PROCESSING OF ION-MOLECULE BEAM SCATTERING DATA: FRAMEWORK OF SCATTERING DIAGRAMS AND DERIVED QUANTITIES

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Received November 17th, 1981

The problem of processing data resulting from ion-molecule beam scattering experiments under single-collision conditions is treated from the point of view of the probability theory. The probability-interpreted quantities characterizing ion-molecule scattering are related to the total and differential cross-section of the process in question.

Since the beginning of ion-molecule beam scattering studies under single-collision conditions results have been presented in the form of contour scattering diagrams. In the first years of the studies, Wolfgang and Cross[1] suggested the use of "Cartesian probabilities" to express the angular and radial distributions of product velocities in the velocity space of the system. The Newton diagram[2] provided a framework for the graphical transformation of the laboratory (LAB) and center-of-mass (CM) coordinate system. This type of data presentation has been generally accepted, with small variations, by most of authors in this field of research[3-8]. Specific changes have been described only briefly and fragmentarily as sections of papers focussed on chemical aspects of the studies. Consequently, the terminology, definitions, and meaning of employed quantities has not been unified satisfactorily.

In this paper we attempt to treat the subject as a whole describing how to obtain from experimental data the basic quantities characterizing a reactive scattering process, including a detailed derivation of their mutual relations. Our treatment systematically uses terms from probability theory and relates the probability-interpreted quantities to the total and differential cross section of the scattering process in question. Although the treatment is generally valid for all chemical particles (atoms, molecules, ions), we restrict ourselves deliberately to ion-molecule processes, where this kind of analysis has been widely applied.

Classical Treatment of an Elementary Chemical Reaction $A + B \rightarrow C + D$ *as a Two-Body Collision*

The main task of the chemical scattering theory is to deduce the asymptotic behaviour of products from the asymptotic behaviour of reactants. By the asymptotic behaviour we mean the behaviour of the chemical particles far enough from the collision center so that no interaction between them may take place. If the molecule A interacts with the molecule B randomly as far as their mutual orientation is concerned (this is the case in most of beam scattering experiments) it does not make any sense to complicate the description of the process by treating A and B as manybody (*i.e.* polyatomic) species. (It would be necessary in any case to average the result of such a description over all relative orientations of A and B).

Because of this reason we may replace the chemical particles by mass points in order to obtain a classical description of the state of the system in external (translational) degrees of freedom. This approach makes it possible to accept from classical two-body collision theory[9] some general conclusions which must be valid for the dynamics of elementary chemical processes as well. The analysis of this approach will then be used as a basis for the interpretation of the quantities measured in a beam experiment under single-collision conditions.

In the asymptotic regions the movement of the particles is uniform (in absence of external forces acting on the system the asymptotic regions are defined by the constant-velocity-vector, *i.e.* uniform motion). We can take advantage of this fact by describing a dynamical state of the system in external degrees of freedom before and after the interaction by means of time-independent velocities of the particles. It is convenient to represent these velocities by points in the velocity space[10] of the system, a Euclidean vector space E_3.

The internal force acting in the system is a central force. The angular momentum is then a constant of motion and the process is confined to a plane, *i.e.* the points representing velocities of the reactants A, B and the products C, D lie in the same plane of the velocity space of the system. Consequently, in order to represent the dynamical state of a two-body system it is sufficient to work only with a two-dimensional subspace E_2 of the velocity space of the system. However, we have to keep in mind that the finite size of real beams makes actually the problem of chemical scattering a three-dimensional problem (see further on). For the sake of simplicity the problem will be treated here in two dimensions, for an extension of the dimension by one is in this case trivial.

Let us assume that $\mathbf{v}_A$, $\mathbf{v}_B$ are the velocity vectors of the reactants in E_2, represented by the mass points A, B of the masses m_A, m_B and of the total mass $M = m_A + m_B$. Let us construct in E_2 an orthogonal coordinate system $\{O; \mathbf{v}_1, \mathbf{v}_2\}$ of the origin O and the unit base vectors $\mathbf{v}_1$, $\mathbf{v}_2$. Let the origin O be located at the intersection of the vectors $\mathbf{v}_A$, $\mathbf{v}_B$ (*i.e.* in the collision center). Changing now the location of the vectors $\mathbf{v}_A$, $\mathbf{v}_B$ by a parallel translation to the distance equal to the norm of each, the vectors $\mathbf{v}_A$, $\mathbf{v}_B$ will represent radius vectors of the velocities which the particles A, B would have if no interaction during the collision occurred (Fig. 1*a*). When speaking about reactant velocities, we will always have in mind these velocities.

