

Effusion and processes on the surface

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A systematic review is given of the various approaches to the theory of molecular flow in the interior of vessels and of molecular effusion into vacuum. The approximate character of the photometric model, widely used at present in effusion calculations, is noted. It is shown that effusion is determined by three factors: 1) kinetics of chemical reactions involving molecular fluxes on the walls of vessels; 2) local kinematics of the reflection of these fluxes by the walls, and 3) shape of the vessel and of the effusion aperture. A detailed analysis is given of each of these factors from both experimental and theoretical standpoints. Attention is drawn to possible applications of neutron-transport theory, and a number of geometric probability theorems, to the effusion problem. Possible, desirable, and essential topics for future theoretical and experimental research into effusion are enumerated. The literature cited covers the period essentially up to the end of 1974.

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"In any chemical situation a large number of atoms are involved, and we have seen that the atoms are all jiggling around in a very random and complicated way. If we could analyze each collision, and be able to follow in detail the motion of each molecule, we might hope to figure out what would happen." ⁽¹⁾, p. 34

"...and lo and behold!, the chemists are almost always correct." ⁽¹⁾, p. 34

R. P. Feynman

1. INTRODUCTION

A. General considerations

Effusion is the slow (with thermal velocities) escape of a gas or vapor from a vessel. Although effusion can also be observed at enhanced pressures (gas-dynamic conditions), we shall confine our attentions to free molecular, or Knudsen, effusion when the mean free path is greater than the linear dimensions of the vessel and of the effusion aperture. This restriction to the Knudsen conditions is dictated by our desire to avoid overloading our discussion with questions connected with homogeneous gas diffusion, which are of independent interest.¹⁾ We shall also almost completely exclude a number of other effects associated with temperature inhomogeneities in the vessels (the fountain effect in helium near the lambda point, the thermomechanical effect

and its inverse, the mechanocaloric effect^(2,14) or with the electric-field distribution.^(2,15) Finally, we shall not consider the physics of beams consisting of particles with energies greater than the thermal energy.

The Knudsen conditions can be achieved either by reducing the pressure inside the vessel or by reducing its characteristic linear dimensions (by using small cavities or capillaries).

The effect of the surface of the vessel and of its shape on the distribution in its interior of the flow of chemically active molecules has frequently been discussed in the review literature.^(2,3) Certain aspects of chromatography^(4,5) and effusion can also be included in this category of problems.

Well before the work of Maxwell and Boltzmann, before the completion of the basic formulation of the kinetic theory of gases, Graham^(2,16) discovered in 1829 that the flux j of a gas of molecular weight M through a porous isothermal partition (at temperature T) was given by the formula

$$j = A(P_1 - P_2) \sqrt{\frac{T}{M}},$$

¹⁾For example, see^(2,13) in connection with the separation of isotopes by thermal diffusion. Processes of this kind normally occur at relatively high pressures; they could be achieved under the Knudsen conditions but with a lower efficiency.

where A is a constant, P_i is the pressure on the two sides of the partition, and j and P_i are functions of time. In 1873, Feddersen^[218] investigated the gas conductance of a nonisothermal porous partition with equal gas pressures on either side. Reynolds^[219] (1879) and Knudsen^[220] (1910) investigated the same effects but with calibrated capillaries inserted into the partition. They developed a theory of the constant A in the formula given above.²⁾ In the steady state, and for sufficiently narrow capillaries, single-component gases satisfy the expression

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}}$$

We shall not describe the entire crown of the genealogical tree of effusion and will confine our attention only to its roots. The most important branches will be mentioned in the course of our exposition. It will be clear from the ensuing description that the kinetics and kinematics of effusion are, to a considerable extent, determined by surface processes—in particular, adsorption—the history of which is older by roughly 100 years: “The 150-year-old history of studies of adsorption contains too many facts, too many theories, and too many names—including those of the leading scientists of each period—for an even partial account to be given here” (1936).^[221]

Much of the historical background is given in various textbooks.^[32, 98, 214, 215, 217] The history of effusion experiments could be used to show that “on average” the number of important parameters that cannot be neglected is an increasing function of time. Those cases in which important problems would appear to be resolved by experiment are relatively rare. The more common situation is that in which only the sphere of influence of individual factors is established. Thus, the scattering of molecules by a surface is determined by the ratio of the heat of adsorption E_a and the energy kT_0 of the incident molecule. The heat of adsorption depends on the composition and state of the surface and of the incident beam. An analysis of the interaction between noble-gas molecular beams and single-crystal metal surfaces was used in^[24] to establish the following classification of scattering processes: 1) quasioelectric scattering (accompanied by diffraction in the case of long de Broglie wavelengths) occurs for $E_a/kT_0 \leq 0.25$; 2) inelastic scattering occurs for $0.25 \leq E_a/kT_0 \leq 2.5$, and 3) adsorption-desorption scattering occurs for $2.5 \leq E_a/kT_0$. Most of the published research on effusion phenomena has been confined to situations in which the third class predominates ($E_a/kT_0 \gg 2.5$).

In view of the foregoing, accurate direct experiments are of paramount importance (see Chaps. 3–5), but there is also considerable hope that the microscopic theory of phenomenological coefficients will turn out to be successful. L. D. Landau, who developed the theory of one of the accommodation coefficients for helium atoms, was a pioneer in this field. This line of re-

search is being developed by Goodman.^[22, 23] The many chemical kinetic coefficients are not as yet covered by the theory. The establishment of connections between the various coefficients would seem to be a promising line of enquiry (see Chap. 3).

B. Who needs effusion and why?

The publication of books^[9, 10] and historical-bibliographical reviews of vacuum phenomena and pumps,^[11, 12] was followed by many original papers in the periodical literature. It will be convenient to review them from a unified standpoint. The numerous reviews concerned with allied questions such as evaporation and condensation,^[13–16] the technology, physics, and chemistry of molecular beams,^[17–20, 97] and the elementary gas-solid interaction^[21–25, 166] do not generally discuss the effusion problem although they do touch upon some of its individual aspects.

The main scientific stimulus to effusion research is the lack of information about the elementary interaction between the particles of real gases among themselves (this is the concern of the crossed molecular beam technique) and with real surfaces. Here, effusion is both a research tool (as a source of molecular beams) and the object of investigation because effusive flow is determined by the elementary interactions between the particles in the interior of effusion cells.

The noticeable increase in interest in effusion has been due to the needs of various technological and scientific processes, including pumping systems,^[7] low-pressure gauges,^[8] measurements of partial evaporation rates, deposition of microelectronic circuits, and production of molecular beams for research in chemistry and physics.

In other words, ideally, one would like to have molecular beams of given intensity, composition, and spatial and energy distributions or, as a minimum requirement, one would like to know what one is dealing with under given real conditions. This also applies to the surface whose interaction with the incident particles is being investigated. Thus, at best, one would like to have a surface with perfect (or given) structure, composition, charge and energy states, and shape, although, in practice, one would be satisfied with adequate knowledge of the properties of the surface.^[154]

Adsorption-desorption or the more complicated heterogeneous chemical reactions occurring on the walls of the effusion vessel have a self-consistent character. The coverage of the surface with adsorbed gases and, occasionally, the more substantial modifications of its physical and chemical properties, are connected with the intensities of the incident particle fluxes. The desorption flux depends on the incident-particle flux and on the state of the surface. Thus, the very nature of the phenomenon impedes the separate investigation of the different individual factors.³⁾

Surface phenomena are important for studies of the

²⁾This phenomenon also drew the attention of Maxwell (see^[217]).

³⁾This idea has been pointed out by Ya. B. Zel'dovich.

interaction between satellites and the upper atmosphere, and research into the composition and temperature of the upper layers of the atmosphere with the aid of meteorological instruments (i. e., effectively, effusion vessels) carried by satellites and rockets involve, in a way, the converse problem, i. e., the scattering of incident molecular fluxes by the interior surfaces of these devices. [222]

Molecular flow in vessels is a typical stochastic process, so that there is a mutually beneficial link between effusion studies, on the one hand, and theories of scattering and propagation of neutrons, sound, protons, and so on. The neutron "bottle," proposed by Zel'dovich, [223] which is based on the ultracold and almost complete containment of neutrons reflected (partly diffusely and partly specularly because of the long de Broglie wavelength) from the walls of the "bottle," is excellently described by traditional effusion terminology.

These questions are closely related to the interaction between gases and porous sorbents and catalyzers. Research in this field is facilitated by the availability of new experimental techniques (new ultrahigh vacuum systems) and new results, some of which are discussed in the present review.

C. Photometric approximation. The Knudsen cell as an analog of a perfect black body

The perfect effusion cell, invented by Knudsen, is the analog of the perfect black body in optics. Again, as in optics, the analogy is not perfect. The disturbing factors are the following: surface diffusion of particles over the walls of the effusion aperture, chemical interactions between the material of the cell and the effusing medium (which may erode the cell or modify its shape), changes in the shape of the cell due to recondensation or simply to the effusion current itself, the linear photometric transformation of the incident flux leaving the surface may not be valid, and the assumption of thermodynamic equilibrium between the vapor-gas mixture and the condensed phases may not be admissible.

Apart from these fundamental difficulties, there are a number of purely technological problems, including the provision of an isothermal cell, fabrication and preparation of the effusion cell, measurement of the required beam parameters, and so on. These matters will be virtually ignored here although they are the source of much anguish to the hard-pressed experimenter.

Let us discuss in greater detail the undeservedly popular [9, 98, 121-123] photometric model of diffusion. In order to avoid complications due to multiple collisions, we shall suppose that the scattering surface is not curved, and will ignore possible transformations of the molecules, assuming that they are stable.

In the case of a single-component vapor, the condensation coefficient is defined by

$$\alpha_c = \frac{\sigma - \varphi}{\sigma - \sigma_0} = \frac{\sigma - \varphi}{\sigma - \varphi_0}, \quad (1.1)$$

where σ and φ are the densities of the incident and departing molecular beams, while σ_0 and φ_0 are the corresponding quantities in equilibrium. From (1.1), we can show that the rule governing the transformation of the incident into the departing flux is

$$\varphi = (1 - \alpha_c) \sigma + \alpha_c \sigma_0 = (1 - \alpha_c) \sigma + \alpha_c \varphi_0. \quad (1.2)$$

This transformation is not necessarily linear because α_c may be a function of σ [87] (see Chap. 3).

When $\alpha_c = \text{const}$, (1.2) yields the photometric approximation in which $\alpha_c \sigma_0 = \alpha_c \varphi_0$ is the purely Langmuir evaporation, $(1 - \alpha_c) \sigma$ is the reflected part, and $(1 - \alpha_c)$ is the reflection coefficient. The departure from linearity increases when chemical transformations have to be taken into account (see below).

D. Fundamentals of effusion models

It is generally clear, that, to determine the composition and the spatial and energy distributions of the particles leaving a vessel of given geometry, we must know the answers to a number of more elementary questions:

1) *Chemical* (or kinetic) series: which reactions involve the "creation" or "loss" of the particles in which we are interested? What are the rates of the individual stages of these processes (including the adsorption-desorption processes)?

2) *Locally-kinematic* series: what are the angles to the internal macro-surface of the vessel at which the particles of different kind and (or) different origin (in the sense of the first series) are desorbed (or reflected)? What is the effect of kinetic characteristics on the spatial and energy distributions?

3) *Macrogeometric* series: how are the solutions of the basic direct effusion problems affected by the geometric parameters of the vessel, the effusion aperture, the molecular source, the distribution of thermal sources and temperature fields, and so on? What is the role of surface and volume diffusion? The latter question can also be considered under the heading of kinetics.

The above categorization is very arbitrary because the three "series" are interdependent. This is reflected in the differential equations for the chemical kinetics (nonseparable variables) and in the integro-differential transport equations which are usually nonlinear. The answers to the above questions are frequently unknown. They are available only occasionally and then only for a small number of special or simplified general conditions (for example, Langmuir adsorption).

We shall define *direct effusion problems* as those involving the calculation and (or) measurement of spatial and energy distributions of the partial (with respect to composition) steady and nonsteady molecular fluxes leaving an effusion vessel. These general problems generate a multitude of more special problems, for example, those encountered in the design of molecular-

beam sources with given parameters, or in effusion metrology in so far as it involves the theory of practical instruments.^[26]

When substantive answers to the first two series of questions are available, the direct effusion problem for any given macrogeometry can be solved (at least, numerically). In Chap. 2, we give an outline solution for the simple (but nonlinear) Langmuir adsorption kinetics, the local cosine distribution, and the cylindrical macrogeometry.

E. Formalization of effusion problems

To describe events in the interior of an effusion cell, we must specify the two parameters σ_i and φ_i as well as the surface coverage θ_i , where i represents a particular material. All these quantities must be known as functions of time t and of position x :

$$\varphi_i = \varphi_i(x, t), \quad (1.3)$$

$$\sigma_i = \sigma_i(x, t), \quad (1.4)$$

$$\theta_i = \theta_i(x, t). \quad (1.5)$$

To describe the kinematic features of the model, we must specify the emission polar diagram which describes the distribution of emitted particles of a given type in the space of the polar coordinates (α). These polar diagrams may vary from point to point and may be functions of time.⁴⁾

$$\Phi_i = \Phi_i(\alpha, x, t). \quad (1.6)$$

To elucidate the effect of macrogeometry, we introduce the probability $K(x, x_1)$ that a particle leaving the point x_1 will reach the point x . The form of this function depends on Φ and on the geometry of the regions under consideration $S(x)$. The effect of the geometry can then be described as follows:

$$\sigma_i(x, t) = \int_{S(x)} \varphi_i(x_1, t_1) K(x, x_1) dS, \quad (1.7)$$

provided particles of different type i retain their identities and do not transform into other particles.

In (1.7), t_1 is the time at which particles should leave regions with coordinates x_1 in order to reach those with coordinates x at time t (this means that t_1 depends on particle velocity and on the distance between x and x_1).

The integral in (1.7) is evaluated over all regions $S(x_1)$ which can send their "representatives" to the neighborhood of the point x .

The only use of (1.3)–(1.7) is in impressing upon us that the situation is complicated. Something much more definite has to be written down before calculations

⁴⁾Since there are published data^[24] on the dependence of the distribution of momenta of the emitted particles on the distribution of the incident momenta, this fact should, strictly speaking, be taken into account in (1.6)–(1.7).^[34] However, this will be ignored here for simplicity (this is the Knudsen hypothesis), but we shall return to this topic in Chap. 4.

can be carried out but, nevertheless, the general ideology of the situation should be as given by (1.3)–(1.7).

In practice, there are various possible combinations of given and required functions φ , σ , θ , Φ , K , and S corresponding to given boundary and initial conditions.

Because it has not been adequately explored, we shall not be concerned here with the very substantial and difficult question of *converse effusion* problems in which the results of effusion measurements performed with practical instruments (i.e., with finite resolution in time, space, composition, energy, and so on) are used to determine, firstly, precisely what has been measured (what happened at entry into the instrument) and, secondly, what has occurred inside the effusion vessel itself. These problems are difficult to solve because they are usually incorrectly posed.^[27] In more complicated cases, (1.7) has to be replaced by very cumbersome sets of nonlinear integral or integrodifferential equations,^[9,10] in which different methods of preparing the particles of a particular kind from different "raw material" and, correspondingly, different "sinks" for these particles, must be taken into account. This cumbersomeness is, generally, characteristic for the kinetic theory of rarefied gases.^[98,225] The words of Sirovich, an active mathematician working in this field,^[227] "We are dealing with a sequence which starts with hopeless generality and ends with special cases amenable to calculation" apply equally well to individual papers and to series of papers.^[226] Frequently, these "special cases" can be treated without recourse to extensive integrodifferential equations. A very sober and objective approach to the situation obtaining in the study of the interaction of gases with solid surfaces is given in Barantsev's book.^[224]⁵⁾ Nevertheless, even there, one finds piles of semiphenomenological coefficients which are difficult both to measure and to calculate.

All these difficulties (both mathematical and physical) will, clearly, be removed only after prolonged, difficult, and substantial experimental studies.

F. Examples of studies of elements of the model

The reflection coefficient $(1 - \alpha_c)$ in (1.2) is the fraction of particles with immeasurably⁶⁾ short adsorption time, and α_c can be interpreted in a more general sense than the condensation coefficient, namely, as the fraction of particles lost as a result of any kind of encounter that may involve the particle on the surface (recombination, decay, association, and so on).

The method of modulated molecular beams, used to measure the adsorption time spectrum, has very con-

⁵⁾This book ignores questions involving adsorption, condensation, and chemical reactions on a surface.

⁶⁾The lower limit of measurable adsorption times has recently been reduced to 10^{-8} sec (see^[30,173]) and the discussion of these papers in Chap. 3). The lower Debye limit is 10^{-14} sec. The minimum characteristic time of interaction between an atom and a surface is also 10^{-13} – 10^{-14} sec.

siderable possibilities and has, in fact, been successful in practice. In this method, the minimum measurable time is restricted by the Maxwellian spreading of the pulse front ($\sim 10^{-5}$ sec) when scattered beams are recorded by traditional detectors, but this can be reduced to $\sim 10^{-7}$ sec in the case of optical detection (which requires sufficiently high molecular- and light-beam intensities). However, even the usual simple studies of adsorption under steady-state conditions will yield the absorption time. For example, when the Langmuir equation is valid, the reciprocal of the adsorption time (i. e., the desorption frequency) is given by

$$\mu = \frac{\varphi - \sigma\theta}{\theta}. \quad (1.8)$$

When φ , σ , and θ have been measured, it is, at least in principle, possible to calculate μ . Why, then, is it necessary to introduce the relatively complicated modulated-beam technique?⁷⁾ There are two reasons: firstly, equations such as (1.8) require very accurate measured values of φ , σ , and θ , which cannot be achieved at present (this is the old difficulty of measuring a small difference between two large numbers) and, secondly, measurements by this method require the formula given by (1.8), i. e., a certain model of the problem whose parameters are established by experiment. When modulated molecular beams are employed, on the other hand, we can investigate the function $\varphi = \varphi(t)$ for a given, e. g., periodic, function $\sigma = \sigma(t)$, so that, by writing down the simple mass-balance equation (which is independent of the model)

$$\dot{\theta} = \sigma - \varphi, \quad (1.9)$$

we can obtain $\varphi = \varphi(\theta, \sigma)$ and hence $\mu = \mu(\theta)$. In the steady state, (1.9) is less substantive:

$$\sigma = \varphi. \quad (1.10)$$

Measurements of μ are based on studies of transient processes of two kinds: 1) nonsteady-state Knudsen diffusion along a long capillary of a calibrated amount of gas or vapor introduced at one end of the capillary,^[45] and 2) the periodic adsorption-desorption process when the adsorbent is exposed to the modulated molecular beam.^[167,168]

Method (1) has been used to determine very small adsorption times [$\mu^{-1} \approx (10^{-5} - 10^{-6})$ sec], but it assumes that μ is independent of θ , it requires a cosine-type polar distribution for the desorption process, it neglects surface diffusion, and, in the variant developed by Clausing,^[45] it does not satisfy modern high-vacuum "hygiene"^[46] although this last difficulty can be overcome.^[46]

Method (2) presupposes a large desorption flux or a high detector efficiency. This is realistic for the surface ionization detector, which restricts the method

⁷⁾We are indebted to V. Z. Belen'kii for useful discussions of this point.

because molecular analysis of the particles incident on the adsorbent and leaving it is then impossible, and materials capable of surface ionization have to be employed.

The obvious solution is to replace the surface-ionization detector by a mass spectrometer using an electron multiplier or photoionization, but this is usually associated with a sharp reduction (by 2-6 orders of magnitude) in the sensitivity or an equivalent reduction in resolution [in the densities σ and φ , in the mass numbers, in the characteristic times of the process (μ^{-1}), in the particle energies, and so on (see^[169-176])].

The solution is to use a periodically repeating process and synchronous storage of the signal.^[54,95,172]

These techniques are, however, still restricted by a lower limit of about 10^{-4} sec for the measured adsorption times.

The adsorption-desorption component of effusion problems is important in connection with the problem of crystal growth, for which the spectrum of surface states, which is expected to have many features, has not as yet been identified.

There is extensive evidence that the density of the two-dimensional adsorbed gas and two-dimensional phase transitions involving its participation are important for heterogeneous reactions. In particular, the careful analysis given in^[62] of the kinetics of nucleation in condensation processes has shown (see also^[63]) that the activity of catalyzers depends on the structure of surface layers. Many of these phenomena have not as yet been taken into account in effusion measurements. It is only during the last 5-10 years that experiments have been carried out at ultralow pressures, using mass-spectroscopic and other measurements of the composition and intensity of incident and desorbing molecular beams. It is shown in^[70,71] that the rate of Langmuir evaporation of NaCl single crystals depends on the presence of relatively small amounts of Ca and on the density of dislocations.

We shall now consider a simple case which illustrates the kinetic aspect of effusion problems.

Voronin^[47] has given a theory of the steady-state effusion of a vapor consisting of monomers M and dimers D . He assumed that the following equilibrium chemical reaction was taking place at each point on the inner surface of the effusion vessel:



He then used this assumption to calculate the angular distributions of the effusing monomers and dimers as functions of the geometric parameters of the effusion vessel and of the equilibrium constants of the reaction (1.11). His results have been confirmed experimentally^[48] and this was noted in^[49,55,56]. It will be shown later (Chap. 5) that this agreement is, to some extent, illusory.

The kinetic graph of chemical transformations which involve the participation, for example, of dimers and

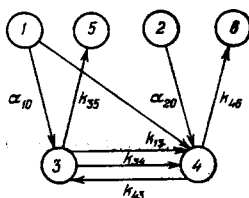


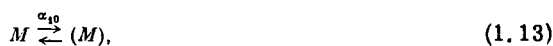
FIG. 1. Graph representing the kinetics of transformations. The reaction rate constants are the same as in (1.12)–(1.16). 1, 2—Monomers and dimers incident on the surface; 3, 4—monomers and dimers adsorbed by the surface; 5, 6—monomers and dimers escaping from the surface.

monomers can be quite complicated. Figure 1 shows transitions between certain states of the monomers and dimers. The number of these states can be readily increased, for example, by introducing all the conceivable positions in the crystal and on its surface. It is much more difficult to identify the leading channels even for the transitions shown in the figure. All that can be done is to arrange the cross sections for these channels in increasing order.^[51]

Let us write down a set of equations corresponding to Fig. 1 that is neither too simple nor too rigorous:

$$\left. \begin{aligned} \dot{\theta}_0 &= -\theta_0(\sigma_1 + \sigma_2) + \theta_1 k_{35} + \theta_2 k_{46} & -\theta_0 \theta_1 \sigma_1 k_{13}, \\ \dot{\theta}_1 &= \theta_0 \sigma_1 & -\theta_1 k_{35} + \theta_2 k_{43} & -\theta_0 \theta_1 \sigma_1 k_{13} - \theta_1^2 k_{34}, \\ \dot{\theta}_2 &= \theta_0 \sigma_2 & -\theta_2(k_{43} + k_{46}) + 2\theta_0 \theta_1 \sigma_1 k_{13} + \theta_2^2 k_{34}, \end{aligned} \right\} \quad (1.12)$$

where, in addition to the symbols defined earlier, we use the rate constants k_{ij} of the following reactions:



It is assumed in (1.12) that the attachment probabilities for the monomers and dimers are $\alpha_{10} = \alpha_{20} = 1$.

The symbols M , D , (M) , and (D) refer to monomers and dimers in the gaseous and adsorbed phases.

It is shown in^[61] that the equilibrium approximation^[47] is valid provided (1) we can neglect collisions between beam monomers and adsorbed monomers, and (2) the rate of desorption of the dimers is much smaller than their dissociation rate. However, direct experiments involving the interaction of an NaCl, $(\text{NaCl})_2$ molecular beam with tantalum^[44, 46, 47] and platinum^[75] targets have shown that some of the dimers $(\text{NaCl})_2$ have adsorption times less than 5×10^{-5} sec and do not succeed in predissociating, so that their concentration in the desorption flux is higher than one would expect from the equilibrium constant. We shall return to the results reported in^[44–46, 74, 75] in Chap. 5.

The escaping fluxes φ_1 and φ_2 are given by

$$\varphi_1 = \theta_1 k_{35}, \quad (1.17)$$

$$\varphi_2 = \theta_2 k_{46}. \quad (1.18)$$

So far, it has not been possible to determine separately

the coefficients k_{ij} . According to^[51], the choice between the competing reaction paths (Fig. 1) in the time-independent case ($\theta_i = 0$) can be made as follows:

1) when $k_{13} \approx 0$, $k_{43} > k_{46}$

$$\varphi_1 = \frac{K}{4} \left(\sqrt{1 + \frac{8(\sigma_1 + 2\sigma_2)}{K}} - 1 \right) \approx \sqrt{a_1 + a_2(\sigma_1 + 2\sigma_2)}, \quad (1.19)$$

2) when $k_{35} \ll \sigma_1 k_{13}$, $k_{43} \gg k_{46}$

$$\varphi_1 \approx \sqrt{b_1 \sigma_1^2 + b_2 (\sigma_1 + 2\sigma_2)}. \quad (1.20)$$

The value of φ_2 is the same in both cases:

$$\varphi_2 = \frac{(\sigma_1 + 2\sigma_2) - \varphi_1}{2}, \quad (1.21)$$

$$K = \frac{k_{43} k_{35}^2}{k_{34} k_{46}}. \quad (1.22)$$

where K is the equilibrium constant. The functional difference between (1.19) and (1.20), taken in conjunction with a comparison with the experiment^[74] on the interaction of NaCl and Na_2Cl_2 molecular beams with a tantalum target, suggests that process (2) predominates. However, much higher experimental precision will be necessary before a reliable identification of the reaction paths can be achieved.

It is important to note here that relationships of form given by (1.22) are valid only in the case of equilibrium in closed isothermal systems (constant number of atoms). Ya. B. Zel'dovich has shown^[229] that the steady-state concentrations of different chemical compounds in such systems do not depend on the path taken by the system to reach this state, and this closes forever any possible discussion on the possibility of different equilibrium states. The system which we are investigating (vessel + effusing material) is not closed^[6] and is not necessarily isothermal because the incident beam of molecules may have a different thermal energy from the substrate or the walls of the vessel. Thus, even the steady state is not necessarily identical with the equilibrium state (although it may be). The general ideology relating to heterogeneous reactions is evidently the same as for the relaxation of different degrees of freedom in a gas,^[230, 231] for which it is possible to establish a hierarchy of characteristic times:

$$\tau_{\text{transl}} \leq \tau_{\text{rot}} \ll \tau_{\text{vib}} < \tau_{\text{chem}}$$

representing, respectively, the translational, rotational, vibrational, and chemical (or electronic) excitations. We shall show below that the analogous hierarchy in the case of collisions between molecular beams is

$$\tau_{\text{transl}} \ll \tau_{\text{ads}} \leq \tau_{\text{chem}}$$

We know of no systematic studies of τ_{vib} and τ_{rot} for heterogeneous interactions, but there are no apparent reasons why these times should not lie somewhere in the middle of the above chains of inequalities.

When particular values of the rate constants k_{ij} are determined, it may be possible to correct the classical

principle of detailed balancing for departures from the Boltzmann distribution and for differences in the translational, rotational, and vibrational temperatures,^[39] for example, as in^[232] (see also the review^[233]). A more detailed discussion of this question would be premature at this time.

The set of equations given by (1.12) refers to the interaction between homogeneous molecular beams and noncurved targets. To investigate these reactions in the vessel, we must also include the integral relationships representing multiple scattering and spatial inhomogeneity of the flux distribution inside the vessel.

The analytic solution of the stochastic integral equation is cumbersome (and, occasionally, not available), so that it is desirable to simplify it, for example, by reducing it to a differential equation. The conditions which must be satisfied before the Smoluchowski equation (for the random motion of chemically stable particles) can be transformed into the differential Fokker-Planck equations, or the diffusion equation, have been discussed by Leontovich^[34] and by Chandrasekhar^[105] (see also the extensive annotated bibliography therein). Diffusion in capillaries, accompanied by chemical reactions, has been investigated by Zel'dovich,^[228] who obtained the widely quoted dependence of the apparent order (and heat) of the chemical reaction on the rates of diffusion, rate of supply of reagents, and true reaction rate. Chambre^[59] has considered the validity of the transition from the integral equation of motion of the chemically active gases along the capillaries to the differential diffusion equation, and has shown that the conditions ensuring the validity of this approximation are

$$\begin{aligned} 1) \quad \alpha_i &\ll 1, \\ 2) \quad \frac{\sqrt{\alpha} L}{2R} &\gg 1, \end{aligned} \quad (1.23)$$

where α_i is a kinetic coefficient (for example, α_c), and L and R are the length and radius of the capillary, respectively. These and other studies of this kind are discussed in detail in^[9] (see also Chaps. 5 and 6). As already noted, before we can evaluate the kernels of the integral equations, we must know the local emission polar diagrams. There is a wide range of possible diagrams of this kind for different beam-surface combinations. They range from those close to δ functions (in the case of diffraction) to almost isotropic distributions (in the case of "strong" chemical interactions, for example—chemisorption; see Chap. 4 for details). We also have the possibility of energy transfer between zero and virtually 100%, i. e., we are dealing with unique research objects (see the next chapter).

G. Results over the last few years. Structure of the remainder of this review

Most experiments on the heterogeneous interaction of the vapor-gas phase with the surface of condensed bodies have been carried out under the notoriously "natural," i. e., very unhygienic, conditions with poorly controlled variation in composition and other properties of the vapor-gas and solid phases. One cannot

but admire the chemists who have succeeded in finding specific catalyzers for many types of chemical transformation, especially since these catalyzers are usually unstable both in use and in manufacture. Satisfactory theories and manufacturing technologies are only just being developed for these materials. There are, in addition, numerous recipes obtained over a long period of time as a result of trial and error (mostly error).

Another area where there is a lack of pure and definite experimental data on heterogeneous interactions is the science of the growth of crystals (which seem to grow in spite of everything, although their quality is not always what it might be).

The majority of the more stable data has accumulated since the advent of ultrahigh-vacuum techniques and molecular beams.

Let us list the most interesting (from our standpoint) results and lines of research for different ranges of values of the parameter $\delta \equiv E_a/kT_g$ (E_a is the heat of adsorption and T_g the beam temperature).

Small values of δ . Investigations of 1) the dynamics and 2) the structure of surface layers which, by the way, have not as yet been taken into account in effusion research. Here, we have the possibility of interesting phenomena involving the scattering of particles inside the effusion vessel with particular orientation of single-crystal walls. 3) Studies of the transfer of translational and rotational energy during collisions between the molecules and the surface. 4) Small-angle scattering of beams of molecules by perfect solid surfaces. This is possible for any value of δ . Studies concerned with small values of δ will be considered in Chap. 4, but they deserve a separate review.

Large values of δ . 1) It has been shown that the time of contact between the incident particles and the target surface is frequently not sufficient for the completion of a number of thermodynamically possible chemical transformations. 2) This time is, however, sufficient for the establishment of complete thermal equilibrium. Both low-temperature and high-temperature beams have been produced (gold and chromium at 300 °C and CsCl at 1800 °C, respectively). 3) As a rule, desorption and evaporation processes are described by an isotropic local cosine distribution. 4) Hysteresis phenomena have been recorded during effective adsorption ($\sigma - \varphi > 0$) and desorption ($\sigma - \varphi < 0$) on the surface of sufficiently perfect single crystals; this was previously observed on porous adsorbents. 5) Particles of different chemical nature have been found to have very different partial angular effusion distributions. 6) Substantial anisotropic effects have been found in the electro- and photodesorption of certain single crystals. 7) It has been established that the structure and valence state of the surface have a considerable influence on the course of heterogeneous processes. 8) It has been noted that an evaporating or desorbing surface may emit fluxes that are greater than in the case of equilibrium, when it receives a particle flux from outside (when $\sigma - \varphi > 0$, $\varphi > \varphi_0$). A simple effusion model is used in Chap. 2 in a numerical solution of the

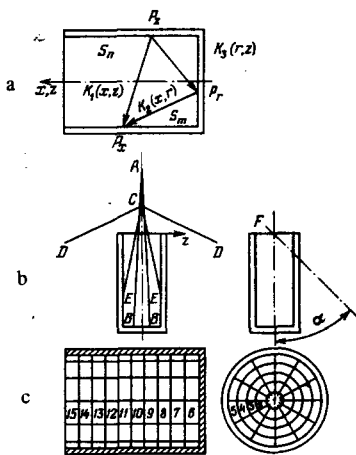


FIG. 2. Coordinate systems for Eqs. (2.1)–(2.8) (S_m —bottom, S_n —lateral surface of cylinder) (a), mutual disposition and displacement of vessel and collimators (b), and method of subdividing the inner surfaces into zones of mutual illumination (c).

problem of the θ , φ , σ distributions and the spatial distributions of effusion through a given set of collimators.

All these phenomena are discussed in greater detail in Chaps. 3–7 but, necessarily, in a condensed form. Moreover, it is shown there how one can borrow some of the results of neutron transport theory (Dirac) and many of the theorems involving geometric probabilities (Crofton, Sylvester, Poincaré) for the description of effusion phenomena. Some calculated and experimental results on the angular distribution of effusion, and certain particular aspects of effusion phenomena, are reproduced. In the final chapter (Chap. 7), we outline certain possible problems for future investigations.

2. A PARTICULAR EFFUSION MODEL

Suppose we have particles of a particular species which participate only in adsorption-desorption reactions and obey the Langmuir kinetics:

$$\dot{\theta} = \sigma - \varphi = \sigma(1 - \theta) - \mu\theta, \quad (2.1)$$

where μ is the reciprocal of the adsorption time.^[30] We shall suppose that the local angular distribution is (in accordance with the Knudsen postulates)

$$\Phi = \Phi_0 \cos \alpha, \quad (2.2)$$

where Φ_0 is the intensity (particles \cdot cm $^{-2}$ \cdot sec $^{-1}$) emitted in the direction normal to the area, and Φ is the intensity at an angle α to the normal. In the more detailed language of photometry, the formula given by (2.2) represents the isotropic brightness of each emitting area element.

We must now find the probability $K(x, x_1)$. To determine this probability, we must know not only the angular distribution but also the geometric characteristics of the vessel (and, in general, the physicochemical fields on its inner surface). Suppose that the vessel is

an isothermal cylinder of length L and radius R (Fig. 2a). It is shown in^[10,28,29] that, for this geometry (axial symmetry), it is possible to determine the following probabilities: $K_1(x, z)$ —the probability that a particle leaving a band near the point z on the cylindrical surface, will strike a band near the point x which is also on the inner cylindrical surface, $K_2(x, r)$ —the probability that a particle leaving a ring of radius r on the bottom of the cylinder will reach a band near the point x on the cylindrical surface, and $K_3(r, z)$ —the probability of the reverse transit of the particle from a band near the point z on the cylindrical surface to the ring of radius r on the bottom of the cylinder.

The above probabilities are given by the following expressions

$$K_1(x, z) = \frac{1}{2} \left\{ 1 - \frac{|x-z|[6R^2+(x-z)^2]}{[4R^2+(x-z)^2]^{3/2}} \right\}, \quad (2.3)$$

$$K_2(x, r) = \frac{2R^2xr(R^2-r^2+x^2)}{[(R^2+r^2+x^2)^2-4R^2r^2]^{3/2}}, \quad (2.4)$$

$$K_3(r, z) = \frac{2R^3z(R^2-r^2+x^2)}{[(R^2+r^2+x^2)^2-4R^2r^2]^{3/2}}. \quad (2.5)$$

Equation (1.7) now assumes the form

$$\sigma(x, t) = \int_{S_i} \varphi \left(z, t - \frac{|x-z|}{v} \right) K_i(x, z) dS(z). \quad (2.6)$$

Let us take the initial condition to be

$$\theta|_{t=0} = \begin{cases} \theta_0 & \text{on } S_m, \\ 0 & \text{on } S_n, \end{cases} \quad (2.7)$$

$$0 \leq \theta(x, t) \leq 1. \quad (2.8)$$

The set of equations given by (2.1)–(2.8) can be used for a programmed solution on a computer. This was done in^[28,29] and typical results of this solution are shown in Fig. 3, which plots the values of θ and σ in different parts of the cylinder (Fig. 2c) at different instants of time.

Let us now consider the influence of the geometry of the molecular-beam collimator and its disposition relative to the effusion vessel.^[28] The effect of the geometry of the measuring system is also discussed in^[40-43].

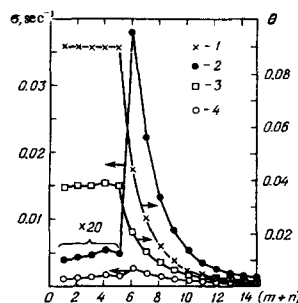


FIG. 3. Distribution of the coverage factor θ and incident flux intensity σ over the inner surface of a cylinder. $m+n$ —number of zone in Fig. 2c, 1— θ , 2— σ for $t=0.116$ sec, 3— θ , 4— σ for $t=1.15$ sec; brace indicates change of scale along the vertical axis. Parameter values: $\mu=10$ sec $^{-1}$, $L=5$ cm, $R=1$ cm, $\theta_0=0.1$; $v=10^4$ cm/sec $^{-1}$.

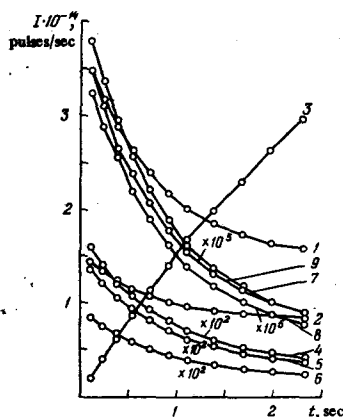


FIG. 4. Detector signal I for different collimator-detector assemblies. The parameters are the same as in Fig. 3. The collimators and the cylinder (Fig. 2b) are made on the same scale. Numbers on curves between 1 and 9 are defined in the following table.

Type of collimator (Fig. 2b)	DCD			ECE			BAB		
Curve No.	1	2	3	4	5	6	7	8	9
Shift along the axis, cm	0	1.33	2.66	0	0.43	0.87	0	0.36	0.72

Figure 2b shows the relative disposition of the effusion cylinder and the three collimators used in the calculations. The collimator consisted of two coaxial circular diaphragms defining the right circular "visibility cones" BAB, DCD, and ECE in the figure. They are the boundaries of regions on the surface of the cylinder from which desorbed and reflected particles can reach the detector after passing through the collimator; the detector is assumed to be perfect, i. e., capable of recording all the particles reaching it with 100% efficiency. Equation (2.6), taken in conjunction with (2.2)–(2.5), differs from the usual Clausing equation^[57] firstly by the fact that it is an equation with a retarded argument, secondly, it is essentially two-dimensional, and thirdly, we have taken into account, for the first time in this type of problem, the equations of adsorption kinetics. The set of equations given by (2.2)–(2.8) is thus analogous to the sorption equations,^[32,33] and its time-independent version is widely used in single-velocity problems in neutron-transport theory.^[35] There is now nothing to prevent us from using results of the kind shown in Fig. 3 (which, in fact, completely describes the situation inside the cylinder) in calculations of the effusion flux from a cylinder. For example, we can determine the Clausing coefficient, i. e., the effective resistance of the cylinder to molecular flow passing through it as a function of the adsorption and geometric characteristics of the vessel (see Chap. 5).

The signal produced by a perfect detector can be calculated as a function of the displacement of the effusion cylinder along the z axis (see Fig. 2b), the rotation about this axis through an angle α (for fixed but demountable collimators), and the time.

We shall not reproduce here the resulting angular distributions, i. e., functions $I(\alpha, z)$, and give only the time dependence (Fig. 4) for fixed α, z . The parameters used in the calculation are given in the caption of Fig. 4.

We note the increase in the detector signal in the case of curve 3, and the fall in the case of the other "geometries." This is due to the broad "field of view" of the collimator DCD and the shift of its "point of view" relative to the axis of the cylinder (by 2.66 cm). In this position, the detector can "see" only the increasing (in time) emission from the orifice of the cylinder (Fig. 3) which is reached by particles from the bottom.

Thus, exactly similar processes (see Fig. 3) occurring in identical cylinders result in different measured curves (Fig. 4) which, unless the true origin of this difference is known, can easily be misinterpreted.

Direct inspection of the effusion angular distributions^[28] leads to the conclusion that they gradually broaden with time and with increasing size of the "pupil" of the collimator. This is a manifestation of the increase in the entropy of the system.

We must now consider in somewhat greater detail the situation in each of the above series of problems defining a composite effusion process.

3. ROLE OF HETEROGENEOUS CHEMICAL KINETICS

A. *A priori* error in the measurement of condensation coefficients. Hysteresis phenomena in adsorption

In our example above, we wrote down (2.1) for the Langmuir adsorption kinetics. These equations can be replaced formally by (or can be combined with) the equations describing the kinetics of any other monomolecular reaction.⁸⁾ In the case of more complicated reactions, for example, the bimolecular reaction, we have to face a complication not only in the chemiketic part but also in the equation for the transport of the reagents and the reaction products.

We recall [see (1.1)] the definition of the condensation coefficient

$$\alpha_c = \frac{\sigma - \psi}{\sigma - \sigma_0} = \frac{\sigma - \psi}{\sigma - \psi_0} \quad (3.1)$$

This expression is used both in the time-independent and in the transient state but, in the case of equilibrium,

⁸⁾ For example, if we are interested only in adsorption kinetics, we have at our disposal an extensive collection of various empirical and semiempirical kinetic equations for adsorption and desorption, including the Langmuir equation [in addition to the ideal equation given by (2.1)], the empirical Langmuir equation which differs from (2.1)], the Roginskii-Zel'dovich equation, the equations of Kwan, Benham-Bart, Temkin, and so on, the corresponding adsorbent distributions over adsorption heats, the adsorption isotherms, and other regularities discussed in the fundamental monographs of Roginskii^[28] and Kiperman.^[30]

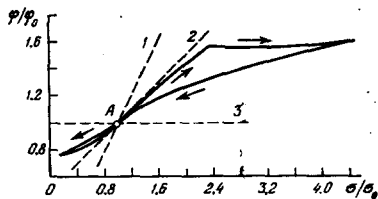


FIG. 5. The $\sigma-\varphi$ transformation (according to the experiment described in [67])—interaction between a KCl beam and the cleavage plane of a KCl single crystal. Equilibrium corresponding to $\sigma=\varphi$ occurs at A. Broken lines correspond to the photometric approximation (1, 2); $\alpha_c=0$ (1), 0.5 (2), and 1 (3).

it gives rise to an indeterminate result, i. e., $\alpha_c=0/0$.

The closer we are to equilibrium, the greater the uncertainty in the measured α_c , and this means that the conditions imposed on the precision of the measuring equipment become increasingly stringent. Simple differentiation of (3.1) yields the following expression for the relative *a priori* uncertainty in α_c as a function of the relative uncertainties $\delta\sigma$ and $\delta\varphi$ in σ and φ :

$$\delta\alpha_c \equiv \frac{d\alpha_c}{\alpha_c} = \frac{\varphi}{|\varphi-\sigma|} (\delta\varphi + \delta\sigma) + \frac{\varphi_0}{|\varphi_0-\sigma|} (\delta\varphi_0 + \delta\sigma). \quad (3.2)$$

The formula for calculating the relative uncertainty in the rate of evaporation (or desorption) as a function of the relative uncertainty in the adsorbent temperature, δT_s , is as follows:

$$\delta\varphi = \frac{E_a}{kT_s} \delta T_s, \quad (3.3)$$

where E_a is the heat of evaporation (or desorption) and k is Boltzmann's constant. The ratio E_a/kT_s may reach values up to about 50, so that, to obtain small $\delta\varphi$, we require very precise temperature measurements. Still higher precision is necessary in the case of measurements of α_c because inspection of (3.2) will show that, for example, the factor $\varphi_0/|\varphi_0-\sigma|$ increases without limit as equilibrium is approached. The exceedingly detailed and particularly accurate measurements reported in [67] ($\pm 0.1\%$ in σ and φ , temperature held constant to within $\pm 0.1^\circ\text{C}$, uncertainty in measured temperature $\pm 0.7^\circ\text{C}$) have revealed important details of the behavior of α_c for KCl molecules on vacuum-cleaved single crystals of KCl. A study was made of the function $\alpha_c = \alpha_c(s, T_s)$, where $s = \sigma/\sigma_0$ and T_s is the surface temperature of the single crystal. Estimates based on

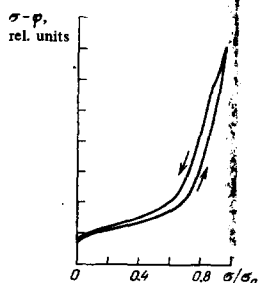


FIG. 6. Hysteresis of the kinetics of adsorption-desorption of water on ZrO_2 (experiment described in [68]).

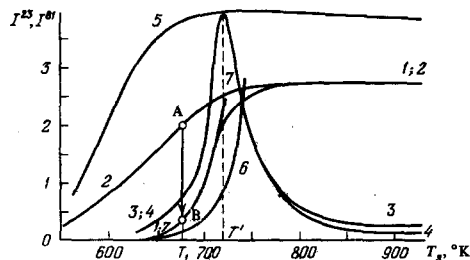


FIG. 7. Desorption [75] of monomers $I^{[23]}$ (1, 2, 6, 7) and dimers $I^{[81]}$ (3-5) of sodium chloride as a function of T_s for different targets. 1—W, Ta; 2, 5—Pt; 3—W; 4—Ta; 6—evaporation without incident beam according to Langmuir; 7—evaporation under an incident beam. T_0 —temperature in the molecular-beam source 933°K . The scale of curves 3-5 is increased by a factor of 3.3, curves 1-5 were obtained for decreasing T_s , 6, 7—increasing T_s (the same for all targets).

(3.2) and (3.3) yield $\delta\alpha_c \sim 10-100\%$. Unfortunately, the uncertainties are not estimated or discussed by the authors of [67]. Nevertheless, we reproduce the data on $\varphi = \varphi(\sigma)$ given in [67] (Fig. 5). We note the similarity between this figure and the data [68] on the adsorption of water on ZrO_2 (Fig. 6). The similarity is greater still when the two sets of results are described in terms of the same coordinates.

Published discussions of the numerous analogous data on the hysteresis properties of adsorption-desorption isotherms (see, for example, [69]) are usually given in terms of the sizes and shapes of adsorbent pores. Data such as those reported in [67, 68] (see also the discussion of [52, 57] given below) suggest other possibilities, including energy inhomogeneity, phase transitions, nucleation, and so on.

A purely kinetic explanation of hysteresis on porous sorbents is given in [234] in terms of the difference between the concentrations of mobile and immobile phases. Zolotarev [194] has shown in detail (in 1971) that, if the desorption process corresponds to the isotherm $a = a(c)$, adsorption occurs on the "correspondence isotherm" $a' = a_0 - a(c)$, where a_0 is the initial adsorption at a given point in the pore and c is the concentration of the mobile phase. But this explanation is not acceptable here.

Recent investigations [141-143] have demonstrated some nontrivial features of the kinetics of migration by diffusion of carbon between the surface and the body of Re and Rh samples.

Figure 7 illustrates the desorption of the monomers NaCl and dimers NaCl_2 from different substrates as a function of the temperature T_s of the substrate, [75] the incident flux σ_i , and the temperature T_0 . At temperatures in excess of T' , the amount of condensate on tungsten and tantalum targets does not increase in proportion to the time of exposure of the target to the beam, the adsorption-desorption equilibrium is established in a relatively short time ($10^{-3}-10^{-5}$ sec), and the accumulation of the condensate comes to an end. For $T_s < T'$, there is an approximately constant rate of accumulation of the condensate (although this rate is different for

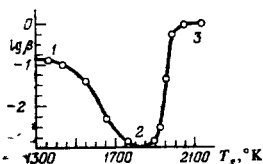


FIG. 8. Degree of dissociation of CsCl for different coverage of iridium with carbon.^[76]

different σ_i and T_s), despite the fact that a proportion of the molecules is reflected (or desorbed). The temperature T' of equilibrium between the incident beam and the condensate increases with increasing σ_i . The shape of curve 5 (platinum target) is essentially different from that of 3 and 4, although, according to the hypothesis put forward in^[47], all these curves should have the same shape. When the measurements are carried out not with a monotonic reduction in temperature T_s (curves 2, 5) but, instead, with gradually increasing T_s , the result is curve 7 (again platinum target). Practically the same curve is obtained (for $T_s < T'$) when T_s is increased sufficiently slowly (curve 1). Over a period of the order of a few tens of seconds, it is possible to observe the kinetic curve of the isothermal transition from curve 2 to curve 1; 7, for example, along the vertical line AB.

A striking feature of curves such as curve 5 is that the reduction in the degree of dissociation of the dimers (above $\sim T'$) is accompanied by an increase in the hysteresis of the desorption curve.⁹⁾ This is naturally explained by a reduction in the dimer adsorption time on the carbon coating covering the platinum, which also reduces the dissociation probability and the probability of nucleation of sodium chloride crystals. This has been confirmed by direct experiment,^[237] in which it was shown, using the apparatus described in^[54], that carbon-free platinum retained sodium chloride particles for a longer time than carbon coated with platinum.

Without going into detailed analysis, it may be concluded that the heterogeneous reaction



proceeds in different ways on different substrates. A phenomenon analogous to that reported in^[52,75] was also observed in^[76-79,141-143] in the case of the reaction



at much higher temperatures (1300–2100 °K) on metals belonging to the platinum group with different carbon coatings.

It was shown in^[76] that the ionization coefficient β , shown in Fig. 8 as a function of temperature, was equal to the degree of dissociation of CsCl, in accordance

⁹⁾In our later paper,^[236] we reported a monotonic transition from curve 5 to the equilibrium curve (virtually curve 4) during a gradual reduction in the concentration of carbon on platinum and iridium.

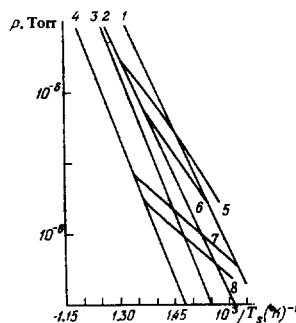


FIG. 9. Partial pressures of monomers (1, 2, 5, 6) and dimers (3, 4, 7, 8) above a sodium chloride film deposited on a tantalum substrate. 2, 4—Langmuir evaporation, 1, 3—Knudsen evaporation. Evaporation under an incident beam and for molecular beam source temperature $T = 1044$ °K (5, 7) and 1015 °K (6, 8).

with (3.5). The amount of carbon on the surface of iridium decreased with increasing surface temperature: it reached a maximum at the point 1, it was equivalent to a monolayer at 2, and was close to 0 at 3. Special experiments showed that carbon has a poisoning effect [for the reaction (3.5)] only when it is present as a two-dimensional crystal lattice but not as a two-dimensional gas.

Results of this kind appear to demand a re-examination of the method based on the use of the double effusion chamber,^[124,125] including the choice and preparation of materials for these chambers and the criterion for the size of the effusion aperture. It is well known^[64] that this aperture must be small enough to ensure chemical equilibrium inside the effusion vessel. However, when the kinetic degree of dissociation of, for example, dimers is low (as in Fig. 7) and the effusion aperture is too large, the amount of effusing dimers may exceed the equilibrium figure [i. e., the amount that would be present for an infinite number of reactions in either direction in (3.4)].

B. Evaporation under variable supersaturation

Figure 9 shows the results^[52,65] of isobaric desorption of NaCl and NaCl_2 from a sodium chloride film evaporated onto tantalum. The authors of these papers refer to their results as "anomalous" mainly because they have not been previously reported. Similar curves have been subsequently recorded^[68] for cadmium films deposited on tungsten (Fig. 10), for the resultant flux of potassium chloride molecules^[67] (without separation into monomers and dimers), and for the (100) surface of a potassium chloride single crystal (Fig. 11^[10]). The overall character of the curves shown in Figs. 9–11 is quite clear. The main feature is that the desorption isobars, plotted in the form $\log \varphi = f[1/T(^{\circ}\text{K})]$

¹⁰⁾The experimental data reported in^[67] were obtained under isothermal conditions ($T_s = \text{const}$); Fig. 11 is the result of a transformation of the data in^[67] into a form expressed in terms of isobaric coordinates, which was carried out by Yu. A. Gel'man, to whom the present author is indebted.

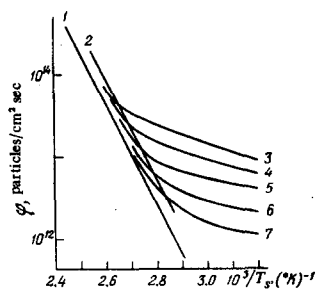


FIG. 10. Desorption isobars for cadmium deposited on tungsten.^[66] 1, 2—Langmuir and Knudsen evaporation. The isobars correspond to the following fluxes on the surface ($\text{cm}^{-2} \text{sec}^{-1}$): 5.9×10^{13} (3), 3.5×10^{13} (4), 1.7×10^{13} (5), 8.8×10^{12} (6), and 4.5×10^{12} (7).

are at an angle to the lines representing Langmuir evaporation and Knudsen effusion. This enables us to conclude that, under steady-state conditions,¹¹⁾ the evaporating body cannot emit more than is predicted by Langmuir, but the flux of departing particles may be greater than predicted by Knudsen.

C. Electron-microscope studies

Detailed kinetic-morphological studies of gold and silver deposits on cleavage planes of alkali halide single crystals have recently been published.^[60,173] Analysis of the experimental data yields the ratios D_s/μ and D_s/μ^2 (D_s is the surface diffusion coefficient) and, hence, the values of D_s and μ separately. We recall these data here because they provide us with a possibility of determining the exceedingly small quantities μ^{-1} and D_s (the data in Table I are based on the results reported in^[80]).

In a sufficiently narrow temperature range, and for low surface coverage; we have

$$\mu = \mu_0 \exp\left(-\frac{E_a}{kT_s}\right), \quad (3.6)$$

$$D_s = D_{0s} \exp\left(-\frac{E_d}{kT_s}\right). \quad (3.7)$$

The exceedingly short lifetimes corresponding to moderately high temperatures lead to an almost complete reflection of gold and silver molecular beams from the corresponding surfaces of the alkali halide crystals. However, as soon as the clusters $(\text{Au})_n$ and $(\text{Ag})_n$ appear with $n > 2$, the gold and silver atoms belonging to these clusters can reside on this surface apparently as long as they do on gold or silver surfaces at the same temperature. Rough estimates of the time of adsorption of gold atoms on a gold adsorbent yield a lifetime of about 300 years at $\sim 500^\circ \text{K}$.

D. Relation between phenomenological coefficients

The phenomenological theory^[115,177] of the interaction between molecules and surfaces can be used with

¹¹⁾ Damped oscillations of desorption have been reported under nonsteady conditions.^[67]

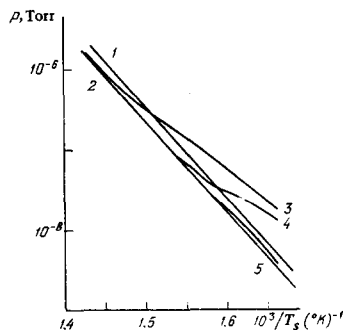


FIG. 11. Desorption isobars for potassium chloride from a cleavage plane of a potassium chloride single crystal, calculated from experimental data.^[67] 1—Knudsen evaporation, 2—Langmuir evaporation; isobars correspond to the following total pressures of the incident flux on the surface (Torr): 3×10^{-7} (3), 3.4×10^{-8} (4), and 3.4×10^{-9} (5).

a sufficiently idealized model to obtain a number of relationships between the various necessary coefficients and parameters characterizing this interaction, namely, the adsorption and desorption rate constants, the attachment, condensation, and accommodation coefficients, the dimensionless inertial and frequency parameters, and the constants of the simple approximation to the interaction potentials.

The main features of a model of this kind are: 1) an interaction potential in the form of a combination of an exponentially decreasing repulsion and a constant attraction with a well depth E_a ; 2) the assumption that the interaction between the adsorbed atoms can be neglected; 3) the classical problem is solved because, for $2 < E_a/kT_s < 100$, the discrete character of the energy levels can be neglected; and 4) the essential parameters of the problem are: the ratio m of the mass m_g of the gas molecule to the mass m_s of the surface atom and the ratio ω of the oscillation frequency ω_g of an adatom to the oscillation frequency ω_s of a surface atom, $\omega = \sqrt{k_g/k_s m}$, where k_g and k_s are the elastic constants representing the bonding of the adatom and the surface atom.

An improved version of the formula for $\mu = \mu(E_a, T_s)$ is given in^[30] (p. 313). The derivation takes into account the compensation effect in the dependence of the pre-exponential factor in the Frenkel formula (3.6) on the heat of adsorption. The result is

TABLE I.^[80] Parameters defining adsorption times and surface diffusion coefficient measured at $T_s = 270\text{--}300^\circ \text{C}$ [see Eqs. (3.6) and (3.7)].

Adsorbate Adsorbent	Au NaCl	Au KCl	Au KBr	Ag NaCl	Ag KCl	Ag KBr
E_a , eV	0.69	0.71	0.79	0.61	0.41	0.47
E_d , eV	0.31	0.27	0.42	1.19	0.08	0.19
μ_0 , sec^{-1}	$1.1 \cdot 10^{12}$	$4.2 \cdot 10^{11}$	$1.2 \cdot 10^{13}$	$4.7 \cdot 10^{11}$	$1.5 \cdot 10^{10}$	$3.7 \cdot 10^{10}$
D_{0s} , $\text{cm}^2 \text{sec}^{-1}$	$3.9 \cdot 10^{-4}$	$2.0 \cdot 10^{-5}$	$1.8 \cdot 10^{-2}$	$5.8 \cdot 10^{-6}$	$3.2 \cdot 10^{-7}$	$2.1 \cdot 10^{-5}$
μ^{-1} (500° K), sec.	$6.6 \cdot 10^{-6}$	$2.9 \cdot 10^{-5}$	$6.5 \cdot 10^{-5}$	$2.6 \cdot 10^{-7}$	$8 \cdot 10^{-8}$	$1.3 \cdot 10^{-6}$
D_s (500° K), $\text{cm}^2 \text{sec}^{-1}$	$3.5 \cdot 10^{-7}$	$6.7 \cdot 10^{-9}$	$1.1 \cdot 10^{-7}$	$1.6 \cdot 10^{-8}$	$2.9 \cdot 10^{-8}$	$5.8 \cdot 10^{-8}$
$\frac{D_s}{\mu}$ (500° K), cm^2	$2.3 \cdot 10^{-12}$	$1.8 \cdot 10^{-13}$	$7.2 \cdot 10^{-12}$	$4.2 \cdot 10^{-15}$	$2.3 \cdot 10^{-15}$	$7.5 \cdot 10^{-14}$

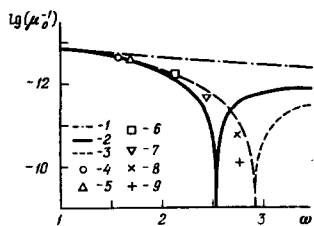


FIG. 12. Pre-exponential factor in the expression for the adsorption time.^[177] 1— $2\pi\omega^{-1}$; 2— $m=1$; 3— $m=0.2$. Experimental data on adsorbate/adsorbent: 4—(Rb/W)^[200]; 5—(Ag/W)^[198]; 6—(Cs/W)^[198]; 7—(Ti/W)^[197]; 8—(Ga/W)^[196]; 9—(Cd/W)^[169]; [μ^{-1}] = sec.

$$\mu = \mu_0 \Gamma(\delta), \quad (3.8)$$

where

$$\Gamma(\delta) = \exp\left(-\delta + \frac{\delta}{a^2}\right) \operatorname{erf}\left(\frac{\sqrt{\delta}}{a}\right), \quad (3.9)$$

$$\delta = \frac{E_a}{kT_s}; \quad (3.10)$$

a is a parameter to be determined experimentally.

Predictions have been made of the effect of the adiabatic interaction at certain resonance frequencies when the probability of capture of a particle becomes much greater. Figure 12 shows examples of graphs of the form $\log(\mu_0^{-1}) = f(\omega, m)$. The values of the characteristic parameters^[115,177] are listed in Table II. An exhaustive review of even the papers on adsorption kinetics alone (not to mention heterogeneous chemistry) published during the last 5–10 years would be a hopelessly difficult task. Nevertheless, this type of information may be of direct importance for the question of effusion. As soon as we take the combination of an effusion vessel and an effusing material, we have to face all the problems of adsorption kinetics, thermodynamics, and other possible interactions.^[89–94,96]

A relatively comprehensive handbook covering all the published material roughly up to 1971–1972 has recently been published.^[164] It includes adsorption characteristics but there is no overlap between the references reviewed in^[164] and those cited in the present paper.

4. LOCAL KINEMATICS. ENERGY TRANSFER

A. Observable and calculable local distributions

The Maxwell-Knudsen hypothesis of diffuse-specular reflection has, up to quite recently, dominated the question of the spatial distribution of molecules reflected by a surface. Very limited information was available on the redistribution of energy among the different degrees of freedom of the gas-surface system.

As noted in the Introduction, the reflection of molecules by a surface depends on the ratio of the depth E_a of the potential well to the energy kT_s of the incident molecule. A more detailed analysis of the dimensionless criteria governing the interaction between a gas and a solid is given in the papers quoted earlier.^[115,117]

In most effusion experiments, $E_a/kT_s \gg 2.5$, and most of the material treated in the present chapter refers to this situation. However, physically clearest results have been obtained for quasielastic and inelastic reflection, and this is very briefly considered at the end of this chapter.

A very objective approach must be adopted to the necessity for working in ultrahigh vacuum. For example, the properties of the surface of a crystal in contact with its saturated vapor are different from those of the surface of the same crystal in ultrahigh vacuum. The structure, composition, and charge state of the surface, and the conditions of energy transfer to the ambient space are different in these two cases.

To estimate the relaxation phenomena during the interaction between molecules and a solid surface, the authors of^[104] proposed to use the solution^[105] of the Fokker-Planck equation in the space of the particle momenta. There is no doubt about the validity of the two limiting results obtained in^[104]: (1) if a particle has a very large adsorption time and a small relaxation time (it rapidly “forgets” its initial momentum), it will leave the surface in accordance with a spatial distribution law that is independent of its prehistory, and (2) conversely, when the adsorption time is small in comparison with the relaxation time for the initial momentum (or when the magnitude of this momentum is relatively large), the particles “remember” their initial states, and the emission law depends on the parameters of the particle beam incident on the surface. The redistribution of energy between the oscillations of a molecule and the lattice phonons, and the effect of this redistribution on the emission characteristics, is also considered in^[104].

The Vallander group^[106] has carried out major work in elucidating the situation in this field and in preparing and carrying out numerical calculations. It has reported calculations on the transformation of microlocal distributions into macrodistributions of emission. The calculations were carried out on the basis of various

TABLE II. Values of the parameters ω and E_a/k (3.10) obtained by comparing the experimental results on adsorption times with the theory in^[115,177].

Adsorbed atom/substrate	Frequency parameter ω	Inertial parameter m	Depth of adsorption well, δ (3.10)	$\frac{E_a}{kT_s}$ (3.6)	Pre-exponential factor in (3.6), μ_0^{-1} , sec	Oscillation period of adatom $2\pi/\omega\Gamma$, sec	Temperature range for T_s , K	Experiment
Cd/W	2.67	0.611	21700	20700	$9.4 \cdot 10^{-11}$	$3.2 \cdot 10^{-13}$	900–1100	169
Ga/W	2.66	0.379	39400	37700	$2.0 \cdot 10^{-11}$	$3.1 \cdot 10^{-13}$	1600–2000	166
Ti/W	2.45	0.260	6300	61300	$2.3 \cdot 10^{-12}$	$2.9 \cdot 10^{-13}$	2000–2500	197
Cs/W	2.14	0.722	33600	32800	$6.3 \cdot 10^{-13}$	$2.5 \cdot 10^{-13}$	600–1100	198
Ag/W	1.72	0.585	35500	33700	$2.8 \cdot 10^{-13}$	$2.0 \cdot 10^{-13}$	1100–1400	199
Rb/W	1.61	0.465	32000	30200	$2.5 \cdot 10^{-13}$	$1.9 \cdot 10^{-13}$	1100–1250	200
Ar/Ag	2.55	0.370	420	380	$4.5 \cdot 10^{-11}$	$5.4 \cdot 10^{-13}$	14–140	201
Rb/Au	2.39	0.102	300	270	$4.2 \cdot 10^{-11}$	$7.0 \cdot 10^{-13}$	10–100	202
Kr/Ag	2.30	0.777	700	530	$1.7 \cdot 10^{-11}$	$4.9 \cdot 10^{-13}$	30–240	201
Ar/Pt	2.30	0.205	1600	1420	$1.4 \cdot 10^{-11}$	$4.6 \cdot 10^{-13}$	70–540	201
Ar/W	2.25	0.218	950	850	$5.9 \cdot 10^{-12}$	$2.7 \cdot 10^{-13}$	40–320	201
Kr/W	2.20	0.456	2250	1950	$4.8 \cdot 10^{-12}$	$2.6 \cdot 10^{-13}$	140–750	201
Ar/Au	2.10	0.203	1200	1010	$1.2 \cdot 10^{-11}$	$6.1 \cdot 10^{-13}$	80–400	201
Xe/Pt	2.10	0.673	3750	3130	$6.6 \cdot 10^{-12}$	$4.2 \cdot 10^{-13}$	310–1250	202
Kr/Pt	2.05	0.430	1050	840	$6.5 \cdot 10^{-12}$	$4.1 \cdot 10^{-13}$	100–350	201
Xe/W	2.02	0.716	4500	3800	$2.7 \cdot 10^{-12}$	$2.4 \cdot 10^{-13}$	370–1120	201
Xe/Ag	1.90	1.217	2000	17700	$7.6 \cdot 10^{-12}$	$4.0 \cdot 10^{-13}$	100–670	201
Xe/Au	1.75	0.666	6000	4400	$5.3 \cdot 10^{-12}$	$5.0 \cdot 10^{-13}$	750–2000	203

assumptions about the structure of the surface (for example, normal Gaussian roughness) and the laws of local emission (specular or cosine reflection), and so on.

The local emission laws for very small areas may differ appreciably from the less local laws for a large area and, therefore, the relative size of areas is an important parameter. A macrosurface is not, by far, a perfectly smooth target, but small elements of it may be regarded as smooth.

Careful analysis of the principle of detailed balancing, given in^[103] for the gas-solid system, has resulted in the replacement of the cosine law by the expression

$$I_{\Omega_c}(\Omega_{\Omega_c}) \cos \theta_c = I_{\Omega_i}(\Omega_i) \cos \theta_i, \quad (4.1)$$

where θ_i is the angle between the direction under consideration and the normal to the area, Ω_i is the solid angle, and $I_{\Omega_i}(\Omega_i)$ is the number of particles scattered per second per unit solid angle Ω_i from the particle flux incident within the solid angle Ω_i . This is the analog of the Helmholtz reciprocity theorem in optics noted in^[91] (p. 65). Experimental data confirming (4.1) and cited in^[103] refer to the interaction between argon and the surface of silver when adsorption capture has a low probability; the result given by (4.1) appears to fail in the limiting cases of large and small values of E_a/kT_s .

The numerous attempts to detect a departure from the cosine distribution for large E_a/kT_s have not been successful (existing anomalies will be noted below) either in the case of Langmuir evaporation^[100] or for the products of a chemical interaction between molecular beams and solid surfaces.^[99] Hopes of detecting a large anisotropy in a manifestation of the anharmonism of crystal lattice oscillations such as, for example, evaporation at sufficiently high temperatures, are generally unjustified and require an experimental precision that cannot usually be achieved.

Nevertheless, there are a few cases of anisotropy in the emission of particles with thermal velocities. The authors of^[178, 183-185] have reported pronounced anisotropy in evaporation kinetics for single crystals of CdS and ZnO, in which the morphological inhomogeneity of different boundaries can be clearly seen.

The considerable departure from cosine emission in the case of PbI^+ and $SnCl^+$ ions obtained from PbI_2 and $SnCl_3$ molecules during surface ionization^[101, 116] has not as yet been explained.

B. Transformation of translational energy and its relation to reflection characteristics

Energy exchange between the translational degrees of freedom of gas molecules and a solid surface is described by the accommodation coefficient α_a , defined by analogy with α_c as follows:

$$\alpha_a = \frac{T_a - T_g}{T_s - T_g}, \quad (4.2)$$

where T_s , T_g , and T_a are, respectively, the temperatures of the surface, the incident gas, and the escaping gas.

Studies have been carried out (again for large values of E_a/kT_s) for the following combinations: 1) $T_g > T_s$ (for example, ^[144] Au and Cr beams on NaCl surface); 2) $T_g < T_s$ (for example, NaCl and Na_2Cl_2 beams on a Ta surface in^[74] and on Ta, W, and Pt surfaces in^[75]; CsCl beam on metals belonging to the platinum group, both pure and coated with carbon^[83, 143]; In beam on Si surface in^[82]). All these experiments showed that $T_g \approx T_s$, i. e., $\alpha_a \approx 1$

This virtually complete accommodation can be used as a unique method of producing either low-temperature or high-temperature molecular beams. As a matter of fact, velocity selectors can be used to produce, for example, a gold molecular beam of appreciable intensity with an effective temperature of $\sim 300^\circ C$ (since the gold vapor pressure at this temperature is $\sim 10^{-22}$ Torr, i. e., cannot be detected) or a CsCl beam at $1800^\circ C$ (since the CsCl vapor pressure is so high, i. e., $\sim 10^3$ Torr, that the molecular flow conditions no longer apply).

We now list a number of methods of determining the translational temperature of molecular beams: (1) measurement of the particle-velocity distribution either with the aid of the Stern velocity selector (see, for example, ^[20]) or by the method involving the deflection of ions produced from the beam under consideration by an electric field; (2) measurement of the time taken by a packet of molecules to traverse a given distance^[180, 181] and (3) measurement of ionization efficiency as a function of time spent by the particles in the ionization space.^[177, 143, 182]

Simultaneous measurements of the lifetimes and the local reflection characteristics for H_2O , O_2 , and Cl_2 on silicon are reported in^[86-88]. No correlation was found between the degree of specular reflection and the particle lifetime on the surface, but it was found that the attachment time depended on the mutual orientation of the beam and target, and the lifetime on the surface was found to increase in the order $H_2 - O_2 - Cl_2$. The high reactivity of silicon probably means that it is desirable to repeat these measurements in a much better vacuum than 10^{-8} Torr.^[88] The reflection of Ar, H_2 , and N_2 by metal targets was investigated experimentally in^[108-114] for much smaller values of E_a/kT_s than those considered above. The connection between incomplete accommodation and the appearance of quasispecular scattering, which was discussed theoretically in^[102-104, 115], was found to be present, and it was confirmed that adsorbed layers were responsible for the energy transfer between beam particles and the surface face.

Figure 13 reproduces some of the results reported in^[114] and clearly shows that an increase in the adsorbed cover on the (111) surface of the platinum single crystal is associated with an increase in the degree of diffuse scattering.

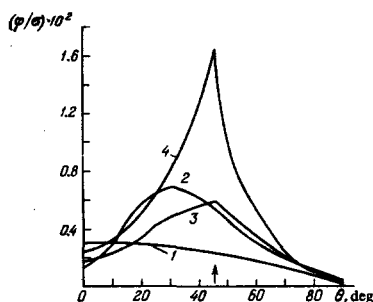


FIG. 13. Reflection characteristics (based on^[114]) for the (111) plane of a platinum single crystal. 1—Cosine reflection for $T_s=300^\circ\text{K}$, $T_o=300^\circ\text{K}$, H_2 , N_2 , CO , Ar beam; low-energy electron diffraction indicated a two-dimensional CO-C (4×2) lattice; 2—reflection of N_2 , $T_s=550^\circ\text{K}$, $T_o=300^\circ\text{K}$; 3—reflection of Ar , $T_s=1000^\circ\text{K}$, $T_o=300^\circ\text{K}$; 4—reflection of H_2 , $T_s=1000^\circ\text{K}$, $T_o=300^\circ\text{K}$; 2-4—clean platinum surface. Arrow indicates the angle of incidence (45°).

C. Structural and dynamic studies

In the course of the last five or six years, many of the well-known effects established by studies of the scattering of thermal neutrons by solids have been found to have analogs in the scattering of molecular beams by crystal surfaces. Neutron beams cannot be used to investigate surfaces because their intensities are relatively low and the scattering cross sections are small. Small-angle x-ray scattering and low-energy electron diffraction can be used to explore surfaces but, usually, involve several atomic layers on the target surface. This gives rise to difficulties in the interpretation of the resulting diffraction patterns and scattering effects.

In this respect, studies involving the use of molecular beams provide information which, in the very least, augments other studies of surface properties and is frequently of interest in itself.

Candidly speaking, most of the investigations performed in the field of effusion under high-vacuum conditions (10^{-9} – 10^{-12} Torr) are either of no interest at all or of only indirect interest because the pressures commonly used in effusion vessels are so high (not less than 10^{-2} – 10^{-7} Torr) that many of the reflection phenomena are lost or smeared out. Nevertheless, new results in this area are interesting, and their implications are very significant, so that we shall briefly list them here although we cannot pretend that this list is complete.

1) As in the case of thermal neutrons, molecular beams can be scattered elastically when E_a/kT_o is sufficiently small. If, in addition, the necessary de Broglie wavelengths can be ensured, it is possible to produce diffraction by surface structures. Historically, the diffraction of He and H_2 molecular beams by the cleavage planes of alkali halide single crystals preceded three-dimensional neutron diffraction.^[208] More recently, the diffraction of He has been detected on the (112) plane of W ^[205,207] and the (110) plane of WC .^[206] The diffraction patterns obtained with D_2 on the (110)

plane of WC ^[209] have been found to be less clear than in the case of helium, and this has been explained by energy transitions involving the participation of rotational degrees of freedom. The traditional studies of diffraction on cleavage planes of alkali halide single crystals have now been extended to adsorption structures of surfaces.^[118]

2) Inelastic scattering of molecular beams has already yielded information both on the dispersion of the frequency of surface oscillations and on the frequency distribution function for these oscillations.^[136,165]

These measurements require a combination of relatively low values of E_a/kT_s and kT_o , so that both the creation and loss of lattice phonons can be recorded.

3) Small-angle scattering of molecular beams by metal surfaces^[145,147] has been used to determine the polarizability of atoms and molecules in the beam, and to elucidate the dependence of the potential describing their interaction with the surface on the distance from the latter.

These results are very fundamental and must be seriously considered. They have been achieved as a result of both experimental and theoretical advances (see, for example, the references cited in^[118,136,146,147,165]).

5. MACROGEOMETRIC ASPECTS OF DIFFUSION

We have already discussed the general features of the laws of photometry and of the theory of propagation of molecular beams in containers, and the difference between them. Let us now list the physical reasons for the inadequacies of the photometric model. They are: 1) the velocity of the molecules is much smaller than the velocity of light and is not constant; 2) the characteristic times of interaction between molecules and solid surfaces lie in a very broad range, whereas photometry does not include kinetics; 3) molecules exhibit the phenomenon of surface diffusion which has no analog in photometry; 4) there is no analog in photometry of the chemical transformation of molecules with the exception, perhaps, of simple removal (in photometry, the absorption of radiation), and 5) the wave nature of matter is neglected in photometry because photometry is part of geometric optics^[119,120] and, in fact, part of *linear* geometric optics.

The restricted validity of the assumption that the transformation of the incident molecular beam into the escaping beam is linear has already been discussed [see (1.2) and thereafter], but this hypothesis has, nevertheless, remained very popular in the theory of molecular beams (see^[9,10] and subsequent publications^[121-123,204] as well as^[9,10,60,61,126,186] which take into account chemical transformations). The same physical model has also been used in Monte Carlo calculations.^[127-131,134]

From the modern standpoint, the photometric approach is restricted in all aspects of the photometric approximation although, occasionally (see below), this model does provide a description of experimental results.

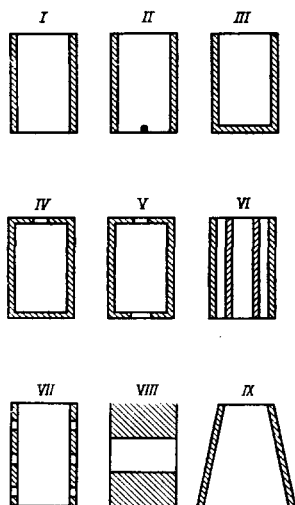


FIG. 14. Standard shapes of effusion vessels under investigation.

We noted in Chap. 1 that, if we have ready-made answers to chemical and locally-kinematic questions relating to the effusion model, and if we know the shape of the effusion vessel, then we can solve the direct effusion problem completely. Most of the emphasis has been placed on the application of modern numerical methods and facilities, since an accurate and purely analytic solution of the problem is not available, partly because of the lack of accurate analytic expressions for the local angular distribution and functions of the form $\alpha_c = \alpha_c(\theta)$, not to mention the kinetic coefficients for the more complicated chemical systems.

A. Summary of shapes discussed in the photometric approximation

As a matter of fact, even the simple Clausing problem has usually been solved only approximately: linear^[37,57] and exponential^[9,10] approximations to the kernel, iteration methods,^[132] reductions to sets of algebraic equations,^[121-123,133] replacement of the integral equation by a differential equation,^[9,10,34,61,105] and some of the other approaches are described in^[120] and are widely scattered through mathematical literature.

In addition to the various vessel shapes discussed previously in^[9,10], Fig. 14 shows nine geometric forms that have recently been discussed in terms of the photometric model (the Roman numbers below correspond to the numeration in Fig. 14):

I—cylindrical tubes and capillaries have been discussed in sufficient detail in^[9,10,11]. The passage of molecules through a rotating cylinder was discussed in^[135]. A calculation was given there of the spatial distribution of H atoms capable of recombination into H₂ on the walls.^[60,61] These last two papers are very similar in their formulation of the problem but report different results. This is connected with the approximate character of the solution^[61] (reduction to the solution of the differential diffusion equation which can distort the flux distribution at exit from the capillary).

II—cylinder with a point source of particles on the axis of the tube.^[21] The flux distribution inside the cylinder has been calculated.

III—cylinder with sources of molecular beams distributed over the bottom in accordance with a given law (this was previously investigated in^[9,10,122,123] but the most complete calculations, including departures from the photometric model, are given in^[28,29]).

IV—the Knudsen effusion cell. The molecular-flux distribution inside a vessel and the resultant single-component effusion flux were calculated in^[122,123] in the photometric approximation, assuming that the effect of the effusion channel could be neglected and the spatial distribution of the effusing molecular fluxes need not be calculated. More rigorous calculations, including the effects of surface diffusion, are discussed below.

V—the flux distributions inside a reactor and the resultant flux through it have been found^[126] for the so-called open reactor with apertures in the bottom and in the lid, the internal surface of which has zones with different particle removal coefficients.

VI—the molecular-flux distribution between coaxial cylinders has been determined in the diffusion approximation, the Clausing coefficient has been found, and certain integral probability characteristics have been obtained in^[137]. These include the mean free path, the probability that the molecule will leave one cylinder for another, and so on (see Chap. 6).

VII—a vapor distributor in the form of a cylinder with perforated walls is analyzed in^[138].

VIII—the cylindrical effusion channel—a fragment of the Knudsen cell—is discussed in detail below.

IX—the molecular-flux distribution inside a cone, and the flux leaving a cone for vacuum through a realistic set of collimators are investigated in^[139]. A similar problem is solved for a conical ring source in^[139]. The conical effusion aperture is discussed in^[140] as a fragment of the Knudsen cell (see below).

This list can be extended by including the experimental studies, the results of which are given below and are partially compared with calculations.^[2]

B. Relationship between the Clausing equation and the more general description

In order to exhibit the relation between the Clausing equation^{[57] 13)} and the more general description,^[28,29] we shall show how the Clausing equation^[57] can be derived from (2.1)–(2.8) (in which, as a first simplifying assumption, possible chemical transformations are not taken into account). In the steady-state variant,

¹²⁾Calculations on the motion of molecular beams in certain vessels and pipes of shapes other than those discussed previously in^[9,10] are given in^[212] and are not referred to here.

¹³⁾We note that the 1932 Clausing paper^[57] was translated from German into English in 1971, indicating that these studies are currently vital.

i. e., without taking retardation into account (second and third assumptions), the equations given by (2.1)–(2.6) can be rewritten in the form

$$\sigma = \varphi, \quad \sigma(x) = \int_{S(x_1)} \varphi(x_1) K(x_1, x) dS(x_1). \quad (5.1)$$

For the one-dimensional case (fourth assumption), taking into account σ_0 , i. e., the contribution of particles entering the capillary, with

$$K(x, x_1) = K(|x - x_1|) \quad (5.2)$$

(fifth assumption), we obtain the Clausius equation in the form^[57]

$$\sigma(x) = \sigma_0(x) + \int_0^l \sigma(x_1) K(|x - x_1|) dx_1. \quad (5.3)$$

We note that we need not specify the form of the equation for the adsorption isotherm in time-independent motion of a molecular flux of gas (or superheated vapor) which does not react chemically with the walls of the vessel (and in the absence of surface diffusion). For example, if we use the Langmuir adsorption model, we can omit the expression $\varphi = (\sigma + \mu)\theta$. The result of this is that (5.3) does not contain coefficients such as the particle removal coefficients. This statement is valid for the resultant flux of particles of the reacting gas if the walls are neither sources nor sinks of particles.

In^[9,10,59–61,126], which we cite in chronological sequence, the effect of chemical reactions on the walls of the vessels was taken into account by introducing the corresponding particle removal coefficients into the integral or differential equation. The following is the equation^[60] for the distribution, in a cylinder, of the flux of atomic hydrogen capable of recombination (in our notation)

$$\sigma(x, \alpha) = \sigma_0(x) + \int_0^l \sigma(x_1, \alpha) [1 - \alpha(x_1)] K(|x - x_1|) dx_1, \quad (5.4)$$

and if we suppose that $\alpha = \text{const}$ we have

$$\sigma(x, \alpha) = \sigma_0(x) + (1 - \alpha) \int_0^l \sigma(x_1, \alpha) K(|x - x_1|) dx_1. \quad (5.5)$$

Equation (5.5) is completely equivalent to the equation describing the propagation of thermal radiation^[120] if we interpret α as the emissive power and $\sigma_0(x)$ as the intrinsic luminosity of the cylinder (without taking reflection into account). The quantity σ_0 was interpreted in^[60] as the distribution of the primary molecular flux density, reaching the cylinder from the gas reservoir, over the walls. It is also possible^[9] to interpret σ_0 as the Langmuir evaporation from the surface of the cylinder; in that case, α is the condensation coefficient [in accordance with (1.1)]. However, since the $\sigma - \varphi$ transformation may be nonlinear, (5.4) is more frequently valid than (5.5).

C. Effects of surface diffusion

The above equations do not take into account surface diffusion which is important when the diffusion free path is comparable with the characteristic linear dimensions of the system.^[36,45] This situation arises in the effusion aperture which is always made as small as possible to ensure vapor saturation during vapor pressure measurements. This question is investigated in detail in^[58,151–153]. Instead of the equation for the flux in the effusion channel, the common practice is to write down the equation for the surface density $n(x)$ of particles on the walls:

$$\frac{1}{E} \nabla^2 n(x) = n(x) - n_e K(0, x) - \int_0^l n(x_1) K(|x - x_1|) dx_1, \quad (5.6)$$

where $E = \mu/D_s$, D_s is the surface diffusion coefficient, n_e is the equilibrium density, $n_e K(0, x)$ is equivalent to σ_0 in (5.5) in the interpretation used in^[60], and the remaining notation is the same as before.

It is considered in^[151] that, when $E \rightarrow \infty$, the equation given by (5.6) becomes identical with (5.3), but this is correct only in the simplest case when Henry's law is valid:

$$n = \Gamma \varphi = \Gamma \sigma, \quad (5.7)$$

where Γ is the Henry constant. Equations (2.1)–(2.8) are more general, but a further term must be added when surface diffusion is important. For example, in the Langmuir model, (2.1) can be modernized to read

$$\dot{\theta} = \sigma - \varphi + D_s' \frac{\partial^2 \theta}{\partial x^2}. \quad (5.8)$$

Since θ is the coverage and n is the surface density, the quantities D_s and D_s' are also different.

It is possible to introduce various other corrections into (2.1)–(2.8) to represent different kinetic details.

We shall now reproduce the individual results^[151–153] to get a feeling for the influence of surface diffusion. Figure 15 shows a Knudsen cell. Three zones can be identified in this system: A—the inner zone which is under the saturated vapor pressure, B—the cylindrical effusion channel (1 in Fig. 15), and C—the external evacuated zone (from which nothing returns to A and B). Equation (5.6) refers to zone B and $n(x)$ is the density distribution on the walls of the channel B, which was found in^[151–153] in an explicit form but is repro-

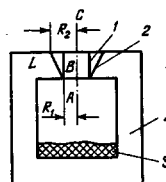


FIG. 15. Two variants of the Knudsen effusion cell. 1—Cylindrical aperture, 2—conical aperture, 3—material under investigation, 4—cell wall. A—inner zone, B—effusion channel, C—outer evacuated zone.

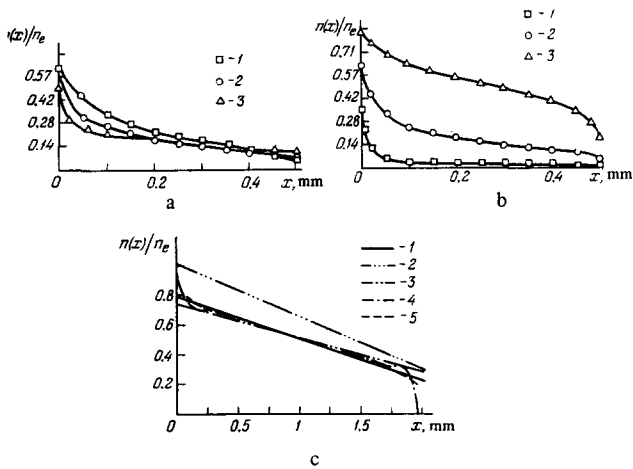


FIG. 16. Density distribution over the surface of the effusion channel. a-b—conical apertures,^[140] c—cylindrical aperture.^[153] a) Cone angle γ (see below Fig. 18) = 30° , $R_1 = 0.05$ cm, $L/R_1 = 1.0$. 1— $E(\text{cm}^2) = 10^4$ (1), 10^5 (2), and 10^7 (3). b) $E = 10^5$ cm², $R_1 = 0.05$ cm; $L/R_1 = 1.0$. 1— $\gamma = 0$, 2— $\gamma = 30^\circ$, 3— $\gamma = 60^\circ$. c) Approximations: 1—data in^[57], 2—data in^[210], 3— $E = 10^7$ cm², 4— $E = 10^4$ cm², 5— $E = 10^2$ cm².

duced here in graphical form because the corresponding analytic expressions are too cumbersome (Fig. 16c).

The effusion flux consists of three components, i. e., the fluxes reaching the vacuum from zone A, from the walls of B, and from the outer surface of the cell C:

$$\Phi_{Ab} = \Phi_A K(0, L), \quad (5.9)$$

$$\Phi_{Bb} = 2\pi R_1 \int_0^L n(x) \mu K(|L-x|) dx, \quad (5.10)$$

$$\Phi_{Cb} = 2\pi R_1 \frac{D_s \sqrt{E} n(L) K_1(\sqrt{E} R_1)}{K_0(\sqrt{E} R_1)}, \quad (5.11)$$

where K_0 and K_1 are modified Bessel functions of the second kind, R_1 and L are, respectively, the radius and length of the effusion aperture, and Φ_A is the equilibrium density of the escaping and incident fluxes on an area equal to the area of the effusion aperture.

For a knife-edge aperture ($L \rightarrow 0$), $\Phi_{Ab}^k = \Phi_A$ and

$$\Phi_{Bb}^k = 0, \quad (5.12)$$

$$\Phi_{Cb}^k = \frac{\pi R_1 D_s \sqrt{E} K_1(\sqrt{E} R_1)}{K_0(\sqrt{E} R_1)}. \quad (5.13)$$

In addition to the effusion probability K_C introduced by Clausing (the Clausing coefficient)

$$K_C = \frac{\Phi_{Ab} + \Phi_{Bb}^k}{\Phi_A}, \quad \Phi_{Bb}^k = \lim_{E \rightarrow \infty} \Phi_{Bb}, \quad (5.14)$$

in modern theory^[151] we introduce the further coefficients

$$K_W = \frac{\Phi_{Ab} + \Phi_{Bb} + \Phi_{Cb}}{\Phi_A}, \quad (5.15)$$

$$K_D = \frac{\Phi_{Ab} + \Phi_{Bb}}{\Phi_A}, \quad (5.16)$$

$$\Phi_A = \frac{\pi R_1^2 P_e}{2\pi m_r k T_0}. \quad (5.17)$$

The total contribution of surface diffusion to the effu-

sion flux will be described as follows:

$$\Phi_{sD} = K_D \Phi_A + \Phi_{Cb} - (\lim_{E \rightarrow \infty} K_D) \Phi_A, \quad (5.18)$$

$$\lim_{E \rightarrow \infty} K_D \equiv K_K, \quad (5.19)$$

$$\beta \equiv \frac{\Phi_{sD}}{K_C \Phi_A}. \quad (5.20)$$

Table III lists the values of the above parameters for two effusion apertures with $E = 10^5$ cm².

Unfortunately the values of E are usually unknown for real combinations of the effusion-cell material and the effusing particles. A partial list is given in Table I whilst values of μ^{-1} are listed in Table II.

The spatial distribution of the effusing flux is calculated in^[152]. Since E is one of the important parameters of this distribution, we have the possibility (which can be enhanced by increasing the number of effusion apertures in the chamber) of determining E by measuring this distribution. Equation (5.6) can then be used together with other sources of information on μ or D_s to determine the other component of E , i. e., D_s or μ .

Calculations similar to those given in^[58,151-153], but for a conical rather than a cylindrical effusion aperture [see Fig. 15, (2)], are reported in^[140] (in all other respects, these calculations are identical). The distributions of the surface density of effusing particles are shown in Figs. 16a and 16b for a conical channel (for different geometric and physical parameters).

The surface density distributions on the inner and outer surfaces of the lid of the effusion chamber are^[152]

$$\frac{n(r)}{n_e} = 1 - \frac{[1 - (n(0)/n_e)] K_0(\sqrt{E} r)}{K_0(\sqrt{E} R_1)}, \quad (5.21)$$

$$\frac{n(L)}{n_e} = \frac{n(L) K_0(\sqrt{E} r)}{n_e K_0(\sqrt{E} R_2)}, \quad (5.22)$$

where r is the distance from the axis of the cell. These expressions also involve the surface densities at the ends of the effusion channel in addition to the previously introduced quantities $n(0)$ and $n(L)$ [cf. Fig. 16].

The total effective effusion transfer coefficient Ψ , which is analogous to K_W in (5.15), but is now given for a conical channel, is shown in Fig. 17 for a number of parameter values.

Finally, we reproduce the results of calculations^[140] of the spatial distribution of the effusion flux for the cell shown in Fig. 15 (2). Figure 18 shows the geometric parameters and the limits of integration for the different components contributing to the spatial distri-

TABLE III.

Size of aperture	L , cm	0.0005	0.0117
	R_1 , cm	0.0058	0.0125
β		0.62	0.17
K_W		1.524	0.789
K_D		0.959	0.679
K_K		0.959	0.686

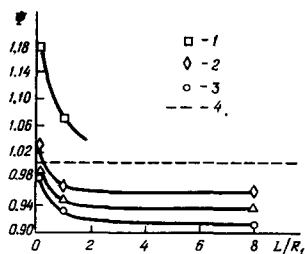


FIG. 17. Integral effusion coefficient^[140] [identical with K_W in (5.15) but for a conical aperture]. $\gamma=30^\circ$, $R_1=0.05$ cm, 1— $E=10^4$ cm⁻², 2— $E=10^7$ cm⁻², 3— $E=\infty$,^[133] 4— $\Psi=1$.

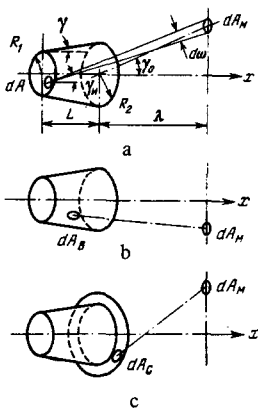


FIG. 18. Calculation of the spatial distribution of effusion flux from a conical effusion aperture. λ —distance from the plane of the target or detector; a — c —limits of integration corresponding to zones A, B, C in Fig. 15.

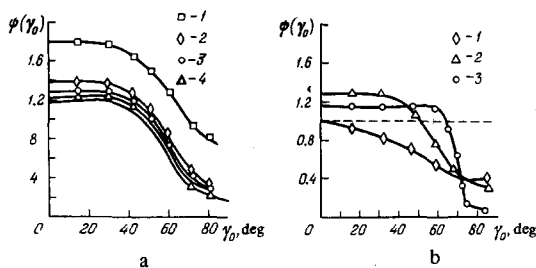


FIG. 19. Partial effusion coefficient^[140] for a conical aperture as a function of γ_0 (see Fig. 18). a) $\gamma=30^\circ$; 1— $E=10^5$ cm⁻², $R_1=0.005$ cm; 2— $E=10^7$ cm⁻², $R_1=0.05$ cm; 3— $E=10^5$ cm⁻², $R_1=0.05$ cm; 4— $E=10^7$ cm⁻², $R_1=0.05$ (see^[133]); b) $E=10^5$ cm⁻², $R_1=0.05$ cm, $L/R_1=1.0$; 1— $\gamma=0^\circ$, 2— $\gamma=30^\circ$, 3— $\gamma=60^\circ$.

TABLE IV. Effusion parameters^[140] for different geometries of the effusion channel (Fig. 18) and inverse square of the diffusion range (E).

No. of series	γ , deg	L/R_1	R_1 , cm	E , cm ⁻²	Ψ ($\gamma_0=0$)	Ψ	K_R	β
1	0	0.0863	0.0058	10 ⁷	1.03	0.99	0.9583	0.034
2	0	0.936	0.0125	10 ⁴	1.62	1.30	0.6866	0.893
3	0	0.936	0.0125	10 ⁵	1.12	0.795	0.6866	0.157
4	0	0.936	0.0125	10 ⁷	1.01	0.698	0.6866	0.016
5	0	8.00	0.050	10 ⁴	1.05	0.232	0.2253	0.031
6	0	8.00	0.050	10 ⁷	1.03	0.229	0.2253	0.018
7	0	1.00	0.050	10 ⁵	1.03	0.698	0.6720	0.039
8	30	1.00	0.050	10 ⁴	1.37	1.064	0.9334	0.140
9	30	1.00	0.050	10 ⁵	1.28	0.967	0.9334	0.037
10	30	1.00	0.050	10 ⁷	1.26	0.947	0.9334	0.015
11	30	1.00	0.005	10 ⁴	4.19	3.950	0.9334	3.23
12	30	1.00	0.005	10 ⁵	1.77	1.49	0.9334	0.587
13	30	1.00	0.005	10 ⁷	1.28	0.966	0.9334	0.035
14	30	0.10	0.050	10 ⁴	1.20	1.17	0.9869	0.185
15	30	0.10	0.050	10 ⁵	1.07	1.03	0.9869	0.044
16	30	0.10	0.050	10 ⁷	1.03	0.992	0.9869	0.005
17	30	8.00	0.050	10 ⁵	1.94	0.955	0.9065	0.054
18	30	8.00	0.050	10 ⁷	1.84	0.934	0.9065	0.030
19	60	1.00	0.050	10 ⁴	1.36	1.21	0.9952	0.216
20	60	1.00	0.050	10 ⁵	1.17	1.04	0.9952	0.045
21	60	1.00	0.050	10 ⁷	1.14	1.01	0.9952	0.005

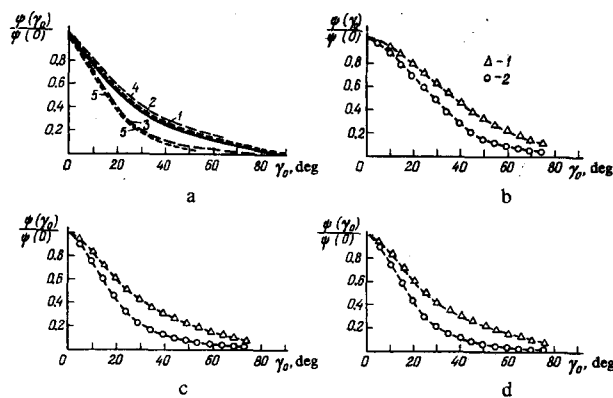


FIG. 20. Comparison^[55] of experimental and theoretical^[37,47,55] partial effusion characteristics for a cylindrical aperture. a) Theoretical curves for CsCl and Cs₂Cl₂ on the assumption that the equilibrium vapor contains 4% Cs₂Cl₂, $L/R=4.0$. 1—Clousing curve for monomer composition, 2—CsCl based on the theoretical results in^[37,47,55], 3—Cs₂Cl₂ data according to the theoretical results in^[37,47,55], 4—CsCl, 5—Cs₂Cl₂ according to^[153], $E=10^3$ cm⁻²; b) $L/R=2.0$, experiments in^[42,48,56]. 1—KCl, 2—K₂Cl₂, theory^[55]; c) same as b) for $L/R=4.0$; d) ditto for CsCl, Cs₂Cl₂ ($L/R=4$).

Figure 19 shows the results of calculations for different parameter sets. Table IV lists the parameters of the cell with a conical effusion aperture; these parameters are analogous to those in Table III.

D. Comparison of calculations with experimental data

The theoretical predictions^[58,151,152] are compared with experimental results in^[153]. Sufficiently good agreement is obtained but the correspondence with the equilibrium dissociation theory^[37,47,48] is better still, especially when the calculations reported in^[37,47] are improved in the way described in^[55]. Figure 20 demonstrates the excellent agreement between experimental and theoretical data. To be objective, we recall once again that we must not be too impressed by this agreement because, firstly, existing direct experiments^[52,75] confirm the equilibrium hypothesis but not for any, by far, combination of a molecular beam and a substrate; secondly, existing phenomenological theories contain too many parameters. All this means that it is usually not too difficult to achieve agreement between theory and experiment, and the latter is frequently less accurate than one would wish.

In a recent study,^[53] the spatial distribution was determined with an angular resolution of 1° for two types of effusion vessel (Fig. 21 shows the type of vessel and Fig. 22 the effusion characteristics), and a qualitative explanation was given of the resulting nontrivial effusion characteristics. An important feature of these results is not only the considerable spatial uniformity of particles of different types, but also the unstable character of the molecular fluxes.

The dynamics of sorption in long capillaries will merely be noted here. This problem, like certain others mentioned only incidentally here, deserves a separate review. This theory (presented in^[187,194] and in the previously mentioned^[4,5,31-33,228]) is, in a sense,

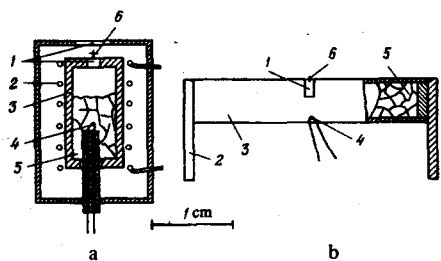


FIG. 21. Design of evaporators^[53] a) 1—effusion aperture, 2—spiral, 3—stainless steel crucible, 4—thermocouple, 5—salt, 6—projection of the axis of rotation perpendicular to the plane of the drawing; b) 1—effusion aperture, 2—current leads, 3—tantalum foil tube, 10 μ thick, 4—thermocouple (the second thermocouple is attached near the current lead; not shown in figure), 5—salt, 6—axis of rotation.

the converse of the theory of effusion. We mention it because the two mathematical formalisms are similar, so that there is a possibility of a mutual enrichment between the two lines of enquiry. For example, the theory of sorption has involved the consideration of a much larger number of models of adsorption kinetics but, on the other hand, it is usually concerned with the

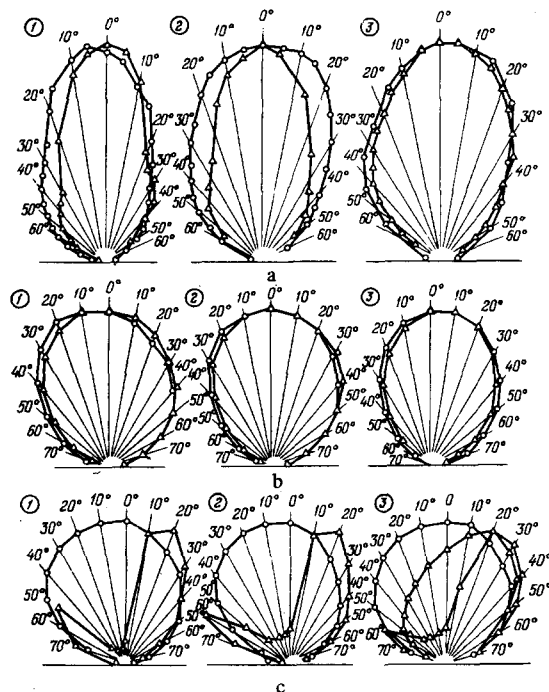


FIG. 22. Angular distributions^[53] of effusion from the evaporators in Fig. 21: \circ —NaCl, Δ —Na₂Cl₂. Curve normalized to maximum partial intensity. a) Effusion characteristics for evaporators shown in Fig. 21a. T_{σ} (°C): 525° (1), 566° (2), and 625° (3). Ratio of maximum flux intensities of monomers and dimers is roughly 2–3; b), c) effusion characteristics for the evaporators in Fig. 21b, ΔT —difference between thermocouple readings in Fig. 21b. T_{σ} (°C)—temperature indicated by central thermocouple. Ratio of monomer and dimer fluxes: for (b) \sim 1–1.5, for (c) 8–10. ΔT for $T_{\sigma}=700^{\circ}\text{C}$ was as follows: for (b) $\Delta T=20^{\circ}$, for (c) $\Delta T=100^{\circ}$, $T_{\sigma}=(^{\circ}\text{C})=$ b) 560 (1), 630 (2), and 700 (3); c) 790 (1), 845 (2), and 890 (3). Evaporator in case (b) was fully loaded; half this charge was used for (c) with central part free from the salt.

TABLE V.

Geometry	$\varphi(l)$	$\langle l \rangle$	$\langle l^2 \rangle$
Infinite parallel planes at distance s from one another	$2a^2/l^3$	$2a$	∞
Sphere of radius R	$l/2R^2$	$4R/3$	$2R^2$
Infinite circular cylinder of radius R	$\frac{16}{\pi} \frac{R^2}{l^3} \int_0^{x_0} \frac{x^4 dx}{2R-x^2 \sqrt{1-x^2}}$, $x_0 = \begin{cases} 1 & \text{if } l > 2R, \\ 1/2R & \text{if } l < 2R \end{cases}$	$2R$	$\frac{16R^2}{3}$

solution of the one-dimensional problem, and phenomena near the ends of the capillaries are usually ignored. The one-dimensional equations of sorption dynamics formulated in the classical paper^[195] have given rise to the theory of chromatography and its very powerful mathematical formalism.^[203]

A multichannel effusion source was proposed, fabricated, and tested by Lucas.^[183] It consists of capillaries, 5 μ in diameter and 2.5 mm long. A plate made up of such capillaries has a transmission of about 50% and a total diameter of 50 mm. The most striking feature of this system is that the axes of all the capillaries intersect at "a single point" on the axis of the plate at 50 mm from it. A helium flux of $\sim 10^{14}$ cm⁻³ was obtained at this focal point for a total consumption of 10^{19} atoms/sec. Very good focusing was achieved: the helium spot in the focal plane had a diameter of 5 mm. The surface flux density was $\sim 10^{18}$ cm⁻² · sec⁻¹, which was comparable with the flux densities obtained by gas-dynamic methods.^[20,136]

6. CERTAIN INTEGRAL CHARACTERISTICS OF EFFUSION VESSELS

A. The method of chords

The method of chords, originally devised by Dirac^[156] to calculate the neutron mean free path in a solid medium, can be used to determine the distances between successive points of collision between particles and the walls of a vessel containing a gas at low pressure. These chords are drawn through the vessel containing the gas, and physically represent the trajectories of the gas particles. The most complete characteristic of the ensemble of such chords is the function representing the length distribution density. We shall consider some examples^[156] of the function $\varphi(l)$, and also the mean lengths $\langle l \rangle$ and the mean squares $\langle l^2 \rangle$, obtained by averaging over $\varphi(l)$. These are listed in Table V, which is based on the data reported in^[156].

The function $\varphi(l)$ for other bodies is also given in^[156], but these expressions are rather cumbersome and will not be reproduced here.

The mean chord length can be calculated from the following simple formula^[155,156]

$$\langle l \rangle = \frac{4V}{S} \quad (6.1)$$

in the case of a three dimensional body (V is the vol-

TABLE VI. Ratio of the mean square chord length to the square of the mean chord for cylindrical cavities of different shape ($Q = \langle l^2 \rangle / \langle l \rangle^2$).

a) Infinite right cylinder

Cylinder cross section	Q
Circular	1.333
Square	1.487
Isosceles triangle	1.648
Regular hexagon	1.397

b) Infinite right cylinder of rectangular cross section with different ratio of the sides of the rectangle, a/b .

a/b	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Q	∞	1.941	1.72	1.621	1.565	1.532	1.511	1.499	1.491	1.488	1.487

c) Gap between two coaxial circular cylinders of radii r and R .

r/R	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.99
Q	1.333	1.368	1.405	1.445	1.490	1.542	1.604	1.681	1.788	1.966	2.467

ume and S the surface area), and

$$\langle l \rangle = \frac{\pi S}{L} \quad (6.2)$$

for a plane figure^[155] of area S and perimeter L . Such simple expressions are not available for the mean square $\langle l^2 \rangle$. This quantity was therefore obtained by the usual averaging over $\varphi(l)$. Tabulations of $Q = \langle l^2 \rangle / \langle l \rangle^2$ for bodies of different shape have been published.^[157]

Table VI shows some of the data taken from^[157]. These tables enable us to put forward the hypothesis that there is one further (in addition to those listed in^[158]) isoperimetric inequality, namely, $Q \geq Q_{cc}$, where Q_{cc} represents the ratio $\langle l^2 \rangle / \langle l \rangle^2$ for an infinite circular cylinder and Q is its value for any other cylinder.

We shall now consider a method^[137] of using the mean lengths to calculate the coefficients of the diffusion and Fokker-Planck equations. In the case of small adsorption times and large times of relaxation of the initial momentum^[105] (average shift not equal to 0), instead of the diffusion equation

$$\frac{\partial W(x, t)}{\partial t} = D \frac{\partial^2 W(x, t)}{\partial x^2}, \quad (6.3)$$

we have the Fokker-Planck equation

$$\frac{\partial W(x, t)}{\partial t} = -\bar{n}(x) \frac{\partial W(x, t)}{\partial x} + D \frac{\partial^2 W(x, t)}{\partial x^2}, \quad (6.4)$$

where $W(x, t)$ is the distribution function for the position of the particle at time t at the point x , and \bar{n} is the number of random walks per unit time

$$\bar{n} = \left(\frac{\langle l \rangle}{u} + \tau \right)^{-1}, \quad (6.5)$$

where \bar{u} is the mean particle velocity and τ is the adsorption time.

In the other limiting case, when (6.3) is valid, i. e., the adsorption times are large and the times of relaxation of the initial momentum of the particle incident on the surface of the vessel are small, the authors of^[137] have calculated $\varphi(x)$, i. e., the distribution density for the probability of displacement along the x axis of the infinite cylinder.

The functions W and φ are related by the following well-known expression

$$\frac{\partial W}{\partial x} = \varphi(x), \quad (6.6)$$

$$\varphi(x) = \frac{1}{2a} \left[1 - \frac{|x| (x^2 + 6a^2)}{(x^2 + 4a^2)^{3/2}} \right], \quad (6.7)$$

where a is the radius of the cylinder.

Table VII lists the values of $\langle l \rangle$, $\langle x^2 \rangle$, and \bar{n} obtained in^[137] for the evaluation of D from the formula

$$D = \frac{1}{2} \bar{n} \langle x^2 \rangle = \frac{1}{2} \left(\frac{\langle l \rangle}{u} + \tau \right)^{-1} \langle x^2 \rangle. \quad (6.8)$$

The motion of molecules in vessels other than capillaries can be described either in terms of the exact integral equations or by transforming from the scalar diffusion equations to the tensor equations by analogy with neutron-transport theory.^[157]

B. The geometric probability approach

Gordon and Ponomarev^[137] have calculated the probability p that a particle leaving an outer cylinder of radius a will strike a coaxial inner cylinder of radius b :

$$p = \frac{b}{a}. \quad (6.9)$$

They write^[137] that the simplicity of this expression "suggests that it is a trivial result but, unfortunately, we have not succeeded in deriving it on the basis of any simple considerations." This result is, in fact, a special case of a more general theorem^[155] on the probability that two convex shells located one inside the other will be cut by a common chord. Thus, for two infinite convex cylinders with arbitrary generators, this probably is given by the ratio of the lengths of the lines cut by the cylinders on an arbitrary plane (non-parallel to the generators). The requirement of con-

TABLE VII.

Geometry Parameters	Infinite cylinder of radius a	Gap between two infinite coaxial circular cylinders with radii $a > b$
$\langle l \rangle$	$2a$	$2a \left(1 - \frac{b^2}{a^2} \right)$
$\langle x^2 \rangle$	$\frac{8a^2}{3}$	$\frac{8a^2}{3} \left[1 - \frac{3}{4} \frac{b}{a} - \frac{3\pi b^2}{a^2} + \frac{3}{4} \left(1 - \frac{\pi}{16} \right) \frac{b^2}{a^2} \right]$
\bar{n}	$\left(\frac{2a}{u} + \tau \right)^{-1}$	$\left[\frac{2a}{u} \left(1 - \frac{b^2}{a^2} \right) + \tau_a + \frac{b}{a} \tau_b \right]^{-1}$

* τ_a and τ_b —adsorption times on the outer and inner cylinder; generally, $\tau_a \neq \tau_b$, for example, because of the possible difference between the materials of the two cylinders or their temperatures.

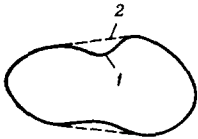


FIG. 23. The probability measure for the number of random straight lines cutting a concave profile (1) is equal to the length of the filament (2) drawn round it.

vexity is not essential since it is usually sufficient to straighten out the profile as shown in Fig. 23 and apply the theorem to this modified outline.

The most important assumption used in deriving the relationships reproduced in the present chapter is that the cosine law is valid for the local emission characteristics. It is only in this case that the density measure for random straight lines in space is invariant under the group of transformations in Euclidean space (see^[155,159] for detailed discussions of the Bertrand paradox). This also refers to Tables VIII and IX which give the recipes for the simple calculation of the probability that particles from one of the infinite cylinders will strike the other (Table VIII), or the probability that they will not reach one of the cylinders after leaving the other because of some obstacle between them (Table IX). These results were obtained more than a hundred years ago^[160,161] and we have rescued them from obscurity because of their possible practical application, not to mention their beauty. The third row in Table VIII corresponds to the "method of stretched filaments," introduced into photometry by Gershun.^[162]

We now consider (again without proof^[161]) the results of Table IX, which lists the formulas of the method of stretched filaments for different possible cases of the mutual disposition of three oval figures. The table begins with the case of two oval figures, also given in Table VIII.

TABLE VIII. Probabilities of simultaneous intersection of two plane convex contours (or infinite cylinders with these profiles) by random straight lines; L_1 and L_2 are contour perimeters.

Mutual disposition of contours	Probability of simultaneous intersection
	$\frac{L_2}{L_1}^*)$ (1)
	$\frac{L_1 + L_2 - L_{12}}{L_1}^{**})$, (2)
	$\frac{L_{12} - L_{12}}{L_1}^{**})$, (3)

where L_{12} is the length of the stretched filament running around both contours

where L_{12} is the length of the stretched filament running around the two contours and intersecting at the point 0; L_{12} is the same quantity as in the preceding disposition of contours

*)Compare with (6.9)

**)Conditional probabilities are indicated. This means that (2) and (3) can be replaced by $(L_1 + L_2 - L_{12})/L_2$ and $(L_{12} - L_{12})/L_2$ if we consider chords that definitely cut the second contours.

TABLE IX.

"Positive" contours	Formulas for the measure of the number of straight lines cutting both oval figures	"Negative" contours
	1) $p_2 = (I \times II) - (I \ II)$ = 1, 2, 3, 4, 5, 6, 1 - 1, 2, 3, 4, 5, 6, 1	
	2) $p_3 = (II \times III) - (II \ III)$ = 1, 2, 3, 4, 5, 1 - 1, 2, 3, 4, 5, 1	
	3) $p_3 = (I \times III) + (II \times III)$ (II III) - D = 2, 7, 8, 9, 4, 3, 2 + 1, 2, 3, 4, 5, 6, 1 - 1, 2, 3, 4, 5, 1 - 8, 1, 4, 3, 2, 6, 7, 8	
	4) $p_3 = (I \ II \ III) + (I \times III)$ + (II \times III) - (I \ III) - (II \ III) - D = 1, 2, 3, 4, 5, 6, 7, 1 + 1, 5, 4, 3, 6, 7, 1 + 2, 5, 4, 3, 8, 2 - 1, 2, 3, 4, 5, 6, 1 - 8, 2, 3, 4, 7, 9, 8 - 1, 9, 8, 4, 3, 2, 5, 6, 1	
	5) $p_3 = (I \times III) + (II \times III)$ - (II \ III) - D = 1, 2, 3, 4, 5, 6, 1 + 7, 8, 4, 3, 2, 9, 10, 7 - 1, 2, 3, 4, 5, 6, 1 - 1, 4, 3, 2, 5, 8, 9, 7, 1	
	6) $p_3 = (I \ II \ III) + (I \times III)$ + (II \times III) - (I \ III) - (II \ III) - D = 1, 2, 3, 4, 5, 6, 7, 1 + 1, 5, 4, 3, 6, 7, 1 + 2, 5, 4, 3, 8, 9, 2 - 1, 2, 3, 4, 5, 6, 1 - 7, 4, 3, 2, 8, 9, 7 - 1, 7, 4, 3, 2, 8, 5, 6, 1	
	7) $p_3 = (I \times III) - (I \ III)$ = 1, 2, 3, 4, 5, 6, 1 - 1, 2, 3, 4, 5, 6, 1	
	8) $p_3 = \Delta_1 - \Delta$ = 1, 2, 3, 4, 5, 6, 2, 7, 3, 8, 1 - 1, 2, 3, 4, 5, 6, 7, 8, 1	
	9) $p_3 = \Delta_1 - \Delta$ = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 1 - 1, 2, 3, 4, 5, 6, 7, 8, 9, 1	
	10) $p_3 = \Delta_2 - \Delta$ = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 1 - 1, 2, 3, 4, 5, 6, 7, 8, 9, 1	
	11) $p_3 = (I \ II \ III) + (I \times II)$ + (I \times III) + (II \times III) - (I \ II) - (I \ III) - (II \ III) - (I) - (II) - (III) = 1, 2, 3, 4, 5, 6, 7, 1 - 1, 2, 3, 4, 5, 6, 7, 1	
	12) $p_3 = 0$	

TABLE X. Values of ΔT° necessary for the detection of a signal ΔP_{Tot} with a probability p for two values of the heat of evaporation $Q_1 = 200$ kcal/mole and $Q_2 = 20$ kcal/mole. $T_E = 1000$ °K, $M = 100$.

$\Delta P (Q_1)$	p			$\Delta P (Q_2)$
	0.52	0.91	0.997	
10 ⁻¹⁰	0.07	0.17	0.3	10 ⁻⁸
10 ⁻¹²	0.7	1.7	3.0	10 ⁻¹⁰
10 ⁻¹⁴	7	17	30	10 ⁻¹²

The table of formulas for the relative number of straight lines cutting all the oval figures consists of three columns: the middle column gives the final formulas, and the left- and right-hand columns reproduce the positive and negative terms in these formulas, respectively. Symbols such as, for example, (I×II) and (I II) indicate that we should take lengths of filaments around the oval figures I and II with and without intersection, respectively. The thick line in the left-hand column shows the "positive" contours, whilst, in the right-hand column, it represents the "negative" contours. Arabic figures in the central column indicate the sequence along the contours. Roman figures label the oval figures.

C. Time constant of an effusion vessel

The relaxation time constant of a vessel, τ , is important for many kinetic investigations. The vessel can be an effusion cell or a molecular-beam detector, or some other system. The formula for a spherical vessel of radius R is given in^[149]:

$$\tau = \left(\frac{4}{3} \frac{R}{u} + \tau_a \right) \frac{S}{S_0} \quad (6.10)$$

[compare this with (6.5)], where S and S_0 are the areas of the inner surface and of the effusion aperture, and τ_a is the adsorption time. When the probability of escape of a particle from a sphere is defined more rigorously (than simply by S_0/S), we have^[140] where V is

$$\tau = \frac{V}{K_i S} \sqrt{\frac{2\pi m_g}{kT_e}} \quad (6.11)$$

where V is the volume of the vessel and the remaining symbols have their usual meaning. Equation (6.11) does not take into account the adsorption time or the various possible complications mentioned in the preceding chapters.

It is therefore better to replace (6.11) with

$$\tau = \frac{1}{K_i} \left(\frac{V}{S} \sqrt{\frac{2\pi m_g}{kT_e}} + \tau_a \right), \quad (6.11')$$

where K_i is one of the effusion coefficients discussed in Chap. 5 (in a special case, the Clausing coefficient K_C and Ψ for a conical aperture).

The effect of adsorption time on the time constant τ is elucidated in^[148] on the assumption that the transit time $\langle l \rangle / \bar{u} \ll \tau_a$ can be neglected and one-half of the surface inside the cell has the time τ_A and the other τ_B . The following formula is derived there:

$$\tau = \frac{\tau_A \tau_B}{\tau_A + \tau_B}. \quad (6.12)$$

The limiting sensitivity with which the vapor pressure can be determined by the Knudsen method is also established in^[148].

For a material of molecular weight M , given pressure and temperature T_e in the effusion chamber, and heat of evaporation Q , we can determine the minimum change ΔT_e which will produce a change in the vapor pressure that will exceed a random fluctuation with given probability. Some numerical results are listed in Table X.

The dependence of the rate of effusion on T_e and M is used in the very effective chromatographic-effusometric devices as a means of determining the molecular weight M (see^[150] and the bibliography therein, which is concerned with a combination of an effusion vessel, a chromatograph, and a mass-spectrometric detector).

7. POSSIBLE FUTURE DEVELOPMENTS

Apart from the lines of enquiry which we have already suggested, in this concluding chapter we shall enumerate problems that should be solved first. Suggestions for subsequent development of this subject are most simply formulated in terms of "lateral" expansion, including:

- 1) new incident particles, i. e., molecular and ion beams that have not yet been investigated;
- 2) new targets, different shapes (including those that may change in the process of effusion) and materials of vessels, nonisothermal targets, and
- 3) new chemical interaction processes (both homogeneous and surface).

It is likely that molecular diffraction studies will cease to be regarded as exotic and will become part and parcel of general diffraction methods, such as x-ray, electron, and neutron diffraction. Success in this field will be largely determined by the future development of stable, high-intensity, monoenergetic beams of atoms and molecules.

It will be necessary, quite soon, to develop beams of particles in given excited states, and also beams of metastable and polarized particles (electrical, magnetic, and spin polarization). Analysis of the scattering of such particles by specially prepared targets will provide important information on surface states.

At all levels and in all areas of research, we have the difficult question of converse problems,^[27] which are still further complicated by the fact that they involve the solution of systems of integrodifferential equations. The problem of the microscopic interpre-

tation of the extensive set of phenomenological coefficients regulating the energy and mass transfer processes which accompany effusion phenomena is just as acute as for example, in radiation transfer theory (see^[211], pp. 254, 255, and 258).

We have not considered in this review the statistical aspects of effusion, which are still in a rudimentary state of development and which should become important at low beam intensities when fluctuation effects become appreciable.^[81-84]

Evidently, the ergodic problem which is almost removed by the uncertainty relation for closed systems (the qualification "almost" is introduced because of the soliton paradox) and which has not even been touched upon for open systems, remains important and interesting.^[83] In effusion, this is the problem of the angular distribution of emission from a vessel when the local angular distribution is either quasispecular or diffractive in character.

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