RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

December 1966

U. D. C. 531.1 : 532.74

THE STUDY OF ELEMENTARY CHEMICAL REACTIONS BY THE MOLECULAR BEAM METHOD

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I. INTRODUCTION

In 1955 a paper[1] was published, demonstrating convincingly for the first time the real possibility of studying chemical reactions accompanying the collision of the molecules of two intersecting beams. It is no exaggeration to say that the publication of this paper opened up a new stage in studies of the mechanism of bimolecular gas reactions and originated a new line of research.

This review examines the present position and some immediate prospects in the use of intersecting molecular beams to study the mechanism of bimolecular gas reactions.

Section I gives a general picture of the molecular beam method, presents some theoretical concepts used in the examination of kinetic problems within the framework of collision theory, and finally discusses the analogy between collisions leading to chemical changes and those responsible for ordinary transfer phenomena in gases.

Section II, after a brief discussion of the experimental technique, describes the chief methods used in the analysis and interpretation of the experimental data.

The concluding Section III is devoted to a detailed examination of the chief experimental results obtained by molecular beam studies of some bimolecular chemical reactions.

Most chemical processes are complex multistage reactions, and only a relatively small proportion correspond to single-stage elementary reactions. It is obvious, however, that each stage in a complex process can in a certain sense be regarded as an elementary reaction, and study of the elementary reactions can in principle lead to a better understanding of the characteristic features of the process as a whole. This explains why in chemical kinetics there is great interest in the study of elementary chemical reactions, of which bimolecular reactions form the most commonly encountered class. The subsequent discussion deals chiefly with these reactions.

One of the main tasks in chemical kinetics is to determine the principal conditions (energetic, configurational, etc.) which must be satisfied by molecules if a chemical reaction is to take place between them. This must be regarded as the fundamental problem, since the frequency with which these conditions are realised in molecular collisions influences the rate of the process and at the same time is comparatively readily determined by familiar methods within the framework of equilibrium statistics, whose applicability is generally assumed.

On the other hand, if the equilibrium approximation is inapplicable, the problem of finding the perturbed distribution functions will also include in the initial stage the determination of the chief microscopic conditions for reaction to take place on collision of the molecules.

The classical methods of kinetic studies[2] cannot take us beyond the limits of the phenomenological Arrhenius equation, leaving to the research worker a considerable degree of freedom in the interpretation of the intimate details of the mechanism of the reaction being studied. Since the activation energy and the steric factor are found by effective statistical averaging over a large number of energy

states and the corresponding collision parameters, these characteristics are insufficient for a complete understanding of the elementary act in a chemical change. Thus there is no guarantee even that theories which provide an obviously correct description of reaction rates are based on correct original hypotheses regarding the mechanism of the elementary process.

This situation makes it extremely desirable to develop and use kinetic methods which are free from this uncertainty. The molecular beam method[3] satisfies these requirements, since, in addition to specifying the translational energy of the colliding particles, it also permits the selection of definite internal stages. In the ideal case it enables a chemical reaction to be conducted with complete control of the energy states and even of the orientations of the reacting molecules.

The molecular beam method is based on the use of a beam of atoms or molecules, produced by a suitable method, as a subject for study, either immediately after its production (in this case the particles of the beam "carry" information on the thermodynamic and physicochemical state of the gas in the formation region) or after the beam has been acted on in some way. The nature of the action on the particles of the beam and the methods used may vary: in all cases — irradiation with a beam of light, reflection from a solid surface, the action of electric or magnetic fields, collision with particles of another beam, etc. — we obtain information on the effects produced by the action. The importance of the molecular beam method in chemical studies is that it is possible in an experiment to record the direct effect of a fairly exactly localised interaction between particles capable of undergoing reaction, so that the effect is not obscured by side reactions or, as is often the case in chemical processes, competing reactions. It is thus possible to isolate an elementary process and to study it over a wide range of controlled collision energies; the localisation of the collision region effectively frees the reaction from the influence of the walls of the reaction vessel. A fairly detailed discussion of the possible applications of the molecular beam method can be found in recent reviews[3-5], and this makes it possible to restrict the present review to a discussion of studies of bimolecular gas reactions.

The ideal arrangement for an experiment to study chemical interaction between molecules corresponds to the use of two intersecting collimated beams homogeneous with respect to velocity, or of one such beam passing through a layer of relatively immobile molecules in a bombarded target. In these cases the emission of the reaction products can be observed within a very narrow range of angles about a certain direction determined by the kinematic conditions to be examined below.

The quantity of reaction products makes it possible to determine the reaction probability or cross-section, and variation of the velocities and internal energies of the particles permits the dependence of the cross-section on these parameters to be found. The position of the maximum and the width of the angular distribution of the products enable in some cases conclusions to be drawn regarding the nature of the distribution between the products of the energy liberated in the reaction, or conclusions regarding the lifetime of the intermediate complex. It is also possible to determine directly the internal energy of the reaction products and the spectrum of their velocities. Thus the extent to which the equilibrium distribution is broken down by the chemical reaction can be established. The reaction products can in turn be used as a beam for secondary scattering.

These are the basic possibilities of the molecular beam method. The level of experimental technique employed does not always permit us to realise them completely. As will be subsequently seen, however, even partial utilisation of these possibilities has enabled us to observe reaction-mechanism details which are quite inaccessible by ordinary methods. The continuous development of experimental technique in the last ten years is bringing these experiments closer to the ideal.

What is the relationship between the microcharacteristics of a chemical reaction (cross-section, threshold energy), determined in experiments with intersecting beams (the same characteristics are obtained in the theoretical analysis of elementary processes), and parameters such as, for example, the rate constant and the activation energy? This question is part of the more general question of the relationship between the microscopic and the macroscopic properties of gaseous systems. It is useful to follow this relationship and to recognise the main assumptions necessary for unambiguous conversion from one set of parameters to the other. Following Eliason and Hirschfelder[6], let us consider a reaction of the type A + B → C + D, taking place in a gas exhibiting a certain distribution of translational and internal energies. By analogy with the analysis of transport in a gas (there is an extremely sound basis for this analogy), it is convenient to regard particles with different internal states (characterised symbolically by the quantum numbers i, j, k, and l) as separate components. This approach is further justified by the fact that intuition suggests that the reactivity should depend on the internal state of the collision partners.

The partial rate of a reaction of the type $A_i + B_j \rightarrow C_k + D_l$ is given by the usual relationship

$$\left(-\frac{dn_{A_i}}{dt}\right)_{ijkl} = k_{ij}^{kl}(T)\, n_{A_i} n_{B_j}, \qquad (1)$$

where n_{A_i} and n_{B_j} are the densities of the molecules A_i and B_j, and $k_{ij}^{kl}(T)$ is the partial rate constant. The overall rate of the chemical reaction (A + B → C + D) measured in kinetic experiments will then be the sum of the partial rates:

$$\left(-\frac{dn_A}{dt}\right) = \sum_{ij}\sum_{kl} k_{ij}^{kl}(T)\, n_{A_i} n_{B_j}. \qquad (2)$$

From kinetic theory, equating the partial reaction rate to the number of collisions leading to reaction[2], we can readily obtain the following relationship in the classical approximation

$$k_{ij}^{kl} = \iiiint f_{A_i} f_{B_j} \overline{I}_{ij}^{kl}(E, 0\varphi)\, g_{ij} \sin\theta\, d\theta\, d\varphi\, dv_{A_i}\, dv_{B_j}, \qquad (3)$$

where f_{A_i} and f_{B_j} are the normalised distribution functions for the velocities $\mathbf{v}_{A_i}$ and $\mathbf{v}_{B_j}$, and $\overline{I}_{ij}^{kl}(E, \theta, \varphi)$ is the differential cross-section for the collision of molecules in states i and j with relative energy E, leading to the formation of product molecules in states k and l, moving at angles θ and φ to the direction of the relative initial velocity g_{ij}. Since in expression (3) only $\overline{I}_{ij}^{kl}(E, \theta, \varphi)$ depends on the angles θ and φ, we can, by integrating with respect to the angles, obtain a new quantity $C_{ij}^{kl}(E)$ — the so-called total reaction cross-section

$$C_{ij}^{kl} = \iint \overline{I}_{ij}^{kl}(E, 0, \varphi) \sin\theta\, d\theta\, d\varphi. \qquad (4)$$

In principle, these two quantities (C_{ij}^{kl} and $\overline{I}_{ij}^{kl}$) represent the final results of both theoretical (quantum-mechanical or classical) calculations and experiments with intersecting beams.