(Such a convention will allow us to depict the product velocities as their radius vectors in the same coordinate system). This coordinate system $\{O; \mathbf{v}_1, \mathbf{v}_2\}$ will be called the laboratory (LAB) system[9]. The radius vectors $\mathbf{v}_A, \mathbf{v}_B$ can be expressed in the LAB system by the expansions

$$\mathbf{v}_A = \sum_{i=1}^{2} v_{Ai}\mathbf{v}_i \tag{1}$$

$$\mathbf{v}_B = \sum_{i=1}^{2} v_{Bi}\mathbf{v}_i\,, \tag{2}$$

where v_{Ai}, v_{Bi} are Cartesian coordinates of the radius vectors in the LAB system. The relative velocity vector $\mathbf{v}_r$ of the reactants A, B, defined by the relation

$$\mathbf{v}_r = \mathbf{v}_A - \mathbf{v}_B \tag{3}$$

has the norm in the LAB system:

$$\|\mathbf{v}_r\| \equiv v_r = (v_{r1}^2 + v_{r2}^2)^{1/2}\,, \tag{4}$$

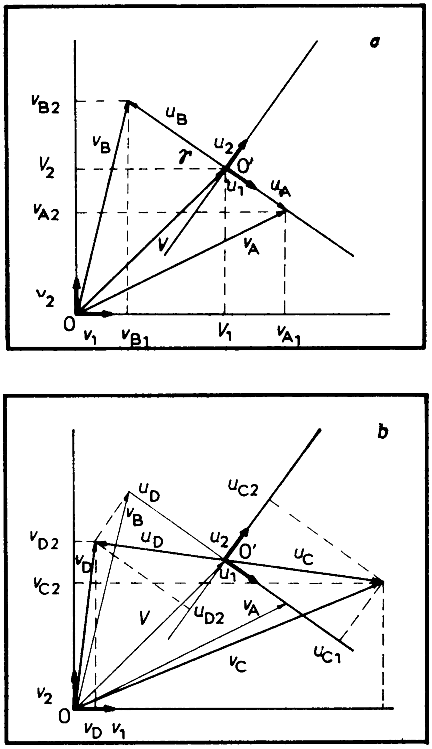

Fig. 1

Laboratory (LAB) and center-of-mass (CM) coordinate systems $\{O; \mathbf{v}_1, \mathbf{v}_2\}$ and $\{O'; \mathbf{u}_1, \mathbf{u}_2\}$, respectively, in the velocity space of the system A + B → C + D. *a*) radius vectors of the reactant velocities and their Cartesian coordinates; *b*) radius vectors of the product velocities and their Cartesian coordinates. The angle of rotation γ of the LAB and CM coordinate systems and the radius vector V of the velocity of the center of mass in the laboratory system are shown as well where

$$v_{\mathrm{ri}} = v_{\mathrm{Ai}} - v_{\mathrm{Bi}}\,, \quad i = 1, 2\,. \tag{5}$$

Let us now construct in E_2 another orthogonal coordinate system $\{O'; \boldsymbol{u}_1, \boldsymbol{u}_2\}$ of the origin O' and the unit base vectors $\boldsymbol{u}_1, \boldsymbol{u}_2$. The expansion of the vector $\boldsymbol{V} = OO'$ in the LAB system has the form:

$$\boldsymbol{V} = \sum_{\mathrm{i}=1}^{2} V_{\mathrm{i}} \boldsymbol{v}_{\mathrm{i}}\,. \tag{6}$$

Let us define the coordinates V_{i} and the angle of rotation γ of the new coordinate system with respect to the LAB system by the following relations:

$$V_{\mathrm{i}} = (m_{\mathrm{A}} v_{\mathrm{Ai}} + m_{\mathrm{B}} v_{\mathrm{Bi}})\, M^{-1} \tag{7}$$

$$\gamma = \arccos\left[(v_{\mathrm{A1}} - v_{\mathrm{B1}})\, v_{\mathrm{r}}^{-1}\right]; \tag{8}$$

the origin O' of the coordinate system $\{O'; \boldsymbol{u}_1, \boldsymbol{u}_2\}$ will then coincide with the point representing the LAB velocity of the center of mass of the reactants A, B; further on, the unit base vector $\boldsymbol{u}_1$ will be parallel with the reactant relative velocity vector $\boldsymbol{v}_{\mathrm{r}}$. The new coordinate system defined by relations (7) and (8) will be called the center-of-mass (CM) system[9]. The expansion of the radius vectors $\boldsymbol{u}_{\mathrm{A}}, \boldsymbol{u}_{\mathrm{B}}$ of the velocities of A, B in the CM system acquires a simple form:

$$\boldsymbol{u}_{\mathrm{A}} = u_{\mathrm{A1}} \boldsymbol{u}_1 \tag{9}$$

$$\boldsymbol{u}_{\mathrm{B}} = u_{\mathrm{B1}} \boldsymbol{u}_1 \tag{10}$$

where $u_{\mathrm{A1}}, u_{\mathrm{B1}}$ are Cartesian coordinates of the radius vectors of the reactant velocities in the CM system. The coordinates $u_{\mathrm{A2}}, u_{\mathrm{B2}}$ are identically equal to zero. Thus we may skip indexing of the coordinates, *i.e.* we define $u_{\mathrm{A1}} \equiv u_{\mathrm{A}}$, $u_{\mathrm{B1}} \equiv u_{\mathrm{B}}$. The reactant relative velocity vector $\boldsymbol{u}_{\mathrm{r}}$ in the CM system defined by the relation

