

MOLECULAR BEAM SCATTERING

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1. Introduction

PROCESSES occurring *via* atomic or molecular collisions are fundamental to chemistry. It is consequently somewhat surprising to see what a relatively small effort has been put into studying such collisions directly. Collisions may be divided into three broad categories: elastic, inelastic, and reactive. In elastic collisions, which normally predominate, the internal energy and quantum states of the collision partners remain unchanged and the only possible observable result is a change in the direction of their relative velocity vector, *i.e.*, an interchange of translational energy only. These elastic encounters are primarily responsible for the macroscopic properties of mass, momentum, and kinetic-energy transfer (diffusion, viscosity, and thermal conductivity). Inelastic collisions are those in which the quantum states of a particle are changed as a result of the collision and will, therefore, generally involve energy transfer between the internal modes of the particles. Reactive collisions comprise those in which chemical reaction occurs and thus, in general, will also involve a change in the mass of the particles. A knowledge of all three types of collision will be required if the details of chemical kinetics are to be successfully interpreted, though in this Review attention will be particularly directed to reactive collisions.

Molecular scattering experiments have enabled these collision processes to be studied without the difficulties of interpretation and inherent loss of detail associated with conventional experiments, where measurement of average properties over a wide distribution of incident energy and internal molecular states are made. Furthermore, in reactions involving a sequence of steps, one step can be isolated and studied.

A number of different experimental configurations¹ have been employed in these scattering experiments. In each case a well-pumped vacuum chamber (about 10^{-7} torr) provides the setting for the experiment. At these pressures the mean free path is many metres and well-defined beams of "molecules" (which in future will be taken to include atoms, free radicals, etc.) can be produced and their scattering either by another beam or by a suitable target investigated. In the arrangement shown in Fig. 1a, for example, a single beam of molecules is produced by the source *A*, collimated

¹ Fraser, "Molecular Rays", Cambridge Univ. Press, Cambridge, 1931; "Advances in Chemical Physics", ed. Ross, Wiley, New York, 1965, vol. X; Datz and Taylor in "Recent Research in Molecular Beams", ed. Estermann, Academic Press, New York, 1959, p. 157; Fite and Datz, *Ann. Rev. Phys. Chem.*, 1963, **14**, 61.

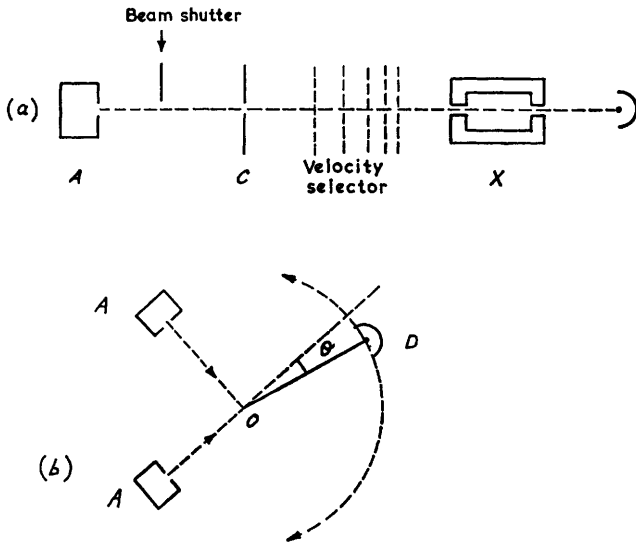


FIG. 1. Schematic illustrations of molecular-beam experiments; (a) single beam for measuring total collision cross-sections for various velocities; (b) crossed-beams for measuring angular dependence of scattering intensity. θ is the angle of scattering in the laboratory co-ordinate system.

by a set of slits at *C* and, after “monochromation” in the velocity selector (which transmits only a narrow range of velocities), passed through the scattering chamber *X* which contains an accurately known pressure of target gas. The beam is finally detected at *D*. The arrangement is thus exactly analogous to the measurement of optical density in a spectrophotometer and by observing the signal intensity recorded at *D* as a function of target-gas pressure, we can measure the total collision cross-section for the interaction of beam and target molecules. These simple arrangements are capable of considerable refinement, for example by selecting particular quantum states of the molecules in the primary beam. The limitation on the resolution and refinement of such selection experiments is at the moment set by the initial beam intensity and signal-to-noise ratio of the detector. An alternative configuration, Fig. 1*b*, uses two well collimated molecular beams arranged to intersect with a definite angle in the scattering centre *O*. The detector in this arrangement is no longer fixed but is rotated about *O*. In this class of experiment a great deal of additional information can be obtained since the angular distribution of scattered material can be measured. Once again the use of selectors is possible but the problems of intensity are much more severe, since the scattered flux will depend upon the product of the two beam intensities. Fortunately, very interesting information can be obtained in some cases with unselected beams. The range of experiments is at present very much dictated

by the techniques for generating and detecting molecular beams so that it is worth examining the experimental aspect more closely.

2. Experimental

(a) Sources.—The most usual source for molecular beams with energies in the thermal range is a small oven maintained at a well-stabilised temperature and provided with a narrow slit through which the molecules can effuse, and, after suitable collimation, form a beam. If the mean free path of molecules in the oven is larger than the slit width, there will be relatively few collisions in the beam and the intensity will be directly proportional to the number of molecules striking the area of the slit, *i.e.*, to the pressure. Unfortunately, we cannot increase the intensity of the beam indefinitely by increasing the pressure, since the onset of collisions in the region of the slit produces a cloud of molecules in front of the slit.² This cloud scatters and attenuates the beam. There is thus an optimum pressure and, correspondingly, a maximum beam intensity, available from sources of this type. The optimum pressure will be approximately that giving a mean free path comparable with the slit width of the oven. For a typical case, a beam 1 cm. high by 0.01 cm. wide, the conditions for effusive flow would require a mean free path in the oven of approximately 0.01 cm. = $1/n\sigma 2^{\frac{1}{2}}$ where σ , the collision cross-section, might be of the order 10^{-13} cm.². The optimum pressure in the oven would then be about 0.03 torr. By kinetic theory the number of molecules striking a detector area A_d in the line of the primary beam but distant l_0 cm. from the source slit of area A_s is:

$$1.12 \times 10^{22} A_s A_d p / l_0^2 (MT)^{\frac{1}{2}}$$

where M , T , and p are the molecular weight, temperature, and pressure of the beam material in the source. Thus primary beam intensities in conventionally sized machines are unlikely to exceed 10^{13} molecules/sec., corresponding in density to a gas at about 10^{-12} torr for normal molecular velocities.