The relationship between these microscopic characteristics and the reaction rate (2) is conveniently followed from the diagram[6] (Fig. 1). If the quantity $P_{ij}^{kl}(E, b, \eta, \theta, \varphi, K)$ is the probability that the collision of molecules of types A_i and B_j (involving the formation of a quasi-molecule with a set of quantum numbers K), with initial impact parameter b, azimuthal angle η, and relative energy E, will lead to the production of molecules C_k and D_l, moving at angles of θ and φ in the [coordinate] system of the centre of mass, the diagram shows the possible routes from the quantity $P_{ij}^{kl}(E, b, \eta, \theta, \varphi, K)$ to the rate constant for the reaction $A + B \rightarrow C + D$. It can be seen from Fig. 1 that in the first stage the corresponding averaging can be carried out in three ways — with respect to the values of K, the initial parameters b and η, and the final parameters θ and φ — each arrow in the diagram representing the successive procedure of averaging with respect to the quantities which are not present in the argument to which the arrow points (the use of arrows is of fundamental significance, since movement in the opposite direction is generally associated with ambiguity). This ambiguity is the main obstacle to verification of the correctness of the original theoretical models by means of ordinary kinetic data. The limited nature of the information on reaction mechanism contained in the averaged quantity $k(T)$ is thus fairly obvious.

The value of the molecular beam method when applied to chemical problems is related to the possibility of studying the mechanisms of the elementary processes corresponding to the lower branches of the diagram in Fig. 1. The unique achievements of the method are that the results obtained on the one hand stimulate the theoretical solution of the problem of the elementary act in a chemical transformation and on the other create the necessary basis for solution of the statistical problem of determining the perturbations of the equilibrium distribution function resulting from the chemical process. The particular solution of the statistical problem for the non-equilibrium situation is associated with the names of Chapman and Enskog, who examined the phenomenon of molecular transport in gases.

There is a very close analogy between the description of the rate of a chemical reaction in a gas and the description of transport phenomena (i.e. viscosity, thermal conductivity, diffusion, etc.)[7]. Before the publication of the well-known studies by Chapman and Enskog[8], the study of transport phenomena was of a particularly phenomenological character, whose defects have become especially clear in recent years. Within the framework of this approach it was almost impossible to predict the behaviour of a substance under conditions differing from those under which the experiment was carried out. The requirements of the technique, which penetrated into a range of temperatures which could not be reproduced in laboratory equipment, emphasised still further the limited nature of this approach (the situation was aggravated by the possibility of dissociation of the gas at high temperatures).

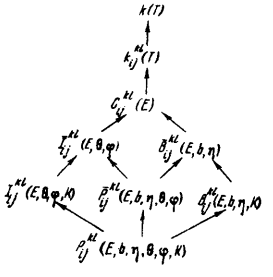


Fig. 1. Diagram illustrating the relationship between the microscopic and the macroscopic characteristics of a chemical transformation.

Chapman and Enskog reduced the description of transport phenomena in monatomic gases to a single basis — the intermolecular forces — and, for a known law of variation in these forces with distance, the determination of the kinetic coefficients became a comparatively simple computational problem. In this way the emphasis in the study of the kinetic properties of gases is being transferred to the problem of determining intermolecular forces[9]. It is extremely tempting to arrive at a similar situation in chemical problems; the immense number of possible collision partners and the limited range of attainable temperatures in this case also lead quite naturally to the necessity for finding a single basis for the description of the phenomena of chemical interaction. In this sense the transition-state theory plays a part which is in some ways analogous to the microscopic approach to the description of transport phenomena. Within the range of applicability of the corresponding approximations, the kinetics of a chemical reaction to a considerable extent reduces to a simple (from the physical viewpoint) basis — the intermolecular forces between the approaching particles. Although in the case of chemical kinetics it cannot yet be said that the main emphasis of research should be transferred entirely to the study of intermolecular forces, there is no doubt that, for reactions with a high energy threshold, studies at this level will be fruitful. Until recently, the only and insufficiently reliable source of information on intermolecular forces for chemically interacting partners was the so-called semi-empirical method of Eyring. The use of the molecular beam method combined with fast computers is opening up another source of such information. This possibility is of great promise and is discussed in Section III.

II. TECHNICAL REALISATION AND INTERPRETATION OF EXPERIMENTS WITH MOLECULAR BEAMS

Since a recent paper[3] described in detail the present state of the experimental technique of the molecular beam method, we shall restrict ourselves to an examination of certain fundamental elements of the technique of working with intersecting beams and the most recent achievements in this field.

As noted above, the chief advantage of the molecular beam method is that it permits control of the energies of the interacting molecules. The only method for isolating particles with a fixed velocity from the beam is by using mechanical selectors[3]. When both beams consist of particles with a fixed velocity, however, there is a sharp decrease in the intensity of the recording signal of the reaction products, and the situation is aggravated by the need to synchronise the arrival of the particles in the region where the beams intersect. At present, therefore, the use of selectors is restricted to one of the beams[10], and quantitative allowance can be made for the scatter thus preserved in the relative collision energies, by analysing the velocities of the products by means of a second velocity

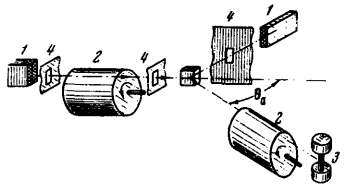


Fig. 2. Diagram of a typical experimental assembly for studying chemical reactions in intersecting beams with thermal velocities:
1) beam sources; 2) mechanical selectors for isolating particles with a given velocity; 3) movable receiver for recording both elastically scattered molecules and reaction products; 4) collimating slits.

selector. This modification must at present be regarded as representing the best arrangement for an experiment with intersecting beams (Fig. 2).

A simple method for ensuring that the collisions being studied involve beams of particles with fixed velocities is to use beams of relatively high energy (10–1000 eV), passing through a gas target, whose molecules can be regarded as virtually stationary. High-energy beams are usually produced[3] by neutralising ion beams which have been brought to fixed velocities electrostatically. An assembly has been described[11] for obtaining fast beams of almost any active atoms, radicals, or molecules in the energy range 600–4000 eV. A typical example of the use of high-energy ion beams can be found in a study[12] of the reaction $N_2^+ + D_2 \rightarrow N_2D^+ + D$.

The number of reactions which can be studied at present is limited by the necessity of ensuring that the particles of the intersecting beams have a relative collision energy greater than the energy thresholds of the reaction. Another restriction is imposed by the method of recording. The most widely used product detector is the differential surface-ionisation detector[1]. The use of this phenomenon for recording obviously limits the possible reaction products to compounds containing alkali-metal atoms. Thus the reactions which have been most extensively studied are those in which one of the partners is potassium, caesium, or rubidium (or, less satisfactorily, lithium or sodium).

This restriction can be overcome by using universal ionisation detectors[3], in which the molecules being studied are ionised by electron impact. Positive ions can be collected by a collector and measured by standard methods. A recently proposed modification[13] uses neutralisation of the space charge in a diode by the positive ions. When ionisation by electron impact is used, the possibility of dissociation must be borne in mind. Partial allowance for this effect can be made by mass-spectrometric observation of the products.