$$\boldsymbol{u}_{\mathrm{r}} = \boldsymbol{u}_{\mathrm{A}} - \boldsymbol{u}_{\mathrm{B}} \tag{11}$$

has the norm

$$\|\boldsymbol{u}_{\mathrm{r}}\| \equiv u_{\mathrm{r}} = (u_{\mathrm{r1}}^2 + u_{\mathrm{r2}}^2)^{1/2} = u_{\mathrm{A}} - u_{\mathrm{B}}\,, \tag{12}$$

where

$$u_{\mathrm{ri}} = u_{\mathrm{Ai}} - u_{\mathrm{Bi}}\,, \quad i = 1, 2\,. \tag{13}$$

The transformation of the Cartesian coordinates of velocities corresponding to the transformation of the coordinate systems is (since $v_{A2}, v_{B1} = 0$, see Fig. 2)

$$u_A = (v_{A1} - V_1)\cos\gamma + V_2 \sin\gamma \qquad (14)$$

$$u_B = -V_1\cos\gamma + (V_2 - v_{B2})\sin\gamma\,. \qquad (15)$$

Using definitions (*7*) and (*8*) these transformations imply:

$$u_A = (m_B/M)\, v_r \qquad (16)$$

$$u_B = -(m_A/M)\, v_r\,. \qquad (17)$$

The basic feature of the transformation of LAB and CM coordinate systems is the conservation of the norm of the reactant relative velocity vector:

$$u_r = u_A - u_B = (m_B/M)\, v_r + (m_A/M)\, v_r = v_r\,. \qquad (18)$$

The relative translational energy of the reactants T (collision energy) is then identical with the kinetic energy of the reactants in the CM system:

$$T = (1/2)\,\mu v_r^2 = (1/2)\,\mu u_r^2\,; \qquad (19)$$

μ is the reduced mass of the reactans: $\mu = (m_A m_B)/M$.

Another advantage of introducing the CM system consists in the form of the momentum conservation law:

$$-m_A u_A = m_B u_B\,; \qquad (20)$$

this relation follows immediately from (*16*) and (*17*).

We will turn now our attention to the products C, D (Fig. 1*b*).

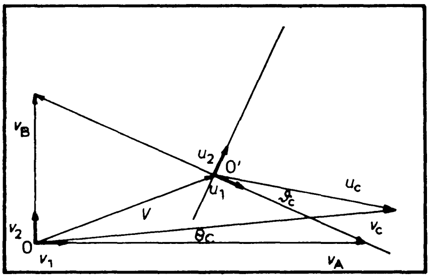

Fig. 2

Newton diagram of the process A + B → → C + D. Radius vectors of product C velocity in the LAB and CM systems and the appropriate LAB and CM scattering angles are shown

Let their velocities be given in the LAB system by the radius vectors $\mathbf{v}_{\mathrm{C}}$, $\mathbf{v}_{\mathrm{D}}$:

$$\mathbf{v}_{\mathrm{C}} = \sum_{\mathrm{i}=1}^{2} v_{\mathrm{Ci}} \mathbf{v}_{\mathrm{i}} \tag{21}$$

$$\mathbf{v}_{\mathrm{D}} = \sum_{\mathrm{i}=1}^{2} v_{\mathrm{Di}} \mathbf{v}_{\mathrm{i}} , \tag{22}$$

where v_{Ci}, v_{Di} are the appropriate Cartesian coordinates in the LAB system. The radius vector of the LAB velocity of the center of mass $\mathbf{V}'$ is defined by the relation:

$$V_{\mathrm{i}}' = (m_{\mathrm{C}} v_{\mathrm{Ci}} + m_{\mathrm{D}} v_{\mathrm{Di}}) M^{-1} , \quad i = 1, 2 . \tag{23}$$

