

IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS*

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A. EXPERIMENTAL INVESTIGATION OF THE VELOCITY DISTRIBUTION OF HYDROGEN MOLECULES DESORBED FROM METAL SURFACES

1. Introduction

An essential step in many chemical reactions occurring at gas-solid interfaces is the associative desorption reaction, $A(\text{ad}) + B(\text{ad}) \rightarrow AB(\text{g})$, where two atoms adsorbed on the surface combine to form a molecule that desorbs to the gas phase. This reaction has been studied in several laboratories¹ by a variety of techniques because of its importance to heterogeneous catalysis, high-temperature oxidation, chemical vapor deposition, and the degassing of metals. Existing data are not sufficiently detailed, however, to provide rigorous tests of theoretical models of the kinetics and energetics of associative desorption. We believe that more rigorous tests will be possible with the unique data obtained by the experimental technique described herein.

It has been generally assumed that the velocity distribution of molecules desorbed from a solid surface corresponds to that of molecules effusing through an orifice from an equilibrium gas phase at a temperature equal to that of the solid. This assumption leads to the expectations: (i) that the spatial distribution of the desorbed molecules will be directly proportional to $\cos \theta$, where θ is the angle of inspection measured from the surface normal; (ii) that the speed distribution at all values of θ will be of the Maxwellian form with temperature equal to that of the solid. Recent results obtained independently in two different laboratories^{2,3} show, however, that the spatial distribution of hydrogen desorbed from nickel deviates markedly from the $\cos \theta$ relation. More specifically, these data indicate that the fraction of the molecules desorbing in the general direction of the surface normal is much greater than that corresponding to the effusion of an equilibrium gas through an orifice. Van Willigen² has reported similar data for the

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(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

desorption of H_2 from palladium and iron, and he interprets these data by means of the simple model.

We propose to measure the speed distribution, as well as the spatial distribution, of hydrogen desorbed from different metals, since the form of the speed distribution is expected to be more sensitive to the desorption mechanism than is the spatial distribution. Also, a more complete description of the state of the desorbed gas is obtained by measuring both distributions, and this will enable us to perform a more stringent test of theoretical models. Although the proposed experiments are limited to H_2 and D_2 , the general technique could be modified so that it applies to any chemical species.

2. Experimental Apparatus

The main components of the apparatus are shown schematically in Fig. IV-1. The vacuum chamber consists in two crosses made from 15-cm ID stainless-steel pipe. Each cross is evacuated by a mercury diffusion pump (Edwards 6M3A) equipped with two

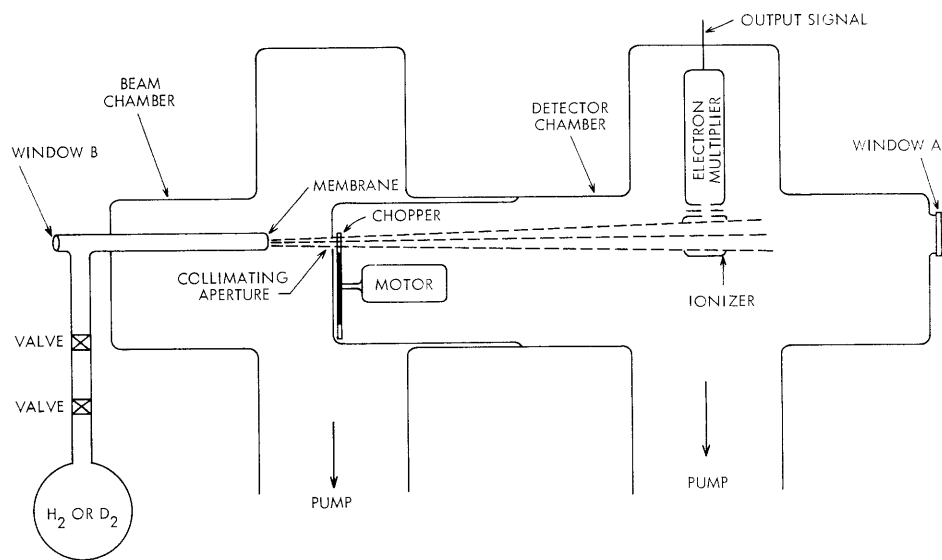


Fig. IV-1. Apparatus for measuring the speed distribution of hydrogen desorbed from metals.

liquid-nitrogen cooled traps in series plus a thermoelectrically cooled baffle. Copper gaskets are employed so that the chamber may be baked during initial evacuation. At present, the ultimate pressure of the system is $\sim 8 \times 10^{-10}$ Torr, and we expect that even lower pressures will be attained in the future.