The universality of ionisation detectors is also a weakness, since the total recording signal is influenced not only by the reaction products but also by the residual gases and particles which have undergone elastic scattering. The influence of the residual-gas background in a laboratory apparatus cannot always be eliminated by improving the vacuum conditions; an effective method of reducing this effect is to modulate the beam and record only the modulated component of the detector current[3]. There still remains, however, the difficulty of recording the products in the region of the "shadow" of the original beam, since it is impossible to separate the currents from the elastically scattered molecules and possible reaction products. This difficulty can be overcome by fitting the receiver with an additional mass filter. A device for selecting ions according to mass can be constructed using either a static magnetic field[14] or the high-frequency electrostatic field of a quadrupole lens[15]. Analysers of the time-of-flight and radio-frequency types also have certain advantages, but when these are used it is more difficult to eliminate the influence of the residual-gas background. The most convenient for these purposes are analysers of the quadrupole type[15,16], which have a high transparency (low ion loss), effective resolution over a wide range of mass numbers and small size. Thus an instrument has been described[16] which makes it possible to record simultaneously ion currents differing by 8 orders of magnitude. These possibilities are of particular interest in connection with the prospects provided by the use of so-called gas-dynamic sources of molecular beams[3], with which beams of heavy molecules having high velocities can be obtained; these, however, contain a certain quantity of light "runaway" gas (H_2).

Interesting possibilities related to the problems examined here are provided by making use of the action of electric and magnetic fields on the beams. The simplest involves the use of an inhomogeneous magnetic field to separate a mixed beam of original atoms and product molecules in the region of the "shadow". The original beam usually comprises paramagnetic alkali-metal atoms; the product molecules are generally diamagnetic, so that, when the mixed beam is passed through an inhomogeneous field, the deflection of the atoms makes it possible to achieve spatial separation of these components. As a result, the receiver is able to record them separately. This method has been used by Herm et al.[17]; in some cases analogous results can be obtained by velocity analysis of the mixed beam using a mechanical selector.

It is more tempting[18,19] to use an inhomogeneous electric field to analyse the rotational states of the reaction products. For a substitution reaction with a marked change in the reduced mass, the initial orbital angular momentum will be converted into the internal angular momentum of the product molecule. As a result of the law of conservation of angular momentum, the rotation is polarised, since the internal momentum vector of the product molecules will coincide with the vector of the initial orbital momentum, perpendicular to the vector of the initial relative velocity. The polarisation will have a marked influence on the deflection of the molecules in an inhomogeneous electric field. Thus analysis of the rotational state of the products makes it possible to establish the influence of the initial orbital momentum on the probability of reaction on collision, i.e. to determine which orbital momenta (impact parameters) make the main contribution to the reaction cross-section. This analysis may allow[19] separation of the vibrational and rotational components of the internal energy of the products.

Let us now examine qualitatively the methods for treating the information obtained in experiments with molecular beams. The primary information obtained in an experiment is the angular distribution of the reaction products, the dependence of the yield of products (total or differential) on the relative collision energy of the particles in the beam, and finally the velocity spectrum of the products moving in a given direction. This primary information must be

interpreted on the basis of various models. In addition to direct recording of the reaction products, study of the elastic scattering of the particles of intersecting beams is also of considerable interest for obtaining the characteristics of a chemical reaction. Thus is due to the fact that the "entry" sections of the potential-energy surface of the reaction for elastic and "inelastic" scattering are the same with adiabatic reactions. Qualitative examination of the characteristic features of elastic scattering is necessary for an understanding of the material which will be presented subsequently.

The dependence on distance of the potential energy of the interaction between two spherically symmetrical particles is often described by a potential of the form

$$V(r) = \frac{\varepsilon}{1-6/\alpha}\left\{\frac{6}{\alpha}\exp\left[\alpha\left(1-\frac{r}{r_m}\right)\right]-\left(\frac{r_m}{r}\right)^6\right\}, \qquad (5)$$

where α is a parameter which makes it possible to vary the steepness of the repulsive part of the potential curve, and the significance of ϵ and r_m is clear from Fig. 3. The curve in Fig. 3 is in some cases conveniently divided into two sections — a monotonic section which can be approximated by a function of the form $V(r) = K/r^n$, and corresponds to repulsion (it defines the interaction of particles with kinetic energy $E \gg \epsilon$), and a non-monotonic section — the latter being the region of the minimum on the curve (significant for energies $E \simeq \epsilon$).

From the elementary theory of scattering[20] it is known that for particles of fixed energy the scattering angle χ depends on the impact parameter b (the smallest distance between the centres of the moving particles in the absence of interaction) and the interaction energy for distances close to that of nearest approach of the interacting particles r_0. In contrast to the case of monotonic potentials, the dependence of the angle of deflection χ on the impact parameter for non-monotonic potentials (with a minimum, see Fig. 3) is ambiguous: equal angles χ may correspond to different values of b. A typical dependence in this case is represented by the curve in Fig. 4*a* (this gives the dependence of χ on b^2, which is proportional to the cross-section of scattering at angles greater than χ). The qualitative characteristics of the experimentally observed angular distribution of the scattered particles can be obtained[21] from the curve in Fig. 4*a* by assuming that the number of particles scattered at a given angle is proportional to the quantity $db^2/d\chi = 2\sigma_T \sin\chi$. From the χ–b^2 relationship we can by differentiation readily obtain the dependence of $db^2/d\psi$ on χ (Fig. 4*b*). Although $db^2/d\chi$ and χ in Fig. 4*b* have different signs, the sense of $db^2/d\chi$ is positive, and under the actual

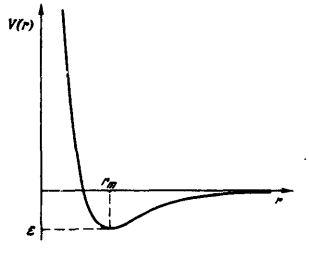


Fig. 3. Typical potential curve for the intermolecular interaction of spherically symmetrical particles.

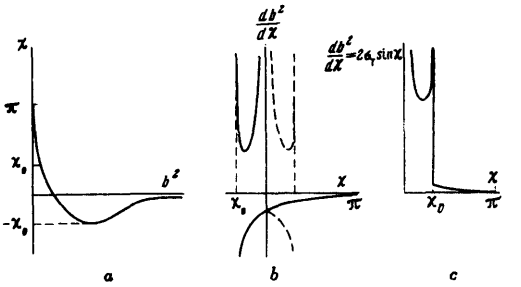


Fig. 4. Construction of the picture of elastic scattering for the interaction described by the potential shown in Fig. 3.

conditions of an experiment it is impossible to distinguish deflections to the right and to the left. Thus the observed scattering picture will correspond to Fig. 4*c*, obtained by transferring the curves (Fig. 4*b*) into the first quadrant, changing the sign, and combining the absolute values of the ordinates of the curves. The right-hand monotonic portion (Fig. 4*c*) corresponds to scattering by the repulsive forces. To study these forces it is most convenient to use the elastic scattering of fast beams of atoms and molecules[22]. Information on these forces is of interest, for example, in connection with the problem of the retardation of fast particles and their transformation into hot atoms.

An extremely useful characteristic of the scattering curve is the emission close to the angle χ_0 (it can be seen from Fig. 4*a* to be linked with the presence of the minimum on the potential curve), which is called the rainbow effect, the angle χ_0 being termed the rainbow angle. The magnitude of this angle, determined by experiment, makes it possible to find unambiguously the depth ϵ of the potential curve (Fig. 3). For non-spherical systems the position of χ_0 depends on the mutual orientation of the molecules. Firsov's discussion[21] was purely classical; quantum-mechanical treatment of this problem[23], without altering the qualitative form of the scattering curve, shifts the position of the rainbow angle slightly to the left of that shown in Fig. 4*c* and smooths out the breaks on the scattering curve. On the basis of the quantitative theory[23] it is now possible to determine from the experimental scattering curves the parameters of the potential curve for the interaction, given in a particular analytical form.