Recently, in attempts to obtain higher beam intensities, some workers have used much greater pressures in their ovens, so that hydrodynamic flow occurs. Under these conditions a "Laval Nozzle",³ in which the collisions between beam molecules serve to "focus" their translational energy in a forward direction, can be used to produce fast beams of very high intensity. Intensities 10^2 — 10^3 greater than those obtained by effusion are available. Such systems by virtue of the large mass flow require very high pumping speeds and are rather akin to hypersonic wind tunnels, and correspondingly expensive. So far they have not become available to chemists. Beams of condensable substances may offer more immediate scope, since relatively inexpensive cryogenic pumps can be used.

² Ramsey, "Molecular Beams", Oxford Univ. Press, Oxford, 1956; Smith "Molecular Beams", Methuen, London, 1955; Hasted, "Physics of Atomic Collisions", Butterworth, London, 1964.

³ Valleau and Deckers, *Canad. J. Chem.*, 1964, **42**, 225.

Atomic and free-radical beams can be formed by effusion from suitable ovens in which dissociation has been brought about by familiar thermal or microwave-electric discharge methods, *e.g.*, hydrogen-atom beams of good intensity have been produced by thermal dissociation in a tungsten tube oven heated to 3000°K electrically.⁴

Very fast beams of neutral molecules have been produced by charge exchange in which, for example, a beam of A⁺ ions with energies in the 10 eV range are fired through a chamber containing a suitable pressure of argon.⁵ Since the cross-section for charge exchange is very much greater than that for momentum transfer a considerable fraction of the ions in the beam will be neutralised without being deflected from the beam. The final fast neutral beam is then obtained by deflecting away the remaining ions with an electric field.

(b) Velocity and State Selection.—It is obviously of interest to study collision processes as a function of the relative velocity and quantum states of each particle both before and after their encounter. In favourable cases this is now possible, though normally the sensitivity of the detector and beam intensity limit the resolution which would otherwise be obtainable.

The distribution of velocities in a molecular beam from an oven at T°K can be obtained from Maxwell's law. The number of molecules $N(v)$ with velocities between v and $v + dv$ in directions within the solid angle $d\omega$ defined by the beam is

$$N(v) = C(d\omega/4\pi)v^2 \exp(-v^2M/2RT)dv$$

But the number of molecules passing through the source slit is proportional to $vN(v) dv$ molecules/cm.²/sec. and thus the distribution of velocities in the beam is

$$I(v) = 2I_0 (2RT/M)^{3/2} v^3 \exp(-v^2M/2RT) \text{ molecules/cm.}^2/\text{sec.}$$

(where I_0 is the total intensity of the beam, all velocities).

In principle, by varying the oven temperature and measuring the resultant signal after some velocity-dependent process has occurred it is possible to reconstruct the details of the velocity dependence. Unfortunately, for accurate results an excessively wide range of temperature is required, so that a more direct method of selection is needed. For velocity selection a mechanical method reminiscent of Fizeau's experiment to measure the velocity of light is most often used. The selector consists of a number (usually 5 or 6) of discs mounted on a shaft which can be rotated at an accurately known speed.⁶ A series of equally spaced slots around the edge of each disc, mutually offset in successive discs, will then obstruct all but a small range of velocities, the transmitted velocity being determined by the

⁴ Martin and Fluendy, *Rev. Sci. Instr.*, 1966, **36**, to be published.

⁵ Devienne, Souquet, and Clapier, *Compt. rend.*, 1963, **256**, 233.

⁶ Hostettler and Bernstein, *Rev. Sci. Instr.*, 1960, **31**, 872.

speed of rotation. Resolutions ($\Delta v/v$ half-intensity width) of 5% are commonly achieved.

The principle of the famous Stern–Gerlach experiment, in which a beam of atoms possessing a magnetic dipole is deflected by an inhomogeneous magnetic field, has also been used for velocity selection, since the deflection is a function of velocity. It is particularly suitable for fast moving projectiles such as hydrogen atoms for which the conventional type of selector would have to be very long.⁷ For scattering experiments a system of offset slits is normally used to filter out unwanted velocities.

The deflection $x(v)$ produced by a given velocity v is

$$x(v) = \frac{1}{2\epsilon} \mu_{\text{eff}} \frac{\partial H}{\partial x} l^2$$

where l = length of field, $\partial H/\partial x$ = magnetic field gradient, ϵ = K.E. of molecules, $\mu_{\text{eff}} = Mg\mu_0$ (M can have values $-J, -J + 1, \dots, J$; g is the Landé factor, and μ_0 is the Bohr magneton).