In the actual experiment a thin metal membrane (Ni, Pd, or Fe) will be welded to the end of the tube shown in Fig. IV-1, and the temperature of this membrane will be controlled by electron-bombardment heating. By filling the tube with H_2 gas, H atoms

(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

will adsorb in the metal and diffuse to the vacuum face of the membrane where they associate and desorb as molecules. This scheme for supplying hydrogen to the test surface has been used successfully by van Willigen,² and it has the advantage of minimizing the pressure of H₂ in the vacuum chamber. (If one wished to study gases that do not permeate readily through metals, then the gas could be supplied to the surface by means of a molecular beam³ rather than by permeation.)

The system is designed to ensure that the pressure is sufficiently low that the velocity distribution of the desorbed molecules will not be altered by gas-phase collisions. A fraction of the desorbed molecules will pass through a collimating aperture (0.1 × 1.0 cm) in the partition between the "beam chamber" and the "detector chamber" (see Fig. IV-1) and then be gated (modulated) by a slotted disc driven by a motor. (Globe #18A103 motor with Barden Bartemp bearing for vacuum service; the motor casing has been provided with water cooling to prevent overheating during operation or bakeout.) These molecules travel 37 cm to a detector where a fraction of the molecules are ionized by electron impact. The ions are accelerated by electrostatic fields into an electron multiplier (EMI 9603/2) to amplify the signal by ~10⁵. As indicated in the block diagram of Fig. IV-2, the output signal from the multiplier is amplified further and then

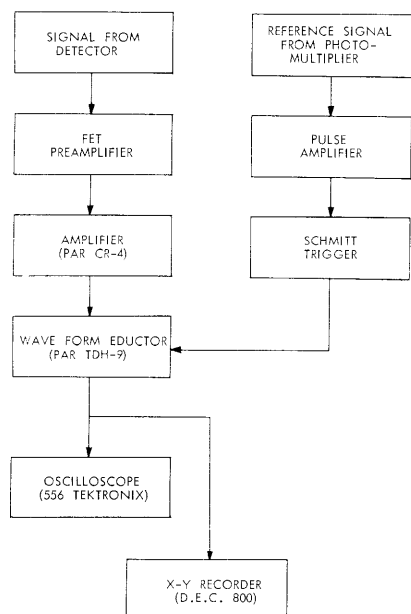


Fig. IV-2. Detector electronics.

fed to a multichannel signal-averaging instrument (waveform eductor, PAR TDH-9) which enhances the signal-to-noise ratio. The waveform eductor is triggered by a reference signal derived from the slotted disc that modulates the beam. (We shall return to this point.) The output signal from the waveform eductor is viewed on an oscilloscope and permanent recordings are made by means of an X-Y recorder.

(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

3. Performance Test

We are now performing a preliminary experiment in which the membrane is simulated by a small slit (0.05×0.5 cm) cut in the end of the tube shown in Fig. IV-1. This provides a simple means for producing a molecular beam of H₂ or D₂ having nearly the same intensity and speed distribution as what we expect to have in the case of desorption from a membrane. Our principal objectives are to determine whether the signal amplitude is sufficiently large relative to the noise and whether the signal waveform is not seriously distorted by the detector and amplifier characteristics.

If the gas pressure in the tube is sufficiently low that the mean-free path is at least an order of magnitude greater than the slit width (0.05 cm), then the molecules effusing through the slit will have a Maxwellian speed distribution which, when expressed in the time-of-flight coordinates appropriate for the present apparatus, is⁴

$$n_s(t) = \frac{F}{aA_d} \left\{ \frac{\tau}{t} \exp(-\tau^2/t^2) - \frac{\tau}{t-t_{co}} \exp\left[-\left(\frac{\tau}{t-t_{co}}\right)^2\right] + \frac{1}{2} \sqrt{\pi} \left[\operatorname{erf}\left(\frac{\tau}{t-t_{co}}\right) - \operatorname{erf}(\tau/t) \right] \right\}, \quad (1)$$

where $n_s(t)$ is the density (molecules/cm³) of the molecular beam in the detector ionizer at time t measured from the instant at which the chopper (the slotted disc) allows molecules to be transmitted, F is the flux of molecules into the ionizer for the case of a DC (unmodulated) beam, A_d is the cross-sectional area of the ionizer (4 cm²), t_{co} is the time that the chopper remains "open," and τ is the characteristic flight time

$$\tau = L/a, \quad (2)$$

where L is the distance from chopper to ionizer (37 cm), and

$$a = (2kT/m)^{1/2} \quad (3)$$

with k being Boltzmann's constant, T the gas temperature, and m the molecular mass. Since the number of ions produced in the ionizer is directly proportional to $n_s(t)$, the detector output signal, $S(t)$, is