For chemical interaction, analysis of the elastic-scattering picture makes it possible to fix the distortions of the scattering curve produced by chemical effects. The magnitude of this distortion can be used[10] to find the probability of the reaction, defined by the relationship

$$P(\chi, E) = \frac{\sigma_{th}(\chi, E) - \sigma_{exp}(\chi, E)}{\sigma_{th}(\chi, E)},$$

where E and χ are the energy and angle of deflection in the [coordinate] system of the centre of mass, and σ_{th} and σ_{exp} the theoretical and experimental values of the differential cross-section of scattering of molecules with energy E at an angle χ. The value of σ_{th} can be calculated from the known potential or by using the parameters of the interaction potential, found from the initial part of the scattering curve, unperturbed by chemical reaction (Fig. 4*c*), on the assumption that this potential is also applicable to those distances of approach at which chemical reaction is possible. It is thus possible to determine the approach distances corresponding to a probability $P(\chi, E)$ different from zero,

i.e. corresponding to the development of chemical reaction, and also the dependence of P on E. It should, however, be noted that the total reaction cross-sections found from $P(\chi, E)$ are greater by a factor of 5–50 than those calculated from the total product flux. An attempt has been made[24] to analyse the possible reasons for this discrepancy, and it has been shown that the rapid descent observed on the experimental scattering curve in the range of large angles can be explained on the basis of an interaction potential in the form of a curve with two minima (the ordinary van der Waals minimum and a "chemical" minimum).

The elastic-scattering curve observed when two beams intersect can be predicted for a known potential for the intermolecular forces. In the absence of a solution to the corresponding dynamic problem, a picture of the angular scattering of the reaction products cannot be constructed in such simple fashion. Nevertheless, in some cases the laws of the conservation of energy and momentum can be used to predict the form of the distribution. Let us examine qualitatively the scheme for this calculation[25], noting that by varying its parameters (for example the dependence of the reaction cross-section on the energy) until the theoretical and experimental curves coincide, it is possible to determine the values of these parameters. Let us assume first for simplicity that the transformation taking place on collision corresponds to a hypothetical addition reaction A + B → AB, whose probability for one collision is unity (we shall not deal here with the reality of these transformations). In this case it is clear that, as a result of the law of conservation of momentum, after the "adhesion" of the particles, the complex AB in a laboratory system of coordinates will move along the vector of the velocity of the mass centre. Thus the form of the observed angular distribution of the complexes would correspond to the law governing the distribution of the vectors of the rate of movement of the mass centres of the colliding particles, and the magnitude of the beam currents would be determined by the cross-section of collision. The direction of the vector is determined by the rule for combining the particle velocity vectors $\mathbf{v}_A$ and $\mathbf{v}_B$ (Fig. 5*a*), so that the distribution of the velocity vectors of the centres of mass will depend exclusively on the distribution of the magnitudes and directions of the initial velocities of the particles in the intersecting beams. For two collimated beams with uniform velocities, the resulting distribution of the products would be needle-shaped. For collimated beams intersecting at right angles, with Maxwell velocity distribution, the distribution will be bell-shaped (Fig. 5*b*) and related unambiguously (within the limits of the assumptions made) to the bell-shaped form of the Maxwell distribution.

If the beams are poorly collimated, the form of the angular distribution will also be influenced by the scatter of the initial directions of the velocities. Anticipating a little, we may note that the indefinite nature of the interpretation, associated with poor collimation of the beam, reduces slightly the value of the information contained in the angular distribution of the products. In recent work, therefore, considerable attention is paid to the analysis of the perturbations of the elastic-scattering curve resulting from chemical interaction. If reaction does not take place at every collision (for example if the cross-section of the reaction depends on the energy), it is clear that the above bell-shaped distribution of the products will be slightly deformed by this relationship.

For the more real process A + B → C + D the distribution of the products will also depend on the masses of the products and the energy liberated in the reaction. Let us examine the simplest features of the decomposition — the formation of two product particles — in more detail[20], since a quantitative analysis of the internal energy of the products can often be carried out on the basis of only one form of angular distribution of the products.

In the system of the centre of mass, the total momentum of the system A–B is zero, and the scattering in this system will take place in such a way that the total momentum remains unchanged. In the diagram in Fig. 6, the elastic scattering corresponds to rotation of a vector of constant magnitude $\mathbf{v}'_A - \mathbf{v}'_B$, and the ends of the velocity vectors of the scattered particles for different angles of scattering lie on circles A and B with radii $\mathbf{v}'_A$ and $\mathbf{v}'_B$. With inelastic scattering the speeds of the particles of the complex AB, which decomposes in the reaction, depend on the initial kinetic energy and the energy liberated in the reaction, and also on the masses of the products C and D. If all directions of scattering of the reaction products are equally probable (this is characteristic of long-lived complexes), the ends of the velocity vectors of the products will lie on circles C and D (the C-circle is not shown) of the velocity diagram in Fig. 6, with radii $\mathbf{v}'_C$ and $\mathbf{v}'_D$ (in the three-dimensional case these circles will be represented by spheres). The directions of motion of the scattered particles in an l-system (laboratory system of coordinates) are determined by the vectors $C + \mathbf{v}'_C$ and $C + \mathbf{v}'_D$, so that products of type D will be observed within a cone whose generating lines are tangents to the D-circle of the diagram in Fig. 6. From Fig. 6 it can be seen (neglecting possible anisotropy of scattering) that the condition for the creation of a preferential direction in the recording of the products is a low rate of recoil $\mathbf{v}'_D$ compared with the speed of the mass centre of C; otherwise, the distribution will be spread out widely in space. The isotropic nature of the scattering of the products in the c-system (the system

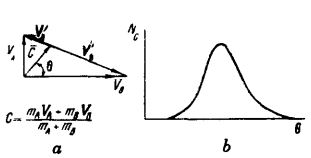


Fig. 5. *a*) Kinematic diagram giving the relationship between velocities in the laboratory coordinate system and the system of the centre of mass; *b*) form of angular distribution of the products.

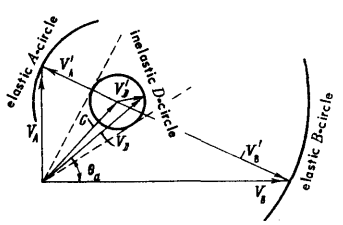


Fig. 6. Kinematic diagram describing qualitatively the main features of the emission of products in the decomposition of the quasi-molecular complex.

of the centre of mass) will be influenced to a marked extent by the lifetime of the complex AB; for schemes with a single simple scattering there should obviously be a preferential direction of scattering for the products.

Returning to Fig. 6, we can see that for isotropic scattering of the products, the compensation of the addition and subtraction of the velocities of recoil from the velocity of the mass centre causes the mean or most probable velocity measured in the l-system to coincide with the latter. For anisotropic decomposition with recoil backwards (relative to $\mathbf{v}'_B$) the velocities in the l-system will be lower than the velocity of the centre of mass, and for recoil forwards they will be higher. Thus by measuring directly the velocities of the product molecules, it is possible to solve the problem of the isotropy of scattering, i.e. the type of reaction mechanism, and also to determine the heat of the reaction $Q = E_1 - E$.

The heat of reaction Q, which is taken to equal the change in the relative kinetic energy, can be expressed

$$Q = \Delta D + \Delta E_{\text{int}},$$

where ΔD is the difference in the energies of bond rupture between reactants and product, and ΔE_{int} the difference in the internal energies of the particles in the initial and the final states. If E is the initial relative energy, the rate of recoil v'_D can be written, from the condition of conservation of energy, in the form

$$v'_D = \left[\frac{2(E+Q)}{M_D(1+M_D/M_C)}\right]^{1/2}.$$

For large positive values of Q, the speed v'_D is high, and the width of the recorded angular distribution of the products will increase considerably; on the other hand, if for a large value of ΔD the experiment reveals a narrow peak in the distribution of the products, this may provide a direct indication of a marked change in the internal energy state of the products ($\Delta D \simeq |\Delta E_{\text{int}}|$).