The momentum conservation in the LAB system can be written as

$$V_{\mathrm{i}} = V_{\mathrm{i}}' , \quad i = 1, 2 . \tag{24}$$

This means, of course, that the product velocities can be expressed as the radius vectors $\mathbf{u}_{\mathrm{C}}$, $\mathbf{u}_{\mathrm{D}}$ in the CM system. The appropriate expansion assumes the form:

$$\mathbf{u}_{\mathrm{C}} = \sum_{\mathrm{i}=1}^{2} u_{\mathrm{Ci}} \mathbf{u}_{\mathrm{i}} \tag{25}$$

$$\mathbf{u}_{\mathrm{D}} = \sum_{\mathrm{i}=1}^{2} u_{\mathrm{Di}} \mathbf{u}_{\mathrm{i}} \tag{26}$$

where u_{Ci}, u_{Di} are the Cartesian coordinates of the product velocities in the CM system. The coordinate transformation corresponding to the transformation of the LAB to the CM system has the following form[10]:

$$u_{\mathrm{C1}} = (v_{\mathrm{C1}} - V_1) \cos \gamma - (v_{\mathrm{C2}} - V_2) \sin \gamma \tag{27}$$

$$u_{\mathrm{C2}} = -(v_{\mathrm{C1}} - V_1) \sin \gamma + (v_{\mathrm{C2}} - V_2) \cos \gamma \tag{28}$$

$$u_{\mathrm{D1}} = (v_{\mathrm{D1}} - V_1) \cos \gamma - (v_{\mathrm{D2}} - V_2) \sin \gamma \tag{29}$$

$$u_{\mathrm{D2}} = -(v_{\mathrm{D1}} - V_1) \sin \gamma + (v_{\mathrm{D2}} - V_2) \cos \gamma . \tag{30}$$

Similarly as for the reactants, we can prove for the products the conservation of the norm of the relative velocity vectors $\mathbf{v}_{\mathrm{r}}' = \mathbf{v}_{\mathrm{C}} - \mathbf{v}_{\mathrm{D}}$ and $\mathbf{u}_{\mathrm{r}}' = \mathbf{u}_{\mathrm{C}} - \mathbf{u}_{\mathrm{D}}$:

$$\|\mathbf{v}_{\mathrm{r}}'\| \equiv v_{\mathrm{r}}' = u_{\mathrm{r}}' \equiv \|\mathbf{u}_{\mathrm{r}}'\| ; \tag{31}$$

the momentum conservation in the CM system is

$$-m_C u_{Ci} = m_D u_{Di}\,, \quad i = 1, 2 \tag{32}$$

and to derive an expression for the product relative translational energy T' (identical with the expression for the product kinetic energy in the CM system):

$$T' = (1/2)\,\mu' v_r'^2 = (1/2)\,\mu' u_r'^2\,; \tag{33}$$

μ' is the reduced mass of the products: $\mu' = (m_C m_D)/M$.

It is a consequence of momentum conservation that a complete information on the product final translational state in the A + B → C + D process can be obtained knowing only one of the product velocities.

In our two-dimensional orthogonal coordinate systems $\{O; \mathbf{v}_1, \mathbf{v}_2\}$ and $\{O'; \mathbf{u}_1, \mathbf{u}_2\}$ we can now introduce polar coordinates[11] of velocities of the j-th particle (j = A, B, C, D) using the Cartesian coordinates of velocities of those particles; the velocity of the j-th particle has in the LAB system the coordinates v_j, Θ_j:

$$v_j = (v_{j1}^2 + v_{j2}^2)^{1/2} \tag{34}$$

$$\Theta_j = \arccos\left[v_{j1}(v_{j1}^2 + v_{j2}^2)^{-1/2}\right]; \tag{35}$$

the polar coordinates in the CM system are u_j, ϑ_j:

$$u_j = (u_{j1}^2 + u_{j2}^2)^{1/2} \tag{36}$$

$$\vartheta_j = \arccos\left[u_{j1}(u_{j1}^2 + u_{j2}^2)^{-1/2}\right]. \tag{37}$$

The polar coordinate transformation corresponding to the transformation of the LAB and CM systems is determined unequivocally by the relations (*27*)–(*30*) and (*34*)–(*37*). We will not write down those explicitly. Let us just note that the momentum conservation in the CM system has in the polar coordinates the form:

$$u_A m_A = u_B m_B \tag{38}$$

$$u_C m_C = u_D m_D\,; \tag{39}$$

the norm of the relative velocity vector is given by the sum:

$$v_r = u_A + u_B \tag{40}$$

$$v'_r = u_C + u_D\,. \qquad (41)$$

Using the last relation we can express the product relative translational energy T' as:

$$T' = (1/2)\,(m_C M/m_D)\,u_C^2\,. \qquad (42)$$

In the arrangement of our experiment the reactant beams intersect at a fixed angle of 90°. This makes it possible (without any further restrictions) to orient the laboratory system in such a way that the base vectors $\mathbf{v}_1$, $\mathbf{v}_2$ will be parallel with the radius vectors $\mathbf{v}_A$, $\mathbf{v}_B$ (Fig. 2). This allows for a simple definition of the product scattering angle. Let us define the scattering angle of the product C in the LAB system as the angle between the radius vector $\mathbf{v}_C$ of the product C and the radius vector $\mathbf{v}_A$ of the reactant A. The LAB scattering angle defined in this manner is then identical with the polar angle Θ_C of the product velocity in the LAB system (*cf.* equation (*35*)). Therefore, we can call directly the polar angle, Θ_C, the laboratory scattering angle (LAB angle) of the product C. Similarly, we can define the scattering angle of the product C in the CM system as the angle between the radius vectors $\mathbf{u}_A$ and $\mathbf{u}_C$. Because the radius vector $\mathbf{u}_A$ is *ex definitione* parallel with the base vector $\mathbf{v}_1$, this scattering angle is identical with the polar angle ϑ_C of the product velocity in the CM system (*cf.* equation (*37*)). We will call the polar angle, ϑ_C, directly the CM scattering angle (CM angle) of the product C. Let us note that the product CM angle is identical with the angle between the relative velocity vectors of reactants and products. The graphical representation of the velocities in the LAB and CM systems in the velocity space such as in Fig. 2 is referred to as the Newton diagram[2].

The Total Cross-Section

Pairs of reactants A + B enter the collision with various values of the impact parameter vector $\mathbf{b}$ (ref.[13]). The continuous set of values of $\|\mathbf{b}\| \equiv b$ ranges from zero to a maximal value, b_{max}, where the process under study still takes place. Each pair, of velocity vectors of mutually randomly oriented reactants in crossed beams defines their relative velocity vector $\mathbf{v}_r$ and for $\mathbf{b} \neq \mathbf{O}$ a plane containing $\mathbf{v}_r$ and $\mathbf{b}$. In this way the beam scattering problem develops into a three-dimensional problem; therefore, our treatment must be transferred into the E_3 velocity space. Let us assume that the values of the reactant relative velocity vectors (defined by various velocity pairs of reactants in beams) differ not very much from the most probable value (as far as their size, direction, and position is concerned). Then, in the first approximation, the vector of so defined most probable reactant relative velocity can be regarded as a mutual cross line of all considered planes determined by the particular reactant pairs.

Radius vectors of velocities of products are located in the planes of radius vectors of velocities of those particular reactants they were formed from. Thus the product velocities in the velocity space are distributed isotropically about the most probable relative velocity vector of the reactants (accordingly to the isotropical distribution of $\boldsymbol{b}$). In other words: if the above mentioned assumptions are fulfilled, the distribution of product velocities about the most probable reactant relative velocity vector must be cylindrically symmetrical.

Let us assume that the dimensions of the detection slit are infinitesimal so that we may apply the differential treatment. The distance R of the geometrical center of the detection slit from the collision center (approximated here as a point) is an instrumental constant. Its position in the LAB coordinate system can be then defined by the angle Θ and by the azimuthal angle Φ (angle with respect to the plane of the two beams). As the particles travel in the field free region between the collision center and the detection slit with a constant velocity, the position of the detection slit can be expressed by the angular coordinates of the detected particles in the LAB system, and *vice versa*.

The number of ions of the species k (k = A, C) reaching the detector is proportional to the number of k-ions passing through the detection slit area dG, and surmounting a stopping potential* ε. As the mass-to-charge ratio of the detected ions is known, the stopping potential ε can be expressed directly in units of kinetic energy. The detector slit area is an instrumental constant for all positions of its geometrical center on a spherical surface of a radius R and with its origin in the collision center. The measured electric current (or the pulse-counted number of particles) is then directly proportional to the intensity of particles of the species k, *i.e.* to the number of particles k passing during a unit time through the unit area perpendicular to it. As the distance R of the geometrical center of the detection slit is an instrumental constant, the area dG of the slit can be expressed angularly as an element $\mathrm{d}\Omega = \sin \Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi$ of the solid angle Ω in the LAB coordinate system of the velocity space.

Let us consider a continuous function $I_k(\varepsilon, \Omega)$ of continuous variables ε, Ω. Here ε represents the applied potential barrier in kinetic energy units, defined on the interval $\varepsilon \in (0; E_{\max})$; Ω is a solid angle, defined on the interval $\Omega \in (0; 4\pi)$ and cutting from the spherical surface $G_{\text{tot}} = 4\pi R^2$ an area of variable size. The intensity $I_A(\varepsilon, \Omega)$ of the ion reactant A differs from zero only over an area in the infinitesimal vicinity of the values $\Theta = 0$ and $\Phi = 0$ (*i.e.* the ion reactant enters the scattering center as a beam and the values $\Theta = 0$ and $\Phi = 0$ are adjusted to its direction). Therefore we can neglect in our consideration the dependence of I_A on Ω and take only $I_A = I_A(\varepsilon)$.

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* We treat here the ion energy analysis by means of a stopping potential, *i.e.* integral energy analyzer, as it is more general; the case of a differential (*e.g.*, a deflection or a TOF energy analyzer) is included in the treatment and its specific features will be pointed out further on in the text.