$$S(t) = \Lambda_n n_s(t), \quad (4)$$

where Λ_n is the detector sensitivity. It is convenient to represent n_s by an equivalent pressure, p_s , defined by

$$p_s = n_s k T_c = 3.1 \times 10^{-17} n_s \text{ (Torr)}, \quad (5)$$

(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

where T_c is the temperature of the chamber walls ($\sim 300^\circ\text{K}$). In this case, Eq. 4 becomes

$$S(t) = \Lambda_p p_s(t), \quad (6)$$

where $\Lambda_p = \Lambda_n/kT_c$. We have experimentally determined Λ_p to be 45 A/Torr for H_2 with a 0.2 mA electron current, a 50 V electron energy, and a voltage of 2500 V applied to the electron multiplier.

Based on the dimensions and pumping speed of the apparatus, we estimate that P_s , the value of p_s for the case of a DC (unmodulated) beam, is given by

$$P_s = 1.17 \times 10^{-6} p_o, \quad (7)$$

where p_o is the H_2 pressure in the molecular beam source (that is, the pressure upstream of the slit). Similarly, we estimate the background pressure in the detector chamber to be

$$p_c = 3.3 \times 10^{-5} p_o. \quad (8)$$

Therefore,

$$P_s/p_c = 3.5 \times 10^{-2} \quad (9)$$

and, since $p_s(t) \leq P_s$, it follows that

$$p_s(t)/p_c \leq 3.5 \times 10^{-2}. \quad (10)$$

That is, less than 3.5% of the ions produced in the ionizer are due to the modulated beam, so it is necessary to: (a) place a blocking capacitor after the electron multiplier to reject the DC component of the total signal, and (b) use a waveform eductor to average out AC components that are due to p_c , mechanical vibrations, and other sources of noise.

In the present test the reference signal is obtained by placing a photomultiplier tube at window A and a light source at window B (see Fig. IV-1). The beam of light passing through the slit and collimating aperture is modulated by the chopper in the same manner as the molecular beam, and the resulting output signal of the photomultiplier tube serves to trigger the waveform eductor periodically at the instant that a slot in the chopper rotates to the position where light is transmitted. (When the slit is replaced by a membrane, the reference signal will be obtained either by placing a magnetic transducer next to the chopper, as has proved to be satisfactory in another apparatus,⁵ or by using the thermal radiation from the heated membrane as the light source for stimulating the present photomultiplier tube.)

(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

The experimental curve shown in Fig. IV-3 was measured under the following conditions: $p_o \approx 3.5 \times 10^{-3}$ Torr, $T_o \approx 300^\circ\text{K}$, $t_{co} = 5 \times 10^{-5}$ sec, $p_c = 1.2 \times 10^{-7}$ Torr, and the background pressure in the beam chamber = 9×10^{-6} Torr. According to Eq. 7,

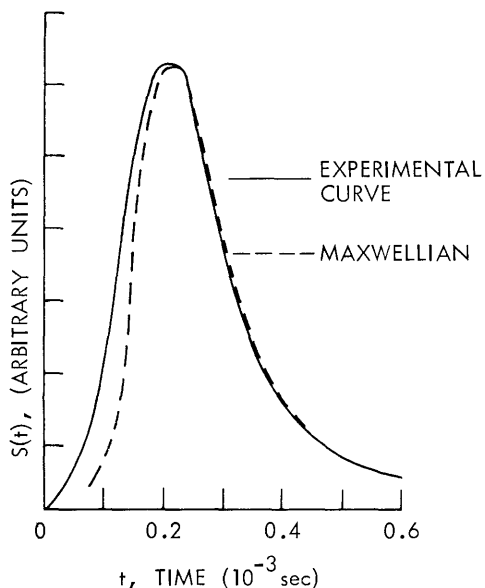


Fig. IV-3. Time-of-flight data for an H_2 molecular beam.

$P_s \approx 4 \times 10^{-9}$ Torr. The dashed curve labelled "Maxwellian" was computed from Eq. 1 for $T = 300^\circ\text{K}$, and its amplitude has been normalized to fit the maximum of the experimental curve. The agreement is good for $t \gg 2 \times 10^{-4}$ sec, and we believe that the agreement for $t < 2 \times 10^{-4}$ sec will be improved when we install a preamplifier adjacent to the electron multiplier output to reduce distortion caused by cable capacitance. (The FET preamplifier shown in Fig. IV-2 was not employed in the present test.)