The value of Q can be effectively decreased only by transfer of part or all of the energy ΔD to internal degrees of freedom of the products. The nature of the angular distribution of the products is more readily used, for quantitative estimation of the fraction of ΔD transferred to internal degrees of freedom, under definite kinematic conditions, in particular for small changes in the reduced mass of the products $\mu_1 = M_C M_D/(M_C + M_D)$ relative to that of the reagents $\mu = M_A M_B/(M_A + M_B)$. In this sense, the reaction $K + HBr \rightarrow KBr + H$, which has been studied in most detail, is inconvenient for energetic analysis, since the width of the angular distribution of the products will be strongly influenced not only by Q but also by non-uniformity of the initial velocities. On the other hand, in the reaction $K + CH_3I \rightarrow KI + CH_3$, for example, these two effects are separate because of the displacement of the maximum in the product distribution from the direction of the vector of the most probable velocity of the mass centre and because of the anisotropy of the decomposition itself. The method of kinematic estimation[26] described below in Section III, while clear and effective, was used because of the imperfect nature of the experimental technique employed; it should be noted that machine calculation[27] has revealed considerable ambiguity in these estimations. Direct determination of the velocities of the products using a selector makes it possible to solve the same problem more accurately for any kinematic conditions.

In addition to the above mechanism of adhesion with subsequent isotropic decomposition of the quasi-molecule AB, use is also made of the concepts of ricochet and stripping mechanisms of interaction on collision, taken from the theory of nuclear reactions. In the first case an atom colliding with a molecule as it were ricochets, carrying away an atom from the latter. The characteristic feature of the stripping mechanism is that the colliding atom and the atom removed by it from the molecule move in a direction which coincides with the initial direction of the colliding atom. An important aspect in stripping is that the interaction of the colliding atom with the target atom takes place as though the other atoms in the molecule were not present.

These two mechanisms, unlike the first, are characterised by the existence of a correlation between the directions of the initial and final relative velocities; the products as it were "remember" the initial state. Stripping chemical reactions take place at large impact parameters, so that they have extremely large cross-sections. On the other hand, ricochet collision is possible only when the particles approach close to one another, so that the cross-sections are much smaller than those for stripping.

In this examination no allowance has been made for the angular momentum of the interacting particles. The total angular momentum (orbital plus internal) of the system should be conserved, and this will influence both the angular distribution of the products and the nature of the redistribution of the internal energies, and also the actual probability of the reaction. For reactions in which the orbital momenta of the products and reactants are much greater than the internal momenta, the direction of the relative velocity will be preserved in determining the form of the distribution curve. For a significant change in the reduced mass of the products relative to the original (e.g. a decrease, as in the case of K–HBr), because the total angular momentum is conserved, the initial energy of orbital motion will be converted chiefly into energy of rotational excitation of the products. With increase in the rate of relative motion and hence in the orbital momentum, increase in the rotational excitation of the products may lead for this system to a decrease in the probability of reaction[10]. A complete analysis of the experimental data should therefore include allowance for the influence of angular momentum.

The experimental data obtained correspond to the laboratory system of coordinates, whereas it is more natural to carry out the theoretical analysis in the centre-of-mass system. Interpretation of the data obtained is thus possible if they are converted to the latter system. This problem usually consists of two parts — conversion from the angles giving the position of the detector in the l-system to the angles in the c-system, and conversion of the beam currents measured in the given detector positions into the differential cross-sections. These procedures have been examined in detail elsewhere[28,29].

III. MAIN RESULTS OF THE STUDY OF CHEMICAL REACTIONS IN INTERSECTING BEAMS

To provide a general picture of the results of the study of chemical reactions using intersecting beams, the Table summarises information on studies of this type, with an indication of the extent to which specific reactions have been studied. It can be seen from the Table that most attention has been paid to the study of substitution in HBr, HCl, CH_3I, and HI molecules, and exchange reactions of the type $H_2 + D \rightarrow HD + H$. For a considerable proportion of the reactions given in the Table, the data are scanty, and these reactions will be specially studied in the future.

TABLE.

Reagents	Observed product	Chief results	Remarks	Ref.
K–HBr	KBr	the total reaction cross-section, its dependence on the collision energy, and the threshold energy of the reaction were measured, and the energy state of the reaction products was analysed. The vibrational and rotational energies of the products were determined	the Cs, Rb–HBr systems have been studied	1, 10, 19, 32, 33, 42, 46
K–HCl K–HI	KCl KI	the total cross-section and its dependence on the collision energy were measured, as also the threshold energy of the reaction	data for the K–HCl system were obtained from observations of the elastic scattering	31
K–$C_nH_{2n+1}I$	KI	the total reaction cross-section was estimated (n = 1, 2). Kinematic analysis established that the greater part of the energy of reaction appears as excitation of internal degrees of freedom of the products. Anisotropy in the emission of the products was established. A numerical analysis was made of the dynamics of collision (n = 1, 2)	analogous studies were made with isopropyl, n-propyl, and n-butyl alcohols as reactants	26, 34, 41, 47, 48
K–CH_3Br	KBr	the total cross-section and the threshold of the reaction were determined	data were obtained from observations of elastic scattering	30
K–Br_2 K–I_2 K–ICl K–IBr	KBr KI KCl KBr	the total cross-sections were estimated. It was concluded that the reaction takes place by a stripping mechanism. A kinematic analysis was made of the energy state of the products. The internal energy of the products was measured directly for the K–Br_2 system	analogous results were obtained when K was replaced by Rb or Cs	17, 33, 35, 37, 43, 46, 49, 50
K–CCl_4 K–CH_2I_2	KCl KI	preliminary study indicates the possibility of a stripping mechanism	analogous results were obtained when K was replaced by Cs	17, 43
Rb–SCl_2	RbCl	a stripping mechanism was established for the reaction. Kinematic analysis indicates marked excitation of the reaction products		43
K–$SnCl_4$ K–PBr_3	KCl KBr	preliminary analysis indicates a reaction mechanism intermediate between stripping and complex formation		
H–D_2 D–H_2	HD	the differential reaction cross-sections were estimated. Suggestions were made regarding the mechanism. Numerical calculations of the dynamics of collision were carried out		38–40, 45
N_2^+–D_2	N_2D^+	the total reaction cross-sections were found over a wide range of energies		12
K–SnI_4			distortion of the elastic-scattering curve was noted for the K–SnI_4, $HgBr_2$, HgI_2, and $HgCl_2$ systems. Suggestions were made regarding the possible influence of chemical reactions	44, 51

1. Reactions of the Type K + HX → KX + H

Substitution has been studied in most detail for X = Br; study of this reaction by the molecular beam method was begun as early as 1955.[1] The first results[1] were later refined[10,31], and we shall restrict ourselves to an examination of the later data. Beck et al.[10] studied the chemical interaction accompanying the intersection of a beam of atoms (K) with fixed velocities and a beam of molecules (HBr) with a Maxwell distribution of velocities. The experimental arrangement was similar to that shown in Fig. 2 and the chief results were as follows. (i) The magnitude and nature of the dependence of the total reaction cross-section on the collision energy E were found, and the energy threshold of the reaction was determined. (ii) The data obtained in the study of the elastic scattering were used to determine the dependence of the probability of the reaction on the impact parameter b or the energy of interaction at the distance of closest approach r_0, this energy being related unambiguously to the impact parameter. (iii) A qualitative explanation was obtained for the experimentally observed dependence of the probability of the reaction on the initial collision energy for a fixed value of r_0.

