm^{2}sec. This is two orders of magnitude greater than the maximum intensity for effusion at room temperature.

A beam of condensing particles is characterized by its low tendency to spread. This is of great value in methodology, as it permits us to maintain a high flow density at great distances from the source. In using mixtures of condensing and non-condensing gases (e.g., N_2 and H_2), a considerable increase in the beam intensity has been observed, as might be expected. Thus, for a mixture 20% N_2 + 80% H_2, the intensity rose thirtyfold in comparison with pure nitrogen at the same pressure. The enrichment of the beam in the heavy condensing particles had the result, e.g., that for an initial mixture 25% H_2 = 75% He, the beam proved to consist of 98.4% hydrogen.

The possibility of obtaining intense beams containing these "aggregates" affords a highly interesting physical object to experimenters working in the region of the liquid state. It is of great interest to study the structure and binding energies of these formations. Such beams also have a certain value as dense gaseous targets and in connection with the problem of injection of fast particles into magnetic traps, since, as is shown in [151], such complexes of particles can be ionized and accelerated.

4. Study of the interaction of molecules with a solid surface. The study of the problem of interaction with a surface has been conducted by various methods for a long time. Here we can consider an ideal ex-

perimental setup to be one in which we detect directly the effect of interaction of a beam of monokinetic particles with a surface having a well-controlled state; the MBM makes possible the closest approach to the realization of this.

The use of the MBM here entails a considerable improvement in the experimental conditions, which is sometimes of fundamental importance in this problem, and makes it possible to simplify the interpretation of the results obtained. The use of the MB in these problems is highly effective from the standpoint of detection, since practically all the particles in the beam participate in the interaction. Hence the useful signal itself will be larger. The study of the phenomenon of diffraction of molecular beams by crystalline planes has already clearly demonstrated the great possibilities of the MBM.

Both in the past and now, much attention has been paid to studying the interaction of beams of metal atoms with a cold surface. Here it has been possible to demonstrate the effect of impurities and of the cleanness of the surface on the efficiency of the process of condensation of the particles of the beam, the laws of migration of the atoms in the deposit, and the structure of the deposit. A detailed analysis of the existing material can be found in [57,152-155].

In the motion of bodies through the upper layers of the atmosphere, their surfaces are subjected to the intensive action of the impinging flow of molecules. This action determines the braking and heating of flying devices.

Among the phenomena that are of interest in this regard and can be successfully studied by the MBM, there are, in particular: (1) the reflection, scattering, and adsorption of impinging particles, (2) the energy exchange between the flow of impinging particles and the surface of the body, (3) the deactivation of excited particles upon collision, surface recombination of atoms and molecules, and of ionized particles to give neutral ones, and the nature of the energy redistribution involved, and (4) the inverse problem of excitation of internal degrees of freedom upon collision, surface dissociation and ionization.

The first studies on the reflection of molecular beams from a surface are the abovementioned studies of Stern. Subsequently, a number of studies have been performed showing that "specular" (diffraction) reflection from a cleavage plane of an LiF crystal is possible only for a very small number of gases (exclusively the light ones). The growing interest in this phenomenon, aroused by the success of the high-altitude flights, has led in recent years to the renewal of intensive work of this problem. Generally one characterizes reflection quantitatively in terms of two quantities, the coefficient of diffuseness f and of specularity (1 − f), in accord with the qualitative notion that one can divide particles into those reflected diffusely and those reflected specularly (with-

out loss of speed). Using these coefficients (along with the coefficient of accommodation α), one can find the aerodynamic characteristics of bodies of practically any shape, and in turn make the best choice among them.

However, this simple qualitative model of the interaction of molecules with a surface, which originally arose only as a working hypothesis, certainly requires testing and corroboration. For this purpose, a new study [154] has been made of the reflection of He and Ar beams from the cleavage plane of an LiF crystal. The results obtained for He completely agree with Stern's results, and some new details were found. However, for Ar it was shown that there are no signs of diffraction at all, and that one cannot construct the scattering diagram by superposition of fluxes of diffusely and specularly reflected particles. Thus, these results do not confirm the hypothesis of diffuse and specular reflection.

References [62,155-157] are also concerned with the testing of this hypothesis; in the latter studies, in particular, they determined the numerical values of the momentum-exchange coefficients, which are the most adequate macroscopic characteristics of the interaction. These coefficients are defined as follows:

$$\sigma_{n,t} = \frac{\Pi_i - \Pi_r}{\Pi_i - \Pi_w} \, ,$$

where Π_i and Π_r are the momenta, either tangential (t) or normal (n), brought in by the incident molecules, or carried away by the reflected ones. The experimental measurement of the angular distribution of the beam molecules reflected from the surface permits us to calculate the numerical values of σ_n and σ_t. The results obtained indicate that σ_n and σ_t can deviate from the values corresponding to the idealized situation, and that the classification of the particles into those reflected diffusely and specularly is not unequivocal. There are grounds to suppose that the numerical values of these coefficients can depend on the absolute value of the velocity of the incident particles. Hence, in obtaining data applicable to aerodynamic problems, we should carry out the experiments of this sort with beams of velocities as close as possible to the actual velocities. We can achieve this, e.g., by using the fast-beam source proposed in [29]. Interesting observations on the laws of reflection of a beam of molecular hydrogen from a tungsten surface have been made in [159]. Here they were able to find the interesting fact, seemingly important from the standpoint of practical application, that the nature of the reflection changes markedly as the surface temperature is varied. It turns out that, as they increased the temperature of the reflecting surface to 2200°C, the completely diffuse distribution of the reflected flux is transformed into a distribution having a distinctly marked directionality, or preferential direction of departure of the reflected particles. This phenomenon took place at lower tem-

peratures (500—800°C) for other materials as well. The author has also observed analogous effects.[157] Thus, a tentative conclusion from the results under discussion might be that the concept of diffuse and specular reflection is inapplicable. Furthermore, the studies carried out distinctly showed the necessity of a great improvement in the vacuum conditions of the experiment.