This procedure will also select the various angular momentum states of the atom. In a slightly different fashion an inhomogeneous electric field can be used to select the rotational states of a molecule having a permanent electric dipole.⁸

Selection of both velocity and rotational states drastically reduces the intensity of the beam. In an effort to combat this, "lens systems" have been devised which will bring molecules with an electric or magnetic dipole moment to a focus and thus increase the effective area of the source.² Quadrupole fields have commonly been used because their field acts perpendicularly towards the central axis and increases with distance from this axis. The behaviour of polar diatomic molecules injected into the field is of two types. If $\mu_{\text{eff}} > 0$, e.g., for the (J, M) states $(0,0)$, $(1,1)$, $(2,2)$, etc., the molecules are deflected away from the axis and are lost. However, if $\mu_{\text{eff}} < 0$, e.g., for the states $(1,0)$, $(2,0)$, etc., the molecules experience a restoring force proportional to their distance from, and directed towards, the central axis. As a result, they execute simple harmonic motion in the xy -plane. For a definite velocity in the z -direction all molecules in a particular rotational state return to the axis at the same half-wavelength position. By varying the voltage across the electrodes, molecules belonging to a state of chosen μ_{eff} can be focused on the detector. An obstacle is placed in the centre of the quadrupole field to shadow the detector against molecules which travel close to the axis and are therefore not much influenced by the field. For molecules with a large range of states there is a considerable degree of overlapping in the deflection pattern and very careful analysis is required if the results are to be unravelled.

Recently the construction of "molecular accelerators" has been started⁹

⁷ Fluendy, *J. Sci. Instr.*, 1965, **42**, 489.

⁸ Kramer and Bernstein, *J. Chem. Phys.*, 1965, **42**, 767.

⁹ Wharton, personal communication, 1965.

in which suitably phased electrostatic radio frequency (R.F.) fields act upon the molecular dipole moment. They can accelerate highly dipolar molecules in states of specified μ_{eff} to translational energies in the region of 10 eV. These devices thus differ from the "passive" filters already discussed in that they transfer whole regions of phase space to a new energy region.

(c) **Detectors.**—The degree of refinement in the way of selection, etc., possible in the experiment is limited by our ability to detect the final signal. Thus while beam intensities are still limited by financial resources, detectors are a most critical part of a beam experiment.

Many different devices have been used or suggested for molecular-beam detection.² They can be conveniently divided into a few categories.

(i) *Chemical or condensation targets.* In these the beam molecules are collected and estimated by some chemical reaction, e.g., a yellow MoO_3 target will show a blue trace of MoO_2 when exposed to atomic hydrogen. These methods are often sensitive but rarely metrical and definitely inconvenient. Recently methods using radioactive counting have seemed more promising.

(ii) *Pressure-measuring detectors.* In these the increase in pressure inside a small receiving vessel exposed via a narrow entry to the beam flux is measured. This is frequently by means of a hot-wire Pirani gauge or some form of ionisation gauge such as that due to Kingdon.¹⁰ This type of detector is almost invariably used with some form of beam modulation so the zero drift and noise associated with pressure fluctuations in the main apparatus are minimised. Their chief advantage is the wide range of substances which can be detected in this manner.

(iii) *Thermal detectors.* Bolometers with a surface active as a catalyst can be used to detect beam molecules which react exothermally on their surface, e.g., atomic hydrogen.¹¹ For very energetic beams the kinetic energy of the impinging molecules will yield sufficient heat.

(iv) *Ionisation methods.* These are perhaps the most important. Basically they involve the ionisation of the molecule followed by its measurement as an electric current through an electrometer or electron multiplier (possibly with a mass spectrometer intervening). In some cases the ionisation may be brought about very simply, e.g., metastable $\text{He}(2S^1)$ will eject an electron on impact with a gold surface. The resulting current will then be a measure of the $\text{He}(2S^1)$ flux.

Surface ionisation detectors have been particularly widely used and are the most sensitive detectors available at present.² In these detectors the ionisation of molecules having a low work function (in practice largely the alkali metals and their compounds) is brought about by collision with a hot wire of high work function, typically tungsten (preferably of a type drawn

¹⁰ Kingdon, *Phys. Rev.*, 1923, 21, 408; Brooks, Thesis, Univ. of California, 1964.

¹¹ Fluendy, *Rev. Sci. Instr.*, 1964, 35, 1606.

from a single crystal of the metal since this emits fewer alkali ions from internal impurities). This approach has been much extended by the use of differential surface ionisation¹² in which two wires, one of high and the other of rather lower work function, are used to distinguish between different species. An important example is the use of tungsten and platinum-alloy wires to differentiate between alkali metals and their halides. By using suitable temperatures and "ageing" treatment for the wires it is possible to arrange for the tungsten wire to ionise a very high proportion (about 90%) of the M and MX molecules striking it, while the platinum wire will only ionise the M plus a very small proportion of the MX molecules striking it. Thus by measuring the flux with both wires and making suitable calibrations the two fluxes can be distinguished. In a typical scattering experiment the currents measured range from 10^{-6} A in the main beam to $\sim 10^{-16}$ A. for some scattered products.

The hot-wire detector is unfortunately very limited in the range of molecules which it will detect. For other substances ionisation can in general be brought about by electron bombardment¹³ (as in a mass spectrometer). A high density of electrons having energies in the 20–50 eV range are concentrated in the path of the beam. The resulting positive ions are passed into a mass spectrometer and the signal of the appropriate mass number observed. This method is considerably less sensitive than the hot wire since only approximately 1 in 10^2 or 10^3 of the molecules in the beam are ionised. Furthermore unless very low pressures are obtained in the detector region there is considerable noise from fragments of the background gas appearing at the relevant mass number. These drawbacks can to some extent be overcome by counting techniques in which the noise and signal can be integrated over long periods.

3. Interpretation of Results

The results of scattering experiments are normally reported in terms of "cross-sections" for particular processes. The area of these cross-sections is a measure of the relative probability of the process. For example consider the situation in which a stationary target molecule is exposed to a flux* of incident molecules.¹⁴ The general differential cross-section $\sigma_{ij}(\omega)$ for scattering into an element of solid angle $d\omega$ accompanied by the change $i \rightarrow j$ is then defined by:

$$\sigma_{ij}(\omega) d\omega = \frac{\text{Number of molecules in state } j \text{ scattered per sec. into } d\omega}{\text{Intensity of incident molecules in state } i}$$

For molecules interacting with centrosymmetric forces (or for the average of many impacts with random orientations) there is complete symmetry

¹² Taylor and Datz, *J. Chem. Phys.*, 1955, 23, 1711.