Assuming a single reaction channel of the process A + B (leading to the products C + D), we can write[14]

$$I_A(\varepsilon = 0) - I'_A(\varepsilon = 0) = I_C(\varepsilon = 0, \Omega = 4\pi), \qquad (43)$$

where $I_A(\varepsilon = 0)$ is the full initial (unattenuated) intensity of the reactant A (zero stopping potential barrier); $I'_A(\varepsilon = 0)$ is the full final (attenuated by the particular single-channel scattering process) intensity of A; and $I_C(\varepsilon = 0, \Omega = 4\pi)$ is the full intensity of the product C (no barrier, entire spherical surface). It holds for $I'_A(\varepsilon = 0)$:

$$I_A(\varepsilon = 0) = I_A(\varepsilon = 0) \exp(-\sigma_{tot} n_B s), \qquad (44)$$

where s is the length of the ion A path through the collision center (in the direction of movement of A), and n_B is the number density of particles of the reactant B; the proportionality constant σ_{tot} is the total cross-section of the process under study. Combining (*43*) and (*44*) one gets

$$I_C(\varepsilon = 0, \Omega = 4\pi) = I_A(\varepsilon = 0) [1 - \exp(-\sigma_{tot} n_B s)]. \qquad (45)$$

The expression in the brackets can be, for small values of the exponent, approximated by the first term of the expansion, and then

$$I_C(\varepsilon = 0, \Omega = 4\pi) = \sigma_{tot} n_B s I_A(\varepsilon = 0) = \sigma_{tot} \xi. \qquad (46)$$

The function $I_C(\varepsilon, \Omega)$, from now on designated as $I(\varepsilon, \Omega)$, represents for fixed values of ε, Ω a number of ions C which appear in a solid angle $\Omega_C < \Omega$ and whose kinetic energy E_C is greater than the barrier ε, *i.e.* $E_C < (E_{max} - \varepsilon) \equiv E$. (The function $I(E, \Omega)$ can be obtained from $I(\varepsilon, \Omega)$ for a fixed value of Ω by the reflection with respect to the line $\varepsilon = E_{max}/2$). The function $I(E, \Omega)$ fulfils all the requirements of a function proportional to a distribution function $F(E, \Omega)$ of continuous random variables E, Θ.

Differentiating the function $I(E, \Omega)$ with respect to E, Ω we obtain a function $i(E, \Omega)$, proportional to the probability density $f(E, \Omega)$ that $E_C < E$, $\Omega_C < \Omega$:

$$\frac{\partial^2 I(E, \Omega)}{\partial E \, \partial \Omega} = i(E, \Omega); \qquad (47)$$

the expression $i(E, \Omega) \, dE \, d\Omega$ is then proportional to the probability that the product LAB kinetic energy falls into the interval $(E; E + dE)$ and that the product appears in the LAB solid angle interval $(\Omega; \Omega + d\Omega)$.

Let us consider a function $J(E, \Omega)$:

$$J(E, \Omega) = \frac{\partial I(E, \Omega)}{\partial \Omega}\,; \tag{48}$$

the expression $J(E, \Omega)\,\mathrm{d}\Omega$ is then proportional (for a fixed value of E) to the probability that the product appears in the interval of the LAB solid angle $(\Omega; \Omega + \mathrm{d}\Omega)$, *i.e.* $\Omega < \Omega_\mathrm{C} < \Omega + \mathrm{d}\Omega$. This solid angle interval intercepts on the surface of the sphere of diameter R and its center in the point O an annular surface. The area of this surface is proportional to $\int \sin \Theta \,\mathrm{d}\Theta\, \mathrm{d}\Phi$; a h^{-1} multiple of the annulus area is then proportional to the area $\mathrm{d}G$ of the detection slit ($h \in (0; 2\pi)$). Thus the function $J(E, \Omega)$ is obviously directly proportional to the measured quantity at a fixed value of E. It holds, of course, that

$$\frac{\partial J(E, \Omega)}{\partial E} = i(E, \Omega)\,. \tag{49}$$

Designating

$$\iint i(E, \Omega)\,\mathrm{d}E\,\mathrm{d}\Omega = I_\mathrm{tot} = I_\mathrm{C}(\varepsilon = 0, \Omega = 4\pi)\,, \tag{50}$$

we have:

$$I(E, \Omega)\, I_\mathrm{tot}^{-1} = F(E, \Omega)\,; \tag{51}$$

it follows from (*51*)

$$f(E, \Omega) = i(E, \Omega)\, I_\mathrm{tot}^{-1} = \frac{\partial J(E, \Omega)}{\partial E}\, I_\mathrm{tot}^{-1}\,. \tag{52}$$

This means that by normalization and differentiation of the measured function $J(E, \Omega)$ with respect to E we obtain the probability density that the detected product has kinetic energy $E_\mathrm{C} < E$ and falls into a solid angle $\Omega_\mathrm{C} < \Omega$.

In conclusion let us note the following: if a differential, instead of an integral, energy analyzer is used, the differentiation with respect to E results from the performance of the analyzer; the measured quantity is in such a case proportional directly to $i(E, \Omega)$.

