A method for determining the mean translational energy of particles desorbed from solid surfaces

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A method for determinig the mean molecular translational energy in gas flows of low intensity (10^{12}—10^{14} molec. s^{-1}) has been proposed. The method was verified using various gases (H_2, N_2, O_2, and CO_2) flowing into a vacuum out of a heated capillary. The translational energies were determined for CO and N_2 molecules desorbing from the surface of polycrystalline Ir. The translational temperature (T_{tr}) measured for CO equals 650±90 K and almost coincides with the surface temperature (T_s = 600 K). In the case of nitrogen molecules, T_{tr} = 4600±500 K at T_s = 500 K. The method proposed is applicable to the determination of the spatial distribution of molecular beam particles.

Key words: desorption; molecular beam, translational energy.

Investigations performed during the past 25 years have shown that desorption of chemisorbed gases from metal surfaces is in many cases essentially a nonequilibrium process,[1,2] *i.e.*, the distribution of particles by their degrees of freedom is not described by the Maxwell—Boltzmann law. In this case the translational temperature of desorbing molecules (T_{tr}) may significantly exceed the surface temperature (T_s).[1—4] Such effects are observed during the recombinational desorption of diatomic gases (H_2, O_2, N_2, and CO), as well as during CO oxidation, when the reverse process (dissociative chemisorption) is activated.

Usually the evidence for emission from the surface of translationally excited particles is that their spatial distribution is strictly oriented normal to the surface and does not obey Knudsen's law:

$$I/I_0 = \cos\varphi, \tag{1}$$

where I_0 and I are the densities of the desorption flow normal to the surface and at an angle φ to it, respectively.

The direct determination of the velocities of desorbing molecules is usually carried out by registering the flight-time of the particles[5,6] or by using velocity selectors.[7] This demands the use of special complex equipment, and during velocity selection it is necessary to have relatively intense molecular beams and vacuum systems with high pumping speeds. But in this case it is possible to determine not only the average velocities of molecules but also the velocity distributions of molecules, which may differ from the Maxwell distribution.[8] Because of the indicated experimental difficulties such measurements have to date been carried out for a limited number of systems characterized by a high density of the desorption flow or by large numbers of analyzed particles making it possible to accumulate the signal. This is the case with hydrogen desorbing from permeable metal membranes[9] and with CO oxidation.[10]

In thermal desorption experiments performed with the use of single crystals or polycrystalline specimens with a smooth surface, the surface area is usually <1 cm^2, therefore the total number of desorbed molecules is equal to 10^{13}—10^{15} and the desorption flow equals 10^{12}—10^{14} molec. s^{-1}

The present work is devoted to the elaboration of a method for determining the mean molecular velocities in gas flows of low intensity (10^{12}—10^{14} molec. s^{-1}). The theoretical basis of the method is the equation for flow density (F/molec. cm^{-2} s^{-1}):

$$F = C\bar{u}, \tag{2}$$

where C is the concentration of molecules in the flow and $\bar{u}$ is their mean velocity. Therefore independent measurements of the F and C values allow one to determine the mean velocity of the particles.

Experimental

The experiments were carried out on a Vacuum Generators UHV apparatus. For development of the method and its calibration an experimental cell was built into the vacuum chamber (Fig. 1). A molecular beam of the gas being investigated was fed through a stainless steel capillary with an inner diameter of 0.6 mm and 50 mm long. The intensity of the gas flow (H_2, N_2, O_2, and CO_2) was set by a fine control leak valve. In each experimental series the gas flow was strictly fixed. The temperature of the capillary was varied from 300 to 1000 K by heating it resistively and measured by means of a Pt—PtRh thermocouple spotwelded close to the exit orifice of the capillary.

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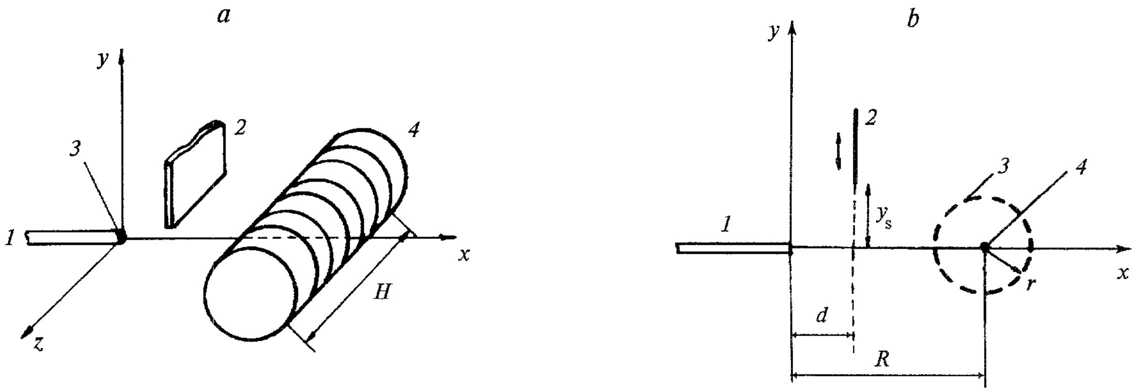