¹³ Weiss, *Rev. Sci. Instr.*, 1961, 32, 397.

¹⁴ Goldstein, "Classical Mechanics", Addison Wesley, Reading, U.S.A., 1950.

* Flux = (Number density of molecules in beam) \times (Velocity of molecules in beam).

about the incident direction, so $d\omega = 2\pi \sin \theta.d\theta$. θ is the scattering angle (between incident and scattered directions). All the information concerning the angular intensity of the scattering is therefore given by the differential cross-section $\sigma(\theta)$. By integrating over θ we obtain the total cross-section σ :

$$\sigma_{ij} = 2\pi \int_0^\pi \sigma_{ij}(\theta) \sin \theta.d\theta$$

The total cross-section is the effective area which the target molecule presents to the incident flux. The transmittance I/I_0 of a beam passing for distance l through a "static" target gas of number density n_B will be $\exp(-n_B l \sigma)$.

When the target molecules are not stationary, the treatment of results is more complicated. Experimental results are measured in laboratory coordinates with the origin at the apparatus scattering centre. For interpretation of results in terms of molecular collisions we must transform to centre-of-mass co-ordinates moving with the centre of mass because we are only interested in the *relative* kinematics of the colliding molecules.¹⁴ Figure 2 shows the velocity vector (or Newton) diagram for the in-plane

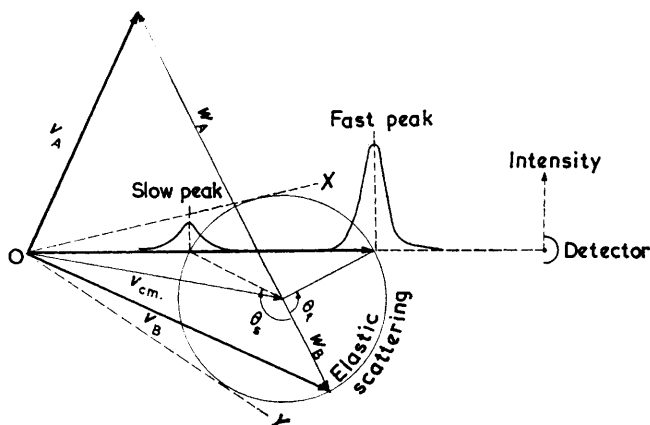


FIG. 2. Newton diagram for scattering from two beams crossing at right angles. Elastic collision of particle B produces rotation of w_B (its relative velocity vector) about the tip of the centre-of-mass vector. For inelastic collisions in which energy is transferred to translational motion w_B would be increased in length as well as rotated.

scattering of two particles A,B crossing at right angles. Beam particles A,B approach the centre of mass with relative velocities w_A, w_B whilst, as can be calculated from Newtonian mechanics, the centre of mass moves at constant velocity $v_{cm} = (m_A v_A + m_B v_B)/(m_A + m_B)$. The relative kinetic energy of the collision is $\frac{1}{2} \mu (v_A^2 + v_B^2)$ where μ is the reduced mass. During elastic collisions the relative velocities remain the same in magnitude but their directions are changed.* The locus of the termini of all

* For scattering in which reaction or energy transfer occurs the magnitude of the vector of scattered B may also change, and may also depend on the angle of scattering.

possible vectors of elastically scattered **B** is a circle of radius w_B . If $w_B < v_{cM}$ the scattered material is confined within the tangents OX, OY of the circle, and there are two relative velocity vectors for **B** scattered in a given direction: a "fast" component arises from scattering through the large centre-of-mass angle θ_F and a "slow" component arises from scattering through the small centre-of-mass angle θ_s . The angular distribution of scattering in the laboratory may thus be radically different from that in the centre-of-mass system. Experimental or laboratory cross-sections and angles have usually to be transformed into centre-of-mass co-ordinates.

In these co-ordinates the scattering problem is equivalent to that for a beam of particles scattered by a potential centred on a fixed target and theoretical interpretations are more easily made.

4. Elastic Scattering

The purely elastic scattering of molecules from spherically symmetric potentials is now rather well understood.¹⁵ The total cross-section results normally show two distinct regions. At high energy the scattering is dominated by the short-range repulsive forces while at low energies the long-range dispersion effects are more important. Measurements of cross-sections for a range of velocities can be used to determine best-fit parameters in a suitable potential function. In particular, interference effects due to the de Broglie wavelength of the particles can often be observed at low energies and provide a very sensitive test for the potential function. In the angular scattering pattern a number of effects (not essentially quantum in origin) can operate to produce structure. Of particular interest is the "rainbow scattering" which can be associated with an extremum in the plot of deflection angle against impact parameter (Figure 3). The extremum is the result of a balance between effects of attractive and repulsive forces. The minimum in this function serves to concentrate extra intensity in the direction of the rainbow angle. Since this angle is primarily related to the ratio of incident kinetic energy to potential well depth an important parameter can be determined quite directly.

Elastic scattering results with good resolution are now becoming available and can be expected to provide our most accurate information about intermolecular potentials.

5. Inelastic and Reactive Scattering

In the field of chemical reactions, those of the type $A + B \rightarrow C + D$ have proved the most amenable to investigation by scattering experiments, since here relatively crude experiments yield much information.

In general, if the transformation of species i to species j (where i and j may be different internal states of the same compound or different chemical

¹⁵ Bernstein, *Science*, 1964, **144**, 141.

species) proceeds by a bimolecular mechanism, then the usual kinetic rate constant, $k_{ij}(T)$, is given by

$$k_{ij}(T) = 2\pi \int_0^\pi \int_0^\infty v_r \sigma_{ij}(\theta, v_r) f(v_r, T) dv_r \sin \theta d\theta$$

where $f(v_r, T)$ is the distribution of relative velocity v_r of the two participants at temperature T and θ is the angle of scattering (in centre-of-mass co-ordinates) resulting from the collision.