Transformation of Independent Variables: Probability Density Distribution of Cartesian and Spherical Coordinates of Velocities in the LAB *and* CM *System*

In order to express the probability density distribution of the coordinates of product velocities in the coordinate systems in the velocity space, we need first of all to transform the variables of the probability density distribution $f(E, \Omega)$.

It holds for the transformation of the LAB kinetic energy E to the LAB velocity v (we will skip indexing of particles remembering that the quantities always refer to the product C):

$$f(E, \Omega)\,\mathrm{d}E\,\mathrm{d}\Omega = f(v, \Omega)\,\mathrm{d}v\,\mathrm{d}\Omega \tag{53}$$

which is a consequence of the conservation of the number of particles (or conservation of probability) in the velocity space; equation (53) implies:

$$f(E, \Omega)\,mv = f(v, \Omega)\,. \tag{54}$$

For the transformation of the variabıes v, Ω to the complete set of spherical variables v, Θ, Φ of the product velocity, we can write another relation reflecting the probability conservation:

$$f(v, \Omega)\,\mathrm{d}v\,\mathrm{d}\Omega = f(v, \Theta, \Phi)\,\mathrm{d}v\,\mathrm{d}\Theta\,\mathrm{d}\Phi\,; \tag{55}$$

it follows from (55):

$$f(v, \Omega)\sin\Theta = f(v, \Theta, \Phi)\,. \tag{56}$$

The meaning of $f(v, \Theta, \Phi)\,\mathrm{d}v\,\mathrm{d}\Theta\,\mathrm{d}\Phi$ is the probability that the product LAB velocity spherical coordinates v_C, Θ_C, Φ_C fit within the following interval: $v < v_C < v + \mathrm{d}v$, $\Theta < \Theta_C < \Theta + \mathrm{d}\Theta$, $\Phi < \Phi_C < \Phi + \mathrm{d}\Phi$.

The remaining transformations are given by the usual Jacobians[11]; Therefore, we will just show the results:

$$f(v, \Theta, \Phi) = v^2 \sin\Theta\, f(v_1, v_2, v_3)\,, \tag{57}$$

where v_1, v_2, v_3 is a complete set of Cartesian coordinates of the product velocity in the LAB system; the meaning of $f(v_1, v_2, v_3)\,\mathrm{d}v_1\,\mathrm{d}v_2\,\mathrm{d}v_3$ is the probability that $v_1 < v_{C1} < v_1 + \mathrm{d}v_1, v_2 < v_{C2} < v_2 + \mathrm{d}v_2, v_3 < c_{C3} < c_3 + \mathrm{d}v_3$.

The transformation of LAB Cartesian coordinates v_1, v_2, v_3 to CM Cartesian coordinates u_1, u_2, u_3 of the product gives

$$f(v_1, v_2, v_3) = f(u_1, u_2, u_3) \tag{58}$$

and the transformation of the CM Cartesian coordinates u_1, u_2, u_3 to the CM spherical coordinates u, ϑ, φ gives

$$f(u_1, u_2, u_3) = (u^2 \sin \vartheta)^{-1} f(u, \vartheta, \varphi) . \qquad (59)$$

The meaning of $f(u_1, u_2, u_3)\, du_1\, du_2\, du_3$ is the probability that $u_1 < u_{C1} < u_1 + du_1$, $u_2 < u_{C2} < u_2 + du_2$, $u_3 < u_{C3} < u_3 + du_3$; analogously, the meaning of $f(u, \vartheta, \varphi)\, du\, d\vartheta\, d\varphi$ is the probability that $u < u_C < u + du$, $\vartheta < \vartheta_C < \vartheta + d\vartheta$, $\varphi < \varphi_C < \varphi + d\varphi$.

By combining (57)–(59) and substituting for $f(v, \Theta, \Phi)$ from (54) and (56) we obtain a very important relation:

$$f(E, \Omega)\, m\, v^{-1} = f(v_1, v_2, v_3) = f(u_1, u_2, u_3) = \\ = (u^2 \sin \vartheta)^{-1} f(u, \vartheta, \varphi) . \qquad (60)$$

Thus by dividing the probability density $f(E, \Omega)$ by the appropriate value of the norm $v = (2E/m)^{1/2}$ we get a quantity proportional to the probability density $f(u_1, u_2, u_3)$.

The probability density distribution $f(u_1, u_2, u_3)$ must reflect the cylindrical symmetry of the scattering pattern with respect to the reactant relative velocity vector. This makes it possible to represent the distribution of product velocities by a cut through the velocity space of the system containing the reactant relative velocity vector. Such a cut is done for instance by the plane of the beams. The plot of the probability density distribution $f(u_1, u_2, u_3)$ in this plane using the contour method is referred to as the scattering diagram[13-15].

