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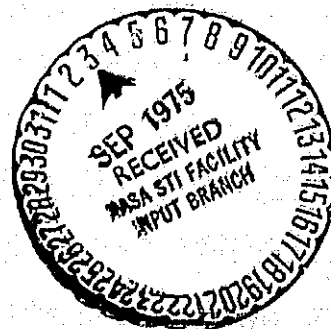
**CHEMISORPTION KINETICS OF HYDROGEN ON
EVAPORATED IRON FILMS**

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Abstract

Measurements have been made of the isothermal adsorption-desorption kinetics for H₂ chemisorbed onto Fe films. The chemisorption process is observed to proceed via a precursor state of adsorbed molecular hydrogen similar to the H₂-Ni system. Reported here are the first measurements of the activation energy for desorption ($\epsilon_d = 5.3 \times 10^{-20}$ J/molecule) and estimates of the values of the fast kinetic rates between the precursor and chemisorbed states. Adsorption into the precursor state does not appear to be activated, but the process connecting the precursor state with the chemisorbed state will, under certain circumstances, be a rate limiting step for adsorption. The effects of contamination of the surface are evidenced in the measurements.

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From measurements conducted with adsorbate temperatures below 100°K, Porter and Tompkins [1] interpreted the chemisorption of H₂ onto Fe surfaces as occurring via an activated process. In studies of the angular distribution of H₂ desorbed from Fe surfaces at 1000°K, Bradley and Stickney [2] concluded that activated adsorption is associated with contamination of the surface and that a clean surface shows little indication of activated adsorption. Reported here are the results of measurements of the isothermal adsorption-desorption kinetics for H₂ chemisorbed onto thin (20 to 50 Å) polycrystalline Fe films at temperatures near 300°K. This work was undertaken to expand our understanding of the general kinetic processes involved and to clarify the previous work, since the chemisorption kinetics of the H₂