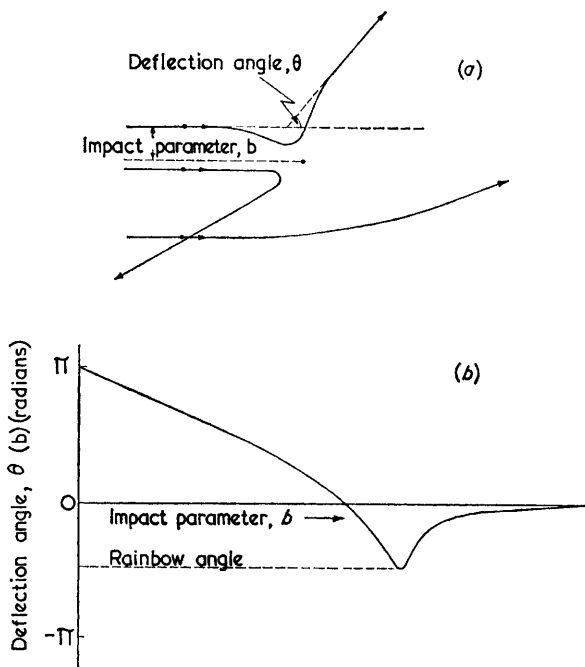


FIG. 3. Elastic scattering by an intermolecular potential with both long-range attractive and short-range repulsive forces. (a) Trajectories of particles with various impact parameters, ' b '. Collisions with small b lead to scattering at wide angles and are dominated by the repulsive part of the potential. For collisions with large b the reverse is true. (b) Variation of deflection with impact parameter.

In deriving a rate constant from measured cross-sections it is not normally necessary to measure differential cross-sections and the angular integration in the equation above is removed by using the appropriate total inelastic cross-section. However, there is as yet no experimental method for measuring such total cross-sections directly. Hitherto, chemical rate processes have been investigated through the rate constant k , usually a k that is a sum governing the formation of products in different rotational and vibrational states. The present state of molecular-beam work is that the angular dependence of $\sigma_{ij}(\theta, v_r)$ for a limited class of chemical reac-

tion is quite well established (and thus some relative total cross-sections are known), but that their velocity or energy dependence is as yet poorly defined, or known over only a small energy range. For this reason, rate constants cannot yet be reliably deduced from cross-sections. It may be noted that if the reaction is too fast, the Maxwellian velocity distribution will no longer hold and other processes then help to determine the overall rate of reaction. For this reason and because on integrating and averaging to obtain a total cross-section details of the angular and energy dependence of $\sigma_{ij}(\theta, v_r)$ are lost, the differential cross-section is of more fundamental interest than k_{ij} in examining a reactive system.

6. Energy-transfer Collisions

The crossed-beam technique is in principle capable of measuring $\sigma_{ij}(\theta, v_r)$ when i and j refer to different rotational or vibrational states of the same chemical species. To measure such an energy-transfer cross-section, the basic scattering experiment of Fig. 1 must be augmented either by measuring the velocity of one of the participants emerging from the collision or (for rotational energy transfer) by determining the rotational state of one of the colliding molecules before and after collision.

The two techniques are illustrated by the two types of experiment that have been performed in this area, namely the transfer of rotational energy in crossed beams of D_2 and K,¹⁶ and rotational transitions in TIF induced by a variety of other molecules.¹⁷ In the deuterium experiments (performed at only one angle of scattering) the conventional Newton diagram gives the velocity of the potassium to be expected from purely elastic scattering; atoms appearing at higher speeds are assumed to have gained extra recoil from rotational de-excitation of deuterium ($j = 2 \rightarrow 0$). Since the energy spacing of the rotational levels of deuterium is an appreciable fraction of the incident kinetic energy, the inelastically scattered potassium at any angle can be separated from elastically scattered potassium by velocity analysis. A small signal due to inelastically scattered potassium having the predicted velocity was observed, yielding a differential cross-section of 0.05 \AA^2 per steradian (at $\theta = 108^\circ$). Calculations indicate¹⁸ that even in the system K-HCl total cross-sections less than 10 \AA^2 are to be expected for transitions among the lowest rotational levels.

In the experiments of Bennewitz and Toennies using rotationally selected TIF, total cross-sections for a range of rotational transitions have been measured. Here, two separate quadrupole fields are used as selector and analyser. Only those molecules that suffer a specified change of J in the collision chamber are refocused and detected. The rotational levels are much more closely spaced than those of D_2 or HCl and the inelastic cross-

¹⁶ Blythe, Grosser, and Bernstein, *J. Chem. Phys.*, 1964, **41**, 1917.

¹⁷ Toennies in "Atomic Collision Processes", ed. McDowell, North-Holland Publishing Co., Amsterdam, 1963, p. 1113.

¹⁸ Lawley and Ross, *J. Chem. Phys.*, 1965, **43**, 2943.

sections are consequently much larger. The observed results have been quantitatively interpreted using an intermolecular potential with an angle-dependent term which is consistent with the observed $\Delta J = \pm 1$ transitions. This type of experiment is one of the few that gives reliable information about the anisotropy in the potential.

The small cross-section to be expected for most collision-induced vibrational transitions makes it unlikely that beam methods will be useful in their investigation for some time to come.

7. Reactive Collisions

In the ideal scattering experiment designed to investigate a chemical reaction, the angular distribution in intensity of one of the scattering products and of one of the elastically scattered reactants is measured. The measurements are performed on mono-energetic beams of molecules in a selected rotational state and repeated for all quantum states of the reactants that are of interest. However, worthwhile velocity selection reduces the intensity of both incident beams by at least a factor of ten, so that subsequent rotational state selection, unless accompanied by efficient focusing, reduces the signal from reaction products almost below detection level. Also, and this is one of the gaps in the method, there is no way of analysing a beam of molecules into their vibrational states; in this respect the method is complementary to infrared emission methods,¹⁹ where the vibrational state of a reaction product is known but not its translational energy. Fortunately, a great deal can be inferred about the nature of reactive collisions, especially the partition of energy in the products, by quite crude experiments using unselected beams.