Let us note that the probability density $f(u_1, u_2, u_3)$ has been called in literature also Cartesian probability[1], Carterian intensity, flux density, and specific intensity[3].

Probability Density Distribution of CM *Scattering Angle and of Product Relative Translational Energy*

The probability density $f(\vartheta)$ of CM product scattering angle ϑ is given by the integral

$$f(\vartheta) = \iint f(u, \vartheta, \varphi)\, du\, d\varphi . \qquad (61)$$

Because of the invariance of $f(u, \vartheta, \varphi)$ with respect to φ (following from the cylindrical symmetry of the product velocity distribution) we can write:

$$f(\vartheta) = 2\pi \int f(u, \vartheta, \varphi)\, du ; \qquad (62)$$

substituting from (59) we have:

$$f(\vartheta) = 2\pi \sin \vartheta \int u^2 f(u_1, u_2, u_3) \, \mathrm{d}u \,. \tag{63}$$

The probability density $P(\vartheta)$ defined by the relation

$$P(\vartheta) = \int u^2 f(u_1, u_2, u_3) \, \mathrm{d}u \tag{64}$$

is proportional to the differential cross-section $\sigma_{\mathrm{diff}}(\vartheta)$; this follows from the definition

$$\sigma_{\mathrm{diff}}(\vartheta) = (2\pi \sin \vartheta)^{-1} \, (\mathrm{d}\sigma_{\mathrm{tot}}/\mathrm{d}\vartheta) \,. \tag{65}$$

In order to prove this statement we recall that

$$i(\vartheta) = f(\vartheta) \, I_{\mathrm{tot}} \,,$$

where

$$i(\vartheta) = \mathrm{d}i_{\mathrm{tot}}/\mathrm{d}\vartheta = \mathrm{d}I_{\mathrm{tot}}/\mathrm{d}\vartheta \,,$$

because

$$i_{\mathrm{tot}} = \int i(\vartheta) \, \mathrm{d}\vartheta = I_{\mathrm{tot}} \,.$$

Then it follows:

$$P(\vartheta) = (2\pi \sin \vartheta)^{-1} \, f(\vartheta) = (2\pi \sin \vartheta)^{-1} \, [i(\vartheta)/I_{\mathrm{tot}}] =$$
$$= (2\pi \sin \vartheta)^{-1} \, \frac{\mathrm{d}I_{\mathrm{tot}}}{I_{\mathrm{tot}} \, \mathrm{d}\vartheta} = (2\pi \sin \vartheta)^{-1} \, (\xi/I_{\mathrm{tot}}) \, (\mathrm{d}\sigma_{\mathrm{tot}}/\mathrm{d}\vartheta)$$

which means that

$$\sigma_{\mathrm{tot}} P(\vartheta) = (2\pi \sin \vartheta)^{-1} \, (\mathrm{d}\sigma_{\mathrm{tot}}/\mathrm{d}\vartheta) = \sigma_{\mathrm{diff}}(\vartheta) \,.$$

Hence, the proportionality constant between $P(\vartheta)$ and $\sigma_{\mathrm{diff}}(\vartheta)$ is the total cross--section.

In order to obtain the probability density $P(T')$ of the product relative translational energy T', we have to derive first the expression for the probability density $P(u)$ of the product CM velocity u (*i.e.* the norm of u_C)

$$P(u) = \iint f(u, \vartheta, \varphi) \, \mathrm{d}\vartheta \, \mathrm{d}\varphi = 2\pi \int f(u, \vartheta, \varphi) \, \mathrm{d}\vartheta \,. \tag{66}$$

Substituting from (*59*) we have:

$$P(u) = 2\pi u^2 \int f(u_1, u_2, u_3) \sin \vartheta \, \mathrm{d}\vartheta \,. \qquad (67)$$

Now we can get the probability density $P(T')$ by the transformation of variables, following from the relation:

$$P(u) \, \mathrm{d}u = P(T') \, \mathrm{d}T' \,. \qquad (68)$$

The substitution from (*42*) gives:

$$P(T') \, u m_C M m_D^{-1} = P(u) \,; \qquad (69)$$

The combination of this relation with (*67*) leads to the final result

$$P(T') = 2\pi m_D (m_C M)^{-1} \, u \int f(u_1, u_2, u_3) \sin \vartheta \, \mathrm{d}\vartheta \,. \qquad (70)$$

The probability density distribution $P(\vartheta)$ *vs* ϑ is often called in literature the CM angular distribution and the probability density distribution $P(T')$ *vs* T' is called the product relative translational energy distribution[4].

Our paper attempts to use consistently the fact that an elementary chemical process occurring in a collision of two particles is investigated in scattering experiments on an ensemble of a large number of reactant pairs. This provides a basis for normalization of the measured product intensities and for their interpretation from the point of view of the probability theory. Such a treatment makes it possible to speak about a probability that a (single) product particle exhibits certain properties.

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Translated by the author (Z. H.).