In the discussion of the method used in the theoretical calculation of the angular distribution of the products it was pointed out that this distribution is determined by that of the initial velocity vectors and by the dependence of the reaction cross-section on the relative collision energy.

It might seem that in this experiment, in which the law governing the distribution of velocities in the beams is known, it should be possible, by comparing the theoretical and experimental distribution curves for the products, to determine the unknown energy dependence of the reaction cross-section. It is found in practice, however, that the distribution of the magnitudes and directions of the relative velocities depends not only on temperature but also on the divergence of the HBr beam. The energy dependence of the cross-section is therefore different for different initial assumptions regarding the divergence of the beam. This ambiguity reduces slightly the value of the information associated with the form of the angular distribution; moreover, it provides another illustration of the limitations of methods using a broad spectrum of initial states (in this case relative energies) of the interacting particles. In the work cited[10,31], a different method was selected for determining the required dependence. For different velocities of the beam of K atoms, the measured product current at the maximum was equated to the maximum on the theoretical curve calculated for the divergence which gave the best agreement between experimental and calculated distribution curves. An energy of 2 kcal $mole^{-1}$ was chosen for the normalisation of the calculated and experimental values of the product current.

The final results of the use of this procedure are shown in Fig. 7; here curves A and C correspond to different assumptions regarding the divergency of the beam of HBr

molecules. The experimental points correspond to different measurements and to selection of the most accurate assumption regarding the divergence of the HBr beam. Although the errors in the determination of the energy corresponding to a given value of the cross-section are fairly large, the shape of the curve, even close to the threshold, can be taken as close to curve D (Fig. 7) calculated for the usual solid-sphere model with a threshold energy $E^* = 0.15$ kcal × × mole^{-1}. The exact value of the threshold energy cannot be determined from these data, but it can hardly be greater than 0.4 kcal mole^{-1}. The slightly indefinite nature of the values obtained in this way can be reduced if we utilise for the analysis the results of a study of the elastic scattering of the same partners. The chief features of elastic scattering have been discussed above (Fig. 4), and for complex molecules this discussion is applicable in the approximation corresponding to spherically symmetrical pair interaction.

In the examination of the elastic scattering of reactive particles having a reaction threshold energy E^*, it is possible in principle to compare a certain limiting scattering angle: for large angles of deflection the elastic-scattering curve is distorted as a result of the partial disappearance of HBr molecules by chemical reaction. The experimental scattering curve in the range of angles smaller than the limiting angle can be used to determine the parameters of the interaction potential; from the latter we can then calculate the curve for purely elastic scattering in the range of angles greater than the limiting angle. Theoretical determination of the limiting angle is difficult, and in the work cited[10] it was determined by the *a priori* condition that the probability $P(\chi, E)$ differed from zero; this rather arbitrary choice was justified by the fact that the results obtained showed little dependence on the magnitude of this angle.

From the definition of probability introduced above, the experimental and theoretical scattering curves can be used to find the dependence of $P(\chi, E)$ on the impact parameter or the related energy of interaction for the distance of closest approach $V(r_0)$. Fig. 8 shows the dependence of the probability $P(\chi, E)$ on the energy $V(r_0)$ for five values of the initial energy of the beam of K atoms. In the energy range $0.2 < V(r_0) < 1.2$ kcal mole^{-1}, the probability curves are clearly separated; at higher values of $V(r_0)$ the experimental errors blur this relationship. The asymptotic values of the probability remain less than unity, and this can be taken as an indication that the steric factor is not equal to unity. For the reaction considered, however, it

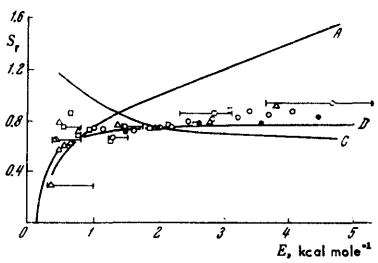


Fig. 7. Experimental dependence of the total cross-section S_r of the reaction K + HBr → KBr + H on the collision energy, and the theoretical curves calculated for various conditions (see text).

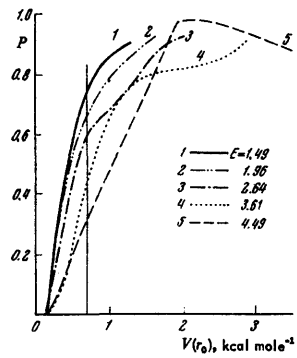


Fig. 8. Experimental dependence of the probability of the reaction K + HBr → KBr + H on the energy of interaction at the point of closest approach for various initial collision energies E.

may be stated that at $b < 2.7$ Å (or for values of $V(r_0) > > 1.2$ kcal mole^{-1}), almost all collisions lead to reaction.

By making use of the expression

$$S_p = 2\pi \int_0^\infty P(\chi, E)\, b db = 2\pi \int_0^\pi (\sigma_r - \sigma_s) \sin\chi\, d\chi,$$

we can find the total cross-section of the reaction S_r for a given relative energy E. Comparison of the S_r–E relationship (the solid circles in Fig. 7) with that obtained on the basis of the procedure described above shows good agreement. The absolute values of the cross-sections show less satisfactory agreement, but this can be attributed to the divergence of the beam of HBr molecules. In this way an absolute value of 34 Å^2 is found for the total cross-section of the reaction with an energy of $E = 2.6$ kcal mole^{-1}.

From the results in Fig. 8 it follows that the reaction probability, whose values correspond to the points of intersection of the curves with the normal to the abscissa, decreases with increase in the relative energy for a fixed distance of closest approach r_0. This effect has been interpreted[10] on the basis of the law of conservation of angular momentum. As a result of the marked change in reduced mass ($\mu_1 \ll \mu$), the final orbital momentum is small, and the condition of conservation of total momentum requires a considerable increase in the internal momentum of the KBr molecule. Thus with increase in the initial rate (or relative energy) there is an increase in the internal momentum (and rotational energy) of the KBr molecule, whereas the proportion of the energy corresponding to translational and vibrational degrees of freedom will decrease. It is known from statistical theory that decrease in the phase volume corresponding to these degrees of freedom should lead to a decrease in the probability of reaction. This probability is evidently zero for those initial energies and the orbital momentum for which, as a result of the conservation conditions, the whole of the final energy is equal to the rotational energy. This condition makes it possible, by extrapolation of the data in Fig. 8, to find independently an extremely important parameter (r_m) of the intermolecular interaction potential.

The conservation laws do not permit definite conclusions to be reached regarding the redistribution of the initial kinetic energy and the energy of reaction ΔD. However, direct measurement of the most probable velocities of the

KBr molecules, by means of a velocity selector[32], made it possible to establish fairly precisely how the energy is distributed between the translational and the internal degrees of freedom of the products. This most probable velocity was found, over a wide range of angles of observation, to be slightly greater than the most probable value of C. On the basis of the arguments examined above, this indicates unambiguously that the KBr is emitted predominantly forwards in the c-system (i.e. in the direction of the vector $\mathbf{v}'_K$).