The energy exchange of particles with a surface is generally characterized by a quantity, the accommodation coefficient, measuring the readjustment of the mean energy of the reflected particles to the value corresponding to the temperature of the surface. Obviously, the mathematical expression for this coefficient will depend on whether the gas is considered to be in motion or not. However, the numerical value, which is determined by the amount of energy lost on the average by an individual particle upon collision, is between unity (complete readjustment) and zero (no energy exchange). Very many studies have been devoted to measuring this coefficient, and practically all of them have been carried out by the so-called "heated" filament method.[160] A detailed analysis of this method and the data obtained can be found in[160-162].

However, a number of defects are inherent in this method,[163] and these can be eliminated by use of the MBM.

Here two methods of measurement are possible. First, by using a mechanical selector, we can study the velocity distribution of the particles reflected from the surface,[164] and if we know the velocity of the incident particles, we can calculate the accommodation coefficient. Using an Na beam, this method has made it possible to demonstrate over the temperature range 500—2000°K that complete accommodation occurs at metal surfaces (Cu, Al, W, MgO) and incomplete accommodation at an LiF crystal surface ($\alpha = 0.7 \pm 0.1$).

In another variant of using the MBM,[163] a monokinetic beam of known velocity is directed at a surface, and the mean velocity of the reflected particles is determined from the time of flight. In this variant, one can directly measure also the times that the molecules spend on the surfaces, provided that they happen to be comparable with the time of flight of the particles from the surface to the detector.[47]

Measurements made by the author have shown that for beams of N_2, CO_2, and Ar of energies ~1.0 eV, capture takes place at metallic surfaces (Cu, Fe, Ta), and the measured lifetimes of the captured particles on the surface amount to tens (10—30) of microseconds.

Along with its obvious value in applications, the study of energy exchange of molecules with a solid body is of independent interest from the standpoint of testing theoretical ideas on this phenomenon.

The theoretical analysis of this phenomenon was largely carried out in the period up to the forties, and has been summarized in a review article by Frenkel'.[165] This analysis leads to two limiting cases: one of them is equivalent to elastic collision of the incident atom with an individual atom of the surface, and the other to impact excitation of an oscillator that approximates the normal vibrations of the crystal structure. The existing experimental data agree poorly with the second possibility, while the elastic system is thoroughly valid only at very large relative energies of collision. Thus the methods of theoretical description of the phenomenon need to be improved, and the basic ways to improve them are noted in the cited reference by Frenkel. In particular, one of the possibilities involves considering the effect of collision of an atom or molecule with a linear chain (or lattice) of elastically (or otherwise) linked atoms, which is a more adequate model of a solid. The results of such a calculation can provide both the energy threshold for capture of the incident particle and the relation of the energy of the reflected particle to its initial energy. An attempt to solve this problem analytically has been made in[166-167].

An experimental study of the interaction of chemically-active atoms (H, O) with a solid surface has been carried out using a modulated beam in[168,62]. In these studies, the particles reflected from the surface were mass-analyzed, and since the ionization cross-sections were known, this permitted quantitative estimates of the fraction of the particles recombining at the surface. In addition, they could estimate an upper limit for the fraction of the dissociation energy borne away by the particles recombining at the surface. In particular,[62] for atomic hydrogen they bear away only 3% of the energy liberated in recombination, while 97% is transferred to the surface. In[168] the temperature-dependence of the probability of recombination of atomic hydrogen at a copper surface was studied in the range 4—100°K. They found a sharp increase in the probability of reflection of atomic hydrogen and deuterium at temperatures of about 4° and 6.5°K, respectively, with a subsequent steep decline at lower temperatures. However, the interpretation of these measurements is hindered, along with other factors, also by the fact that the effective surface varies in nature with varying temperature, owing to condensation of the residual gases. Gradual decrease in temperature involves the formation on the studied copper surface of successive layers of ice, frozen nitrogen, oxygen, and molecular hydrogen. They also studied the condensation on a surface of beams of the molecular gases H_2, N_2, O_2, and H_2O.[168] The use of the MBM involves alluring possibilities of studying inelastic processes in collisions with a surface.

At present, for example, the study of the deactivation of electronically-excited particles at a wall is of great interest. This phenomenon can be studied

experimentally by using beams produced from a gas that has passed through a high-frequency electrodeless discharge. Here we can obtain the necessary information by measuring the ionization curves for the direct beam and that reflected from the surface.

An inelastic process at a surface widely studied by the MBM is surface ionization, which has been discussed in [170,171].

In the problem under discussion here, the study of process of adsorption interaction of molecules with a surface occupies an important place. However, the progress in this field has been greatly limited by the defects in the traditional methods. The MBM provides the experimenter with a powerful means of studying this problem, as it affords the important feature of working in as high a vacuum as possible, i.e., with as clean surfaces as possible. The results of[169] are of great interest in this regard. This study was concerned with the designing and building of an apparatus permitting one to study with an MB the effects of adsorption interaction in a vacuum of the order of 10^{-10} mm Hg.

Intensive growth has occurred in recent years, both in the technique of the molecular-beam method, and in the possibilities of applying it to advantage. The advances in the field of technique and the results of applying the method indicate how promising it is, and that it is absolutely necessary to include this method in the arsenal of experimental means of solving the problems of molecular physics.

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