There are two types of practical beam experiment. In the first the intensity of elastic scattering of one of the *unchanged* reactants (usually K or Cs) is measured as a function of angle.

Greene, Ross, and their co-workers²⁰ have investigated the elastic scattering of K from a variety of halogen-containing compounds, *e.g.*, the hydrogen halides, CH₃Br, and Br₂. In favourable cases (K-CH₃Br, K-HBr, K-HI) a scattering pattern of the general form shown in Fig. 4a was obtained. These experiments were performed with a detector sensitive only to K and the authors have interpreted the marked loss of intensity at large angles of scattering as due entirely to removal of K by reaction. By assuming that the elastic scattering at small angles (arising primarily from collisions with large impact parameters) is unaffected by the reactive process, the elastic potential parameters can be found. These parameters can then be used to predict the complete elastic scattering pattern in the absence of reaction. Thus, the total number of K atoms lost per second can be obtained by integration of the difference between predicted and

¹⁹ Polanyi, *J. Chem. Phys.*, 1959, **31**, 1338.

²⁰ Beck, Greene, and Ross, *J. Chem. Phys.*, 1962, **37**, 2895; Ackermann, Greene, Moursund, and Ross, *J. Chem. Phys.*, 1964, **41**, 1183.

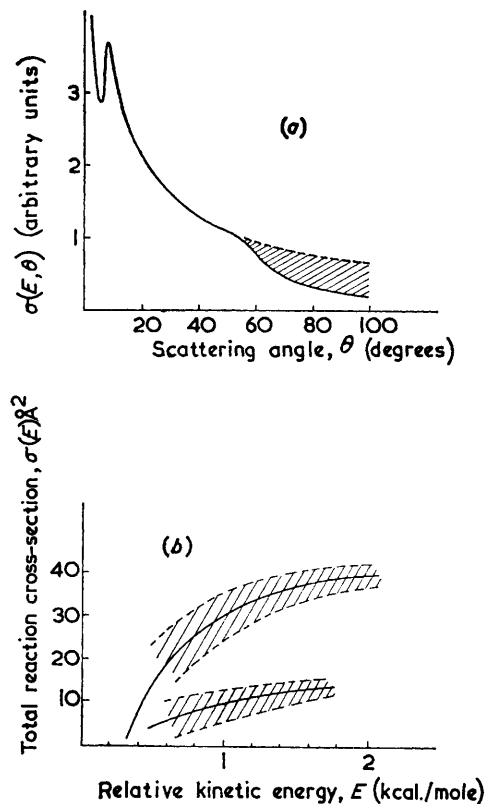


FIG. 4. Experimental results for chemically reactive systems. (a) The general elastic scattering pattern for the system $K + HX$. The shaded area indicates the loss of K due to chemical reaction. (b) The energy-dependence of the total reaction cross-section for $K + CH_3Br$. The shaded area indicates the spread of experimental results. The upper curve comes from the K loss method and the lower from direct measurement of KBr .

observed signal. In order to obtain the absolute total reaction cross-section, the number of molecules lost per second must be divided by the incident flux of potassium atoms and the number of target molecules in the volume of intersection of the two beams. Absolute values are difficult to obtain, but relative values for different target molecules or for different incident energies can be measured to a precision of perhaps 20%.

In the case of $K-BHr$ the product KBr has been detected in the same experiment and this constitutes the second, direct approach to measuring reaction cross-sections which we shall discuss in more detail later. In this reaction the value of σ_{react} obtained by the former indirect method is about 34 \AA^2 ($E_{\text{rel}} = 1 \text{ kcal./mole}$), while the direct method gives a value between three and eight times smaller than this depending on the experimental conditions. For the system $K-HI$ the values obtained by the two methods are 31 \AA^2 and 14 \AA^2 , respectively.

The cross-section obtained purely from observations of the scattering of K must be an upper limit since a decrease in scattered intensity at large angles could be also produced by a softening of the inner wall of the intermolecular potential, as an inspection of typical classical trajectories shows.

If the deficiency in scattered K at various angles (compared with that calculated by assuming a potential falling off with the sixth power of the distance) is plotted against the corresponding distances of closest approach, y , very similar curves are obtained over the whole range of experimental energies: anomalous scattering sets in below the same critical distance of closest approach in every case. This strongly suggests that in subtracting from a hypothetical, purely elastic scattering pattern a property of the potential energy surface has been obtained, but whether this property is due exclusively to reaction has yet to be settled. It being noted that the critical distance of closest approach in the K-HBr experiments corresponds almost exactly to the equilibrium K-Br distance in KBr, the potential energy $V(y)$ corresponding to the critical distance of closest approach is interpreted as the activation energy for reaction. [These critical values of $V(y)$ are all positive and thus two molecules starting from rest and moving together under the influence of their mutual attraction could never penetrate to the required separation.] This leads to the following values for the activation energies: K-HCl, 0.5 kcal./mole, K-HBr < 0.4 kcal./mole, K-HI 0.2 kcal./mole.

In principle, activation energies can also be obtained simply from curves of total reaction cross-section σ plotted against relative kinetic energy E . Fig. 4b shows Greene and Ross's result for the K-HBr reaction, where a low threshold is discernable. More precise velocity selection of the reactant beams and better collimation are necessary before the threshold behaviour can be clarified and the activation energy accurately measured in this way. There is some evidence in the work of these authors of a second step appearing in $\sigma(E)$, possibly at a point where a new vibrational level of the product becomes accessible. The Arrhenius equation $k(T) \propto \exp(-E^*/kT)$ is broadly compatible with a variety of step-like $\sigma(E)$ functions.