Since the beam of K atoms has a fixed velocity (the beam of HBr molecules has a velocity distribution close to the Maxwell distribution), the geometric locus of the ends of possible velocity vectors of the mass centre will be the normal to the v_K axis at the point $v = m_K V_K/(m_K + m_{HBr})$ (see Fig. 9). When points on this straight line are used to construct circles with radii corresponding to different values of the heat of reaction Q (≥ 0.1 kcal mole^{-1}), the points of intersection of the possible velocity vectors $\mathbf{v}'_{KBr}$ with these circles, for decompositions involving forward emission of the KBr molecules (at an angle of 0° in the c-system), are found to lie on the almost straight vertical lines, corresponding to different values of Q, shown in Fig. 9*b*. The range of possible values of Q is not too great, from -1.85 kcal mole^{-1} for an endothermic reaction with total transfer of the energy to internal degrees of freedom (zero recoil velocity) up to 5 kcal mole^{-1} for the total transfer of the energy of reaction ΔD to the translational energy of the products. We can therefore restrict ourselves to a small number of vertical straight lines (Fig. 9*b* shows only the straight lines for $Q \geq 0$). We can plot on this diagram the measured most probable velocities of the KBr molecules for different angles of observation θ_a, and draw a smooth curve through these points (the values of the probable velocities given earlier[32] have since been slightly corrected[33]). It can then be seen from Fig. 9*b* that this curve intersects the vector of the most probable relative velocity at a point through which the line for Q = 0.5 kcal mole^{-1} also passes; hence the most probable exothermic heat of reaction is ~ 0.5 kcal mole^{-1}, and almost all the energy of reaction is used up in internal excitation of the products (the reaction can be regarded as thermoneutral). It has thus been possible to confirm by direct experiment the long-discussed assumption that reactions involving alkali-metal atoms and halogens lead to transfer of the greater part of the energy of reaction into internal degrees of freedom.

The reactions for substituents X = Cl (slightly endothermic reaction) or I were studied by Ackerman et al.[31] on the assembly described by Beck et al.[10] The total cross-sections of the reactions for E = 2 kcal mole^{-1} were found to be 28 Å^2 for K–HI and 3.9 Å^2 for K–HCl.

A method analogous to that described above was used to find the dependence of the probability of reaction on $V(r_0)$, the interaction energy at the point of closest approach. For the K–HCl system the threshold value $V_n(r_0) = 0.55 \pm 0.1$ kcal mole^{-1} was clearly fixed. The plot of this dependence shows two additional breaks. Since their positions are given by the expression $V_n(r_0) + v(\hbar\nu)$, they may be due to the formation of products in different vibrational states (v = 1 and 2). For the K–HI system the behaviour of the probability function is quite different: it shows a sharp ascent beginning from a threshold energy $V_n(r_0) = 0.2$ kcal × × mole^{-1}, after which there is no dependence on $V(r_0)$ and only a weak dependence on E. No significant energy dependence of the total reaction cross-section has been found for either system.

2. Reactions of the Type $K + C_nH_{2n+1}I \rightarrow KI + C_nH_{2n+1}$.

Reactions of this type, unlike those examined above, are characterised by a comparatively small change in the reduced mass. This feature makes it possible, even for two beams which do not have fixed velocities, to make a quantitative analysis of the energies of the products and to establish anisotropy in their emission. A typical picture of the angular distribution of the products for the K–CH_3I system is shown in Fig. 10 (the curves correspond to two different experiments and the broken line gives the calculated curve). A rough estimate of the total cross-section of reaction gives for the K–CH_3I system the value 35 Å^2. Variation of the source temperature for the beam of K atoms indicated[26] that the activation energy of this reaction is small and does not exceed 0.3 kcal mole^{-1}.

Detailed kinematic analysis of the K–CH_3I system[26] gives interesting results. For a molecule of the product KI, the recoil velocity in the c-system may have different directions and magnitudes determined by the relationship

$$v'_{KI} = \left[\frac{M_{CH_3}}{M_{KI}}\,\frac{2(E+Q)}{M_{KI}+M_{CH_3}}\right]^{1/2}.$$

The ends of the possible recoil velocity vectors in the planar case (Fig. 10) lie on circles with radius v'_{KI}. In the scale diagram in Fig. 10 these circles are shown for various values of Q up to 25 kcal mole^{-1} (the difference in the energies of rupture of the C–I and K–I bonds). It can be seen from Fig. 10 that large values of Q (>5) correspond to recoil velocities close to or greater than the velocity of the centre

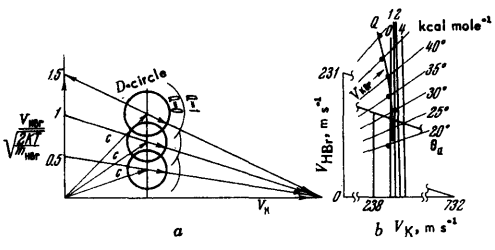


Fig. 9. Kinematic scale diagram for determining the internal energy of the products of the reaction K + HBr → KBr + H.

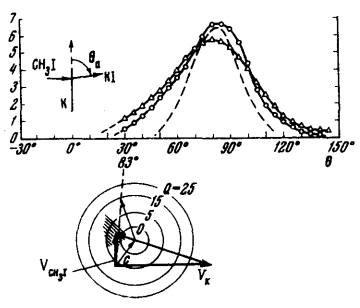


Fig. 10. Angular distribution of the products of the reaction K + CH_3I → KI + CH_3 and kinematic diagram explaining the marked internal excitation of the products.

of mass C. Thus, whereas for $Q = 0$ the range of possible appearance angles of KI lies between 40° and 70°, we find that for $Q = 6$ kcal mole^{-1} KI can be observed for any angle in the l-system. It can thus be seen from the diagram that the observed maximum in the product current for the angle $\theta_a = 83°$ in the l-system can be attributed only to the result of anisotropic emission with recoil of KI molecules backwards ("ricochet"), i.e. in the opposite direction to the velocity of the K atoms (in the c-system). When allowance is made for the cylindrical symmetry of the emission with respect to the relative velocity vector (Fig. 10), it is found that the observed current in the region of the maximum yield of products can be realised only for values of Q not exceeding 5 kcal mole^{-1}, so that ~ 80% of the energy of reaction is used up in excitation of the products.

A more accurate estimate is possible when a mechanical selector is used. Analogous results are also obtained when the number of carbon atoms $n = 2$, and also when K atoms are replaced by Cs or Rb.[26] For systems containing propyl or butyl groups it was found that the radical group has no steric influence (equal reaction cross-sections) and that the final kinetic energy of the products decreases with increase in the mass of the radical group.

For reactions involving alkyl halides, a comparison has recently been made of the calculated (by means of an electronic computer) and experimental angular distributions of the reaction products. Support has been obtained for the qualitative conclusions and quantitative estimations discussed above, but it follows from the calculations that the experimental data can be described satisfactorily with a slightly greater scatter in the values of Q and χ than appeared earlier. This ambiguity is associated with the absence of velocity selection[34].

Study of the K–CH_3Br system[30] using a beam of K atoms of fixed velocity shows that the dependence of P on E for a fixed value of r_0 is opposite to that observed for the K–HBr system (Fig. 9). The reaction probability P does not exceed 0.8, and increases sharply from 0 to this value at a threshold energy $V_n(r_0) = 0.25$ kcal mole^{-1}.

3. Reactions of the Type $X_2 + A \rightarrow XA + X$

The reactions of this type which have been studied, with X = halogen and A = alkali-metal atom are given in the Table. For the Cs–Br_2 system, the elastic-scattering curve does not show a rainbow peak, and the curve descends rapidly even in the range of relatively small angles; these distortions of the scattering curve clearly indicate a high value for the reaction cross-section[35]. In contrast to the systems examined earlier, comparison of the forms of the calculated and experimental curves for the angular distribution of the products shows considerable divergence: in particular, there is a marked difference in the positions of the maxima on these curves. This lack of agreement can be eliminated by making the theoretical calculation on the assumption that the Cs atom interacts only with one Br atom and that the bond between the atoms in the molecule can be neglected (impulse approximation). This impulse scheme corresponds to abandonment of the model which assumes the formation of a complex or composite molecule. As usual, the spectrum of possible recoil velocities of the products is determined by the heat of reaction and the initial energy E; estimates[35] show that, if the final kinetic energy is, for example, $2.2E$, the reaction products are "smeared" over a solid angle of 4π. Since the experiments revealed a narrow distribution peak at $\theta_a = 8$, it must be concluded that not more than 0.5–1 kcal mole^{-1} is transferred to the translational energy of the products and that all the remaining available energy (~ 99% of ΔD) is used up in internal excitation of the CsBr.