4. Proposed Program

The rate of permeation of hydrogen through a nickel membrane of thickness ℓ (mm) and temperature T ($^\circ\text{K}$) given by⁶

$$R = \frac{3.75 \times 10^{17}}{\ell} \left(p_1^{1/2} - p_2^{1/2} \right) \exp(-6970/T) \frac{\text{molecules}}{\text{cm}^2 \text{ sec}}, \quad (11)$$

where p_1 and p_2 are the hydrogen pressures (Torr) on the two sides of the membrane. Therefore, we would expect the permeation rate to be $\sim 1.5 \times 10^{17} \text{ cm}^{-2} \text{ sec}^{-1}$ for the following conditions: $\ell = 0.5$ mm, $p_1 = 760$ Torr, $p_2 \leq 1 \times 10^{-6}$ Torr, $T = 1150^\circ\text{C}$.

(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

Based on the dimensions of the present apparatus and an assumed membrane surface area of $\sim 0.1 \text{ cm}^2$, we estimate that for the above-mentioned conditions the density of desorbed hydrogen in the detector ionizer will correspond to an equivalent pressure, P_s , of $\sim 3 \times 10^{-10}$ Torr. Since this value of P_s is $\sim 1/13$ the value associated with the preliminary experiment described in the preceding section, we are confident that the proposed measurements can be performed after slight improvements in the detector electronics.

We propose to measure the speed distributions of H_2 and D_2 desorbed from both polycrystalline and monocrystalline surfaces of one or more metals (for example, Ni, Fe, Pd). Spatial distribution measurements will be performed either by (a) modifying the apparatus so that the membrane surface may be tilted at different angles relative to the center line of the detector, or (b) constructing a simple apparatus similar to that used by van Willigan.² We plan to determine the effects of surface impurities on the speed and spatial distributions by intentionally contaminating the membrane with oxygen and/or carbon.

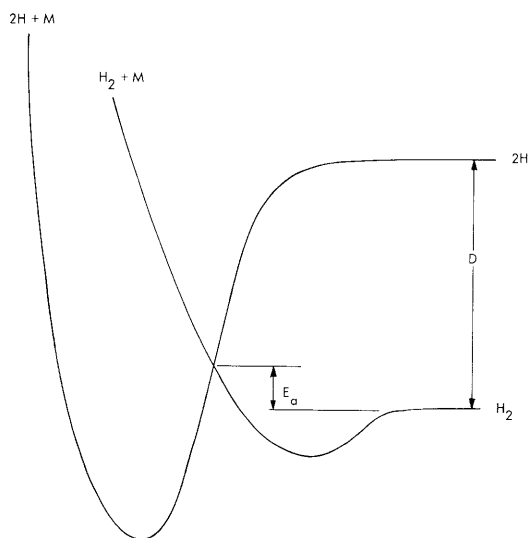


Fig. IV-4.

Schematic representation of the gas-solid interaction potentials for the case of activated dissociative adsorption of H_2 on the surface of solid M. E_a is the activation energy separating the molecular ($\text{H}_2 + \text{M}$) and atomic ($2\text{H} + \text{M}$) adsorption states, and D is the dissociative energy of H_2 .

As an illustration of how the experimental results may be used to test models of associative desorption, we consider briefly the model of activated adsorption suggested by Lennard-Jones,⁷ in 1932. According to this model, the impinging molecules must surmount an energy barrier E_a if they are to dissociate and adsorb as atoms on the metal surface M (see Fig. IV-4.) Therefore, an impinging molecule having speed v and angle of incidence θ must satisfy the condition

$$\frac{1}{2} m(v \cos \theta)^2 \geq E_a \quad (12)$$

(IV. PHYSICAL ELECTRONICS AND SURFACE PHYSICS)

in order to reach the atomic adsorption state. Arguments based on the principle of detailed balancing lead to the conclusion that the condition represented by Eq. 12 also applies to the desorbed molecules if local equilibrium exists in the adsorbate phase. (These arguments have been presented in detail by Batty and Stickney.⁸) That is, the speed distribution function of the desorbed molecules would be zero for $v < v^*$ and it would have the Maxwellian form for $v \geq v^*$, where the critical speed, v^* , is equal to $(2E_a/m)^{1/2} \sec \theta$ according to Eq. 12. Although this model is extremely crude and ignores the apparent evidence against activated adsorption, van Willigen² has demonstrated that it provides a possible explanation of his experimental data on the spatial distributions of H_2 desorbed from different metals. It would be of interest to see if the results of the proposed speed distribution measurements show a deficiency of slow molecules as predicted by the model.

A. E. Dabiri, R. E. Stickney

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