In the second type of reactive scattering experiment, in which the angular distribution of one of the products is measured, the earlier experiments used unselected Maxwellian beams of alkali atoms and halides in order to keep the flux of the product high. An inspection of the Newton diagram for the K-HX system, Fig. 5a, indicates that because of the very small mass ratio of the products ($m_H:m_{KX}$) the potassium halide is largely concentrated near the centre-of-mass vector, leading to a high intensity of product in that direction. Thus, the integrated flux and hence the reaction cross-section can be measured more accurately than in, say, the systems K + CH₃I or K + Br₂ where the product is spread out over a larger solid angle Fig. 5b.

The reactions of Cs and K with the lower alkyl halides, and later with

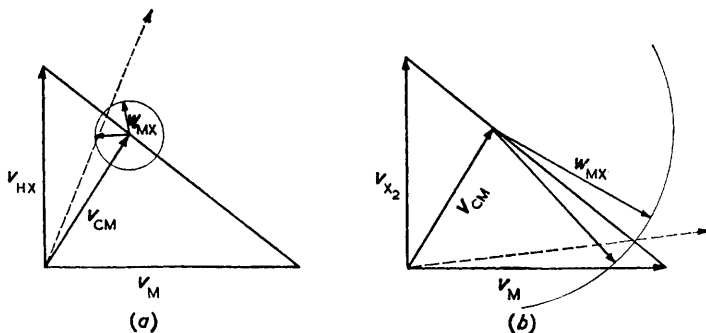


FIG. 5. Newton diagrams for extreme types of reactive encounter. In (a) the product rebounds in the backward direction and there is a large change in reduced mass. In (b) the reaction is followed by forward scattering and there is little change in reduced mass. Only typical final relative velocity vectors of the detected products are shown and a broken line indicates the general direction in the laboratory in which maximum intensity of scattered product is observed.

other small halogen-containing molecules,²¹ have been investigated by Herschbach and his co-workers. Maxwellian beams were used in the earlier experiments and the angular distribution of the alkali halide measured. In some of the most recent experiments in this series, a magnetic field in front of the detector has been used to discriminate unambiguously between the paramagnetic alkali metals and their diamagnetic halides and the large reaction cross-sections reported for some of these systems have been confirmed.

The reaction cross-sections obtained (all for incident energies *ca.* 1 kcal./mole) range from *ca.* 10 \AA^2 for the lower alkyl halides to $> 100 \text{ \AA}^2$ for Cs-Br₂, K-Br₂, Cs-ICl, Cs-IBr, and Cs-I₂.^{22,23} The results from about a dozen different systems seem to fall into two groups, those with large and those with small ($< 30 \text{ \AA}^2$) reaction cross-sections, though it is perhaps accidental that relatively few intermediate cases have been found. Equally important, an analysis of the angular distribution of the scattered product also shows a division into two classes. In the first type, most of the alkali halide produced continues to travel roughly in the direction of the potassium beam; the angular distribution is strongly peaked between 5° and 20° in laboratory co-ordinates measured from the alkali-atom beam. This is in contrast to the reactions of small cross-sections, in which most of the alkali halide product is scattered backwards, *i.e.*, an observer travelling at the centre of mass would see the two reactants approaching from the left and from the right respectively, colliding at his point of observation, and the alkali halide formed returning roughly in the direction from which the

²¹ Herschbach, *Discuss. Faraday Soc.*, 1962, 33, 149; Wilson, Kwei, Norris, Herm, Birely, and Herschbach, *J. Chem. Phys.*, 1964, 41, 1154.

²² Datz and Minturn, *J. Chem. Phys.*, 1964, 41, 1153.

²³ Helbing and Pauly, *Z. Physik*, 1964, 179, 16; Gersing, Hundhausen, and Pauly, *Z. Physik*, 1963, 171, 349.

alkali atoms came. It is also significant that no rainbow angle²³ is observed in the potassium scattering pattern in the large cross-section cases.

The general Newton diagram shows that the direction in which a scattered product is observed in the laboratory depends both on the angle through which the relative velocity vector is turned (the angle of scattering in relative co-ordinates), on the change in reduced mass, and on the change in length of w *i.e.*, on the final relative kinetic energy. In order for the scattering to be strongly peaked in the forward direction in the laboratory co-ordinate system, the angle of scattering θ must be small and the final relative kinetic energy of the same order of magnitude as the initial value. Since all the reactions studied are exothermic (*e.g.*, for $K + RHal$, $\Delta E \approx -20$ kcal./mole), the conservation of energy indicates that up to 90% of the heat of reaction goes into internal modes of the products. These conclusions are in keeping with other kinetic results, especially those from use of the sodium flame technique,²⁴ but in contrast to results from the study of the reactions of hydrogen atoms with the halogens by a flow technique.²⁵

It has also been found by Herschbach²⁶ that there is no appreciable steric hindrance effect in going from methyl halide to butyl halide; this indicates a considerable orientating force in collisions of small impact parameter which line up the molecular partner in the required orientation for reaction. If this were not the case, then one would not expect the rapid rise of transition probability to almost unity with decreasing impact parameter found in the work of Greene and Ross.

Few experiments have been performed on reactive systems with measurement of the velocity of one of the product species. This is, of course, the most direct way of assessing the partition of energy between internal and translational modes and the use of a velocity selector on a product beam (if the primary beams are monoenergetic) does not result in the loss of intensity necessarily accompanying velocity selection of the primary beams.

The velocity distributions of KBr scattered from crossed-beams of velocity-selected K and thermal HBr and Br₂ have been measured by Grosser, Blythe, and Bernstein.²⁷ At any particular angle of observation the KBr velocity was found to be distributed about a well-defined maximum, the most probable velocity varying somewhat with the angle of observation. Should the latter effect remain after conversion to relative velocities, it might perhaps be due to the amount of energy taken up in rotational excitation of KBr changing with the angle of scattering. The result clearly emerged that the final kinetic energy was no more than 0.5 ± 0.5 kcal./mole greater than the initial relative kinetic energy, out of 5.1 kcal./mole liberated in reaction.