The agreement between the experimental curve and the results of the calculation according to the impulse mechanism also leads to the conclusion that this reaction corresponds to the class of reactions of the stripping type. Indications of this mechanism were obtained for analogous systems[36] using beams of K, Rb, and Cs and of Br_2, I_2, ICl, and IBr which did not have fixed velocities. Estimation of the total reaction cross-section for these systems leads to values of the order of 100 Å^2. For these systems the reactions are strongly exothermic (ΔD = 40–50 kcal × × mole^{-1}), but the final kinetic energy of the greater part of the products (in the region of the intensity peak), e.g. in reactions involving Br_2 and I_2 molecules, does not exceed ~ 1 kcal mole^{-1}. Thus the products have a high vibrational excitation (the rotational energy is restricted by the conservation of angular momentum). Direct measurements of the velocities of the products using a selector, carried out recently[33,37] for the K–Br_2 system, show that the spectrum of internal energies of the KBr molecules is extremely broad, extending from 4 to 17 kcal mole^{-1}. Moreover, it may be concluded from the experimental results that the angular distribution of the products in the c-system corresponds to their emission forwards within a cone having an angle of divergence of ~ 30°.

Marked internal excitation of the products takes place also with the Cs–ICl and Cs–IBr systems; here, in the estimation of the vibrational excitation, allowance must be made also for the possibility of reactions leading to products of the type CsI or CsCl (the detector will not distinguish, for example, CsI and CsBr molecules). The high reaction cross-sections and the predominant emission of the products forwards (in the direction of motion of the alkali-metal atom) in these systems again indicates that the reaction takes place by a stripping mechanism.

4. The Reactions $H_2 + D \rightarrow HD + H$ and $D_2 + H \rightarrow HD + D$

Even the first results of a study of these reactions are of considerable interest[38,39], in connection with the possibility of comparing the experimental data with theoretical analysis. The most detailed information was obtained by Datz and Taylor[38], who compared theoretical and experimental angular distribution curves for the products HD (Fig. 11). The section of the curve shown by the broken line in Fig. 11 corresponds to extrapolation of the experimental points into the range, inaccessible to measurement, of the "shadow" of the beam of D, containing a small but significant quantity of HD, The calculated angular distribution of the velocity vectors of the centres of mass is shown by the solid curve and the points correspond to different experiments.

The slight (10–15°) symmetrical broadening of the experimental curve in comparison with the theoretical curve (Fig. 11) can be explained in two ways. It may result either from formation of a short-lived linear complex or from strong excitation of the molecules of the products. A scheme of phase detection[38] makes it possible to estimate the times of flight or the velocities of the HD molecules; this estimate is incompatible with the second possibility, so that there is greater justification for the assumption that a short-lived

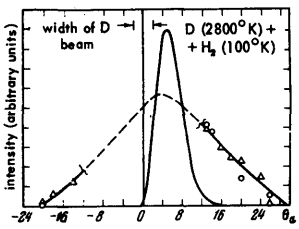


Fig. 11. Angular distribution of the products of the isotopic substitution $H_2 + D \rightarrow HD + H$ (the broken line gives the extrapolation of the experimental points and the solid curve gives the results of the theoretical calculation).

complex is formed, leading to the appearance of non-excited products. The experimental data for these reactions are as yet scanty and unreliable, but numerical analysis of the dynamics of the collisions of the D and H_2 molecules [40] also shows that for this system the direct-interaction scheme is preferable to the collision-complex model.

5. Numerical Methods

To conclude this review of experimental studies of chemical interaction in intersecting beams with thermal velocities, we must consider another extremely promising approach which makes use of fast computers for model calculations on elementary reactions. This approach is of interest in two respects: firstly, it reveals certain details of the mechanism of a chemical transformation inaccessible to present-day experimental technique and shows possible directions for subsequent experiments; and secondly, it will supplement the semi-empirical method for determining potential-energy surfaces.

Numerical methods have been used [40,41] to analyse the dynamics of collisions leading to the reactions $CH_3I + K \rightarrow$ $\rightarrow KI + CH_3$ and $H_2 + D \rightarrow HD + H$. The method involves essentially direct integration of the equations of motion for the approaching atoms and molecules, i.e. exact calculation of the classical trajectories of motion of three or more atoms. By tracing the trajectories of individual parties with time, it is possuble to pick out those which correspond to the appearance of a new combined state and hence determine the reaction cross-section. By varying the parameters of the calculation, we can find the most favourable conditions for the reaction. In the specific case of the $K-CH_3I$ system, the calculations are simplified by assuming that the methyl group behaves approximately as a separate structureless particle with the same mass, the potential of whose interaction with the I atom is the same as that for CH_3. The classical collision trajectories of these partners are computed for different initial conditions, and the familiar Monte Carlo method is used to obtain results averaged over the real distributions of the impact parameters, orientations, and vibration phases [45]. Experiments with intersecting beams permit direct comparison with the results of the calculations, and if correspondence is observed for some results, it maybe expected that other theoretical results, which cannot be directly compared with experimental data (because the latter are not available), are also applicable. On the other hand, by comparing the corresponding results of calculations and experiments and subsequently achieving better agreement, we can readily refine the form of the potential-energy surface.

One may ask to what extent we are justified in describing the motion of atoms in a chemical interaction by classical equations of motion. A number of factors indicate that this is possible — the large masses of the particles, the adiabatic nature of the chemical transformation, the many-quantum nature of the process of bond rupture in the original molecule and of bond formation in the product molecule, etc.

The quantum-mechanical treatment of elementary chemical processes is at present in its early stages. This, together with the considerable mathematical difficulties encountered in the quantum calculations, forces us to use a classical treatment in those cases where it is justified. In the final analysis, justification for the classical description must be provided by agreement between experimental data and calculations.

In particular, for the $K-CH_3I$ system [41], numerical calculation leads to agreement between the available data and makes it possible to find the lifetime of the complexes formed in a collision, their configuration, and a number of other relevant details. An interesting conclusion, following from the results of experiments and calculations on the dynamics of the collisions for the simplest reacting systems (e.g. $K-CH_3I$ and H_2-D), is that the reaction takes place in a short time interval, corresponding to the transit time in the interaction range. Numerical calculations have not as yet given any indication of the formation of the quasi-molecular complexes (albeit short-lived) used in the transition-state theory.

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The above discussion leads to the following conclusions.

Use of the molecular beam method to study elementary chemical reactions (and also processes of energy exchange for internal degrees of freedom and interaction with a solid surface) gives valuable information on important details of reaction mechanisms.

The intensive development of experimental technique is leading to a continuous increase in the volume of information which can be obtained in experiments with molecular beams. We now have the real possibility of controlling not only the initial state of the reagents — the molecules of the intersecting beams — but also the final energy state of the reaction products. Further extension of these studies is possible by making use of the latest achievements in the production of intense beams with electron-volt energies and methods for their detection.

The possibility of using this method to study the internal energy state of reaction products is of intrinsic value in connection with the problem of stimulated radiation.

Comparison of experimental data with numerical calculations of the dynamics of collisions accompanied by chemical transformation may give information on the properties of potential-energy surfaces and supplement the semi-empirical method for their determination. The numerical method also makes it possible to reveal a number of details of the chemical interaction which cannot be determined experimentally (the lifetime of the complex, its configuration, etc.) and stimulates the organisation of new experiments to detect the effects predicted by the calculation.

The study of reactions accompanying the intersection of beams whose molecules have been excited beforehand is of considerable interest. These studies are most conveniently carried out by the molecular beam method.

The results obtained up to the present and the observed general trend towards an extension of these studies indicate the need for the rapid introduction and extensive utilisation of this method in the appropriate research organisations of the Soviet Union.

A number of papers [47-58] on the subject of this review have been published since the present manuscript was submitted.

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