Fig. 1. Disposition of the main components of the experimental cell in the vacuum chamber (*a*) and their section in the *x*0*y* plane (*b*). *a*: *1*, capillary; *2*, shield; *3*, thermocouple; *4*, gauge head. *b*: *1*, capillary; *2*, shield; *3*, anode; *4*, ion collector. Dimensions/mm: $H = 45$, $d = 6$, $r = 12.5$, $R = 24$.

A nude Bayard—Alpert[11] ionization gauge, whose detector was placed near the exit orifice of the capillary was used as the registering device. Between the capillary and the detector a metal foil shield fastened on a manipulator was placed. This allowed one to partly or completely intercept the gas stream directed from the capillary into the ionization space of the gauge head.

In experiments to determine the mean velocities of molecules the readings of the gauge (average molecular concentrations in the detector ionization space) were registered with a completely closed or open shield (C_0 and C_1, respectively). For determination of the spatial distribution of molecules in the beam the indications of the gauge (C_2) were registered as a function of the coordinate of the lower edge of the shield (y_s, see Fig. 1, *b*).

The method described above was worked out with the aim of using it for measuring the kinetic energy of molecules desorbing from metal surfaces. This part of the work was done for the systems CO/Ir and N_2/Ir.

The key experiments were carried out on the same set-up after the following conversions: the shield mounted on the manipulator was replaced by a support with the specimen (10×3 mm^2) cut out from an iridium ribbon 20 μm thick. The manipulator allowed one to rotate the specimen around the y axis and move it along the x and z axes. In the study of CO desorption, labeled ^{13}CO adsorbed on the specimen at 20 °C was used. The desorption of N_2 molecules took place as a result of a temperature programmed reaction (TPR) during the decomposition of NO adsorbed on the specimen at 20 °C.

In these experiments the readings of the Bayard—Alpert gauge were registered for two positions of the specimen. In the first case the specimen was oriented in such a way that the desorbing particles could not directly enter the ionization space. In the second one the specimen was turned with its plane carrying the adsorbate towards the gauge head so that all desorbing particles would traverse the gauge head ionization space. In the first case the obtained signal (C_0) is proportional to the flow of desorbing particles and in the second one the measured signal (C_1) is the sum of C_0 and the particle concentration in the desorption flow.

Carrying out thermal desorption experiments in this way corresponds to experiments with an effusion molecular beam in which the shield is closed or entirely open.

Measurements performed when the system was pumped out only by an ion pump showed that the difference between the signals C_1 and C_0 is negligible, which results in a large error in determinations of the velocities of the desorbing particles. This is due, first of all, to the low concentration of particles in the desorption flow at the heating rates necessary for detailed registering of the thermal desorption spectrum.

To increase the pumping speed an additional sublimation pump was used, which evaporated the titanium onto the surface of the vacuum chamber. In this case it was necessary to measure the total pumping speed by both the ion and sublimation pumps. This was done in the following way: at a fixed leak-in of the gas being investigated (^{13}CO or N_2) and with only the ion pump operating the partial pressure of this gas in the vacuum chamber was registered; after that the sublimation pump was switched on and from the pressure decrease, provided the pumping speed of the ion pump was known, the total pumping speed was found, which for both gases was equal to 700±70 L s^{-1}.

Results and Discussion

Measurement of the mean velocities of the effusion beam molecules. When the shield is entirely closed the molecules do not fly directly from the capillary to the gauge head and the value C_0 corresponds to the concentration of gas in the vacuum chamber, which is determined by the leak-in of gas from the capillary (L) and the pumping speed (S).

$$L = SC_0 \tag{3}$$

Under the conditions of the experiment the leak-in from the capillary is two orders of magnitude higher than the leak-in from other sources, and therefore the latter may be neglected.

When the shield is open the value C_1 exceeds C_0 since, besides the background concentration of molecules (C_0), the primary particles of the molecular beam which pass through the gauge head ionization space are registered. Let us denote the effective cross-section of the molecular beam in the ionization space as σ_b and the cross-section of the gauge ionization space itself, which is "seen" from the exit end of the capillary, as σ_i. When

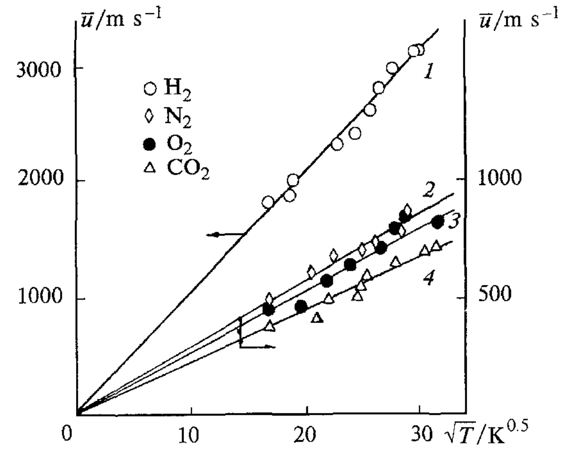

Fig. 2. Mean velocities ($\bar{u}$) of molecular beam particles for different gases as function of temperature (T). Points are experimental data. Straight lines (*1—4*) are results of calculations by Eq. (7) for different molecules: H_2 (*1*), N_2 (*2*), O_2 (*3*), and CO_2 (*4*).

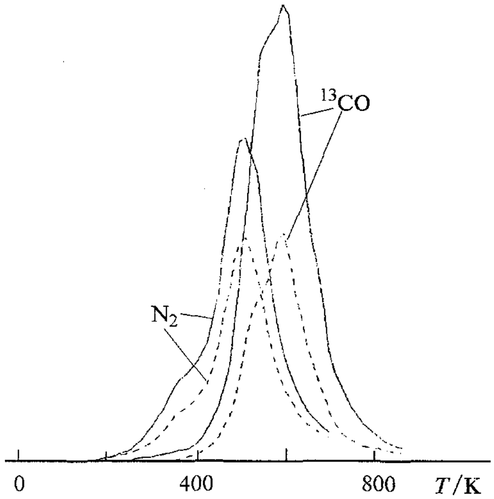

Fig. 3. Spectra of the thermal desorption of ^{13}CO and N_2 from Ir. Solid line: the specimen is oriented towards the gauge detector. Dashed lines: the specimen is in the position in which the gauge registers the secondary particles only.

$\sigma_b < \sigma_i$ the following relationship for the C_l value may be written:

$$\sigma_i C_l = \sigma_i C_0 + \sigma_b C, \quad (4)$$

where C is the concentration of the molecular beam.

It is easy to express the density of the flow in terms of the leak-in, which, coupled with Eq. (3), gives

$$F = L/\sigma_b = SC_0/\sigma_b. \quad (5)$$

Using Eqs. (2), (4), and (5) we obtain

$$\bar{u} = F/C = \frac{SC_0}{\sigma_i(C_l - C_0)}. \quad (6)$$

The cross-section σ_i determined from the dimensions of the gauge head ionization space limited by the anode was equal to 9.5 cm^2.

The S values of the ion pump for the gases studied at pressures of *ca.* 1 · 10^{-8} Torr are listed below:

Gas	H_2	N_2	CO	O_2	CO_2
S/L s^{-1}	270	100	100	57	100

Treatment of the results by Eq. (6) using the parameters listed above gives mean velocities coinciding with theoretical values within the limits of error of 10—15 %.

The results of determinations of mean velocities for molecules of various gases as functions of temperature are shown in Fig. 2. It can be seen that for all of the gases studied (H_2, O_2, N_2, and CO_2) the measured mean velocities, in accord with the kinetic theory,

$$\bar{u} = \sqrt{8kT/\pi M} \quad (7)$$

are proportional to $\sqrt{T}$ and inversely proportional to $\sqrt{M}$ (where T and M are the absolute temperature and molecular mass, respectively).

Determination of the mean velocities of desorbing molecules. As was shown by preliminary investigations,[11] the spatial distribution of the desorption flow of the CO/Ir system follows the cosine law (see Eq. (1)), whereas in the case of N_2, which is a product of NO decomposition on the surface of Ir, the spatial distribution is directed normal to the surface and is described by the empirical equation

$$I/I_0 = \cos^n\varphi, \quad (8)$$

where $n = 2.8$.

These facts indicate that in the first case one may expect the emission of CO molecules whose translational temperature is equal to the surface temperature, and in the second case translationally excited N_2 molecules will be emitted.

The thermal desorption spectra of the ^{13}CO/Ir and N_2/Ir systems shown in Fig. 3 were obtained for the two positions of the specimen. Calculations of the velocities of the ^{13}CO molecules in the maximum of the thermal desorption peak by Eq. (6) give a value of 690±50 m s^{-1}. This corresponds to a translational temperature of the desorbing particles equal to 650±90 K, which is close to the surface temperature (T_s = 600 K). This result agrees with that expected and may serve as a verification of the applicability of this method for measuring the velocities of desorbing molecules.

Desorption of N_2 from the surface of Ir leads to an entirely different result. Calculation of the velocity of N_2 molecules in the maximum of the thermal desorption peak (T_{max} = 500 K) by Eq. (6) gives a value of 1840±300 m s^{-1} which corresponds to a translational temperature equal to 4600±1500 K whereas T_s = 500 K.

If it is assumed that all of the surplus translational energy is caused by the adsorption activation barrier, then the value of this barrier would be equal to

34±12 kJ mol^{-1}. We tried to estimate the activation energy for dissociative chemisorption from the spatial distribution of desorption flow of the nitrogen molecules. For this purpose we approximated the observed distribution not by the empirical Eq. (8) but by the Van Willigen equation:[12]

$$I/I_0 = \frac{\varepsilon + \cos^2\varphi}{(\varepsilon + 1)\cos\varphi} \cdot \exp\left(-\varepsilon \tan^2\varphi\right), \qquad (9)$$

which involves the chemisorption activation energy ($E = \varepsilon kT$).

This estimate gives $E = 5\pm1$ kJ mol^{-1}, which differs greatly from the value obtained from the mean kinetic energy of N_2 molecules desorbing from the surface of Ir. The reason for such a difference may be that Eq. (9) is true for an ideally flat surface, whereas in the present work the specimen was prepared from a polycrystalline ribbon with some surface roughness.

The presence of even slight surface roughness causes appreciable broadening of the spatial distribution of the desorption flow[13] resulting in greatly understated values of the activation energy of chemisorption when Eq. (9) is used. Small bends in the metal foil plane may also give rise to broadening of the spatial distribution of the desorption flow similar to the effects induced by surface roughness.

If it is assumed that the roughness coefficient γ (the ratio of the true surface area to the geometric one) is equal to 1.2 then the true value of the exponent n in Eq. (8), according to our calculations,[13] will be equal to 15±2 and the barrier to chemisorption activation will, correspondingly, be equal to 31±4 kJ mol^{-1} The latter value coincides within the limits of error with the value of $E = 34\pm12$ kJ mol^{-1} obtained from measurements of the translational energy of N_2 molecules desorbing from the Ir surface.

The value of $\gamma = 1.2$ is quite possible for the polycrystalline ribbon surface. For example, for similar platinum specimens we obtained $\gamma = 1.08\pm0.02$ (see Ref. 14).

Determination of spatial distribution of molecules in a beam. Experiments in which a portion of the particle flow exiting from the capillary was intercepted made it possible to obtain information on the spatial distribution of the molecules in the flow.

Figure 4 shows the dependence of gauge readings (C_2) on the shield position (y_s) in $(C_2 - C_0)/(C_1 - C_0) = f(y_s)$ coordinates for an air flow at 20 °C (experimental points). Similar dependences were also obtained for other gases studied at various temperatures.

We managed to express the dependence obtained analytically. During molecular flow of a gas out of the capillary the density of the flow is to a considerable extent concentrated along the capillary axis and can be described by the empirical equation

$$F = F_0 \cos^n\alpha, \qquad (10)$$

where F_0 is the flow density for molecules flying along the capillary axis, α is the angle between this axis and the direction of particle motion, n is an exponent greater than 1. When n increases the flow becomes more concentrated along the capillary axis.

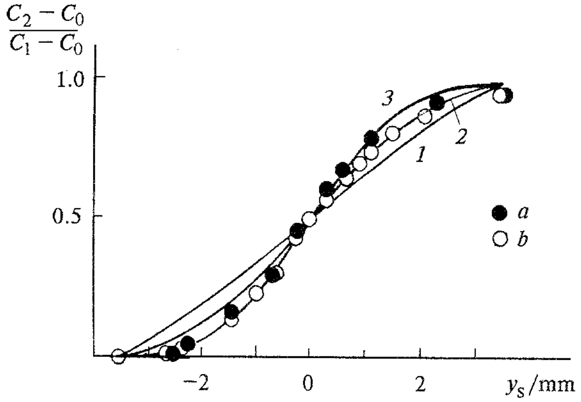

Fig. 4. Normalized dependence of the gauge readings (C_2) on the coordinate of the lower edge of the shield (y_s). Pressure ranges (p/Torr): 10^{-9} (*a*) and 10^{-8} (*b*). The curves were calculated by Eq. (14) at n = 1 (*1*), 10 (*2*), and 20 (*3*). C_0 and C are gauge readings at completely closed and open positions of the shield, correspondingly.

In order to derive the equation necessary to describe the experimental dependence of the gauge readings on the shield position we introduce the following coordinates (see Fig. 1): for the origin of coordinates we adopt the exit end of the capillary, the x axis is directed along the capillary axis and the z axis will, correspondingly, be perpendicular to the plane of the drawing. In subsequent treatment spherical polar coordinates that are "tied" to the given Cartesian coordinates, with polar and azimuthal angles denoted as θ and φ, respectively, will be used.

It is easy to show that in these coordinates

$$\cos\alpha = \sin\theta \cos\varphi. \qquad (11)$$

Taking into consideration Eqs. (10) and (11), the concentration of primary particles arriving from the capillary in the gauge ionization space, which is proportional to their flow, may be written as follows:

$$C_2 - C_0 \approx I = \iint\limits_{\Omega} F_0 R^2 \cos^n\varphi \sin^{n+1}\theta \, d\varphi \, d\theta\,, \qquad (12)$$

where Ω is the spatial angle embracing the trajectories of the primary particles that enter the gauge head ionization space limited by the gauge size and the shield; R is the distance between the capillary and the gauge head (see Fig. 1).

Inserting the pertinent integration limits we obtain

$$I = F_0 R^2 \int\limits_{\theta_1}^{\theta_2} \sin^{n+1}\theta \, d\theta \int\limits_{\varphi_1}^{\varphi_2} \cos^n\varphi \, d\theta\,, \qquad (13)$$

where $\theta_1 = \pi/2 + \tan^{-1}[H/(2R)]$; $\theta_2 = \pi/2 - \tan^{-1}[H/(2R)]$; $\varphi_1 = -\arcsin(r/R)$; $\varphi_2 = \tan^{-1}(d/y_s)$; the parameters d, r, R, and H are shown in Fig. 1.

In the case of a completely open shield the corresponding concentration (C_1-C_0) is expressed by an integral identical to the integral of Eq. (13) but with a different upper limit. The upper limit φ_2 appearing in the integral of Eq. (13) and depending on the shield coordinates should be replaced by $\varphi_3 = \arcsin(r/R)$, the angle determined by the dimensions of the ionization space of the gauge.

Thus the required ratio $(C_2-C_0)/(C_1-C_0)$ may be written as

$$(C_2 - C_0) / (C_1 - C_0) = \int_{\varphi_1}^{\varphi_2} \cos^n\varphi d\varphi \int_{\varphi_1}^{\varphi_3} \cos^n\varphi d\theta. \qquad (14)$$

The integrals appearing in Eq. (14) can easily be calculated for any integer values of n and only the first one depends on the shield coordinate y_s.

In Fig. 4, besides the experimental data, the results of calculations by Eq. (14) are displayed at various n values. From this figure we notice a satisfactory fit of the equation to the experimental data at $n = 15 \pm 5$, which gives a value of 30—40° for the flow half-width.

The proposed method for determining mean velocities and spatial distributions of molecular flows has been successfully verified by experiment which showed its applicability to low intensity molecular beams and desorption flows.

The extreme simplicity of the method, in particular the use of the same vacuum gauge for all of the measurements, and also the fact that relative concentrations are used in Eqs. (6) and (14), makes it possible to avoid significant systematic errors.

An important characteristic of the method is that the ionization gauge measures the total concentration of various particles. This should be taken into account in cases when simultaneous desorption of different substances takes place. To correct for this possibility it is necessary to carry out simultaneous measurements of mass spectra of desorbing particles and to try to use the latter for separating individual thermal desorption peaks from the ionization gauge signal. In our opinion this is the main limitation on the use of the proposed method for measuring the velocities of molecules desorbing from a surface.

This method may also be used for characterizing molecular beams.

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