²³ Polanyi, "Atomic Reactions", Williams and Norgate, London, 1932.

²⁵ Airey, Getty, Polanyi, and Snelling, *J. Chem. Phys.*, 1964, **41**, 3255.

²⁶ Herschbach, *Applied Optics, Supple. 2 on Chemical Lasers*, 1965, p. 128.

²⁷ Grosser, Blythe, and Bernstein, *J. Chem. Phys.*, 1965, **43**, 1268; Grosser and Bernstein, *J. Chem. Phys.*, 1965, **43**, 1140.

Recently Moulton and Herschbach^{27a} have further probed the energies and angular distributions of scattered product molecules using chemiluminescence. For example, vibrationally hot KBr^+ , from crossed beams of $\text{K} + \text{Br}_2$, entered a second scattering chamber containing a Na cross-beam. Electronically excited K^* atoms were generated by a chemical exchange process,



and light emitted from K^* was observed with a photomultiplier. Through this sort of experiment molecular beam scattering and infrared emission studies will eventually combine.

8. Models and Theories of Chemical Reaction

As a result of work with molecular beams, a certain amount is known about the details of a particular group of reactions, the reactions of potassium and caesium with a variety of halides. The features of these reactions that any model must account for, at least qualitatively, are as follows: (i) Two rather distinct classes of reaction can be distinguished, "rebound" and "stripping" reactions. The former is characterised by small reaction cross-section (*ca.* 10 \AA^2) and by backward scattering of alkali halide product, the latter by larger cross-section and by forward scattering. (ii) The energy released in the reaction goes almost entirely into internal modes of motion. (iii) All the reactions have activation energies less than 1 kcal./mole.

It is at once clear from the angular distributions observed that all the reactions studied proceed directly, not *via* a long-lived collision complex. If such a complex were formed, and its lifetime exceeded its period of rotation, then the Newton diagram shows that, depending on the change in reduced mass, a single (or possibly a double) peak symmetrically placed in the direction of the centre of mass or a very broad distribution of product without pronounced peaking would be observed. Further insight into the meaning of (i) above can be obtained by use of the ideas of elastic scattering. A large cross-section for an inelastic process means that a wide range of impact parameters is effective in inducing the change and there is a loose correlation between the strength of the ordinary intermolecular potential (as measured, for instance, by the Lennard-Jones parameter ϵ) and the choice between recoil and stripping mechanisms. The larger the intermolecular force, the more trajectories are drawn in to some critical distance of approach. Nevertheless, it is hard to escape the conclusion that a somewhat more specific effect is operating, and the occurrence of a charge-transfer mechanism was suggested many years ago in connection with the large cross-section observed in some sodium-flame experiments.²⁴ The ionisation energy and electron affinity of the two reactants may be such that even at

^{27a} Moulton and Herschbach, *J. Chem. Phys.*, 1966, **44**, 3010.

a separation of *ca.* 10 Å the state of the colliding system rapidly changes from that of a molecular pair to a vibrationally excited ionic pair. From then on, Coulombic forces within the newly formed molecule take over and the reaction proceeds rapidly to completion. Considerations of angular momentum, together with the unusual nature of the potential-energy surface, seem to be responsible for the strong forward scattering.

Features (ii) and (iii) are also directly concerned with the nature of the potential-energy surface. If the system is regarded as moving over this surface in the course of reaction then the state of the products of an exothermic reaction depends upon the change in reduced mass accompanying reaction and upon the steepness of the entrance and exit valleys. This point has been discussed by Simons²⁸ and Polanyi²⁵ in contrasting the reaction of sodium atoms and hydrogen atoms.

The small activation energy observed in these reactions becomes a parameter to be used in the construction of potential-energy surfaces. These surfaces are then used in what is at the moment the most complete calculation of reaction rates, the Monte Carlo simulation method.²⁹ This method assumes that though the potential energy of interaction of reactants and products must be determined by quantum mechanics, the motion of the constituent atoms or groups through the force field obtained in this way can be found by classical mechanics. When the classical equations of motion are solved, the probability of reaction for the various impact parameters sampled is obtained, together with the angular distribution of the products and the classical degree of excitation of the products. These calculations were performed with the results of scattering experiments in mind, and some of the above features have been reproduced.

It is clear that molecular scattering measurements have a very considerable future in the study of chemical reactions. Up to the present the experiments have been confined to a rather narrow class of reaction. The mechanisms observed may thus not be very typical. In particular it can be expected that some reactions will proceed *via* relatively long-lived complexes. By analogy with nuclear reactions of the "compound nucleus" type it can be expected that the energy dependence of their reactive and elastic cross-sections will yield considerable information.

Improvements in technique can be expected to broaden the range of reactions in which the scattering products can be observed directly. Recently mass spectrometer detectors have been used in the determination of total cross-sections for the mutual scattering of the inert gases and of hydrogen and deuterium.³⁰ Nevertheless, for most reactions the reactive cross-section will remain too small for direct investigation. In

²⁸ Simons, *Nature*, 1960, **186**, 551.

²⁹ Bunker, *Scientific American*, 1964, **211**, 100; Karplus and Roff, *J. Chem. Phys.*, 1964, **41**, 1267; Kuntz, Nemeth, Polanyi, Rosner, and Young, *J. Chem. Phys.*, 1966, **44**, 1168.

³⁰ Buren, Feltgen, Gaide, Helbing, and Pauly, *Phys. Letters*, 1965, **18**, 282; Landorf and Mueller, *ibid.*, 1966, **19**, 658.

these cases the elastic scattering pattern (possibly of super-thermal beams) is capable of yielding considerable information about the potential surface accessible at the relative kinetic energy of the beams. By observing separately the mutual scattering of reactants and products the lower reaches of the entrance and exit valleys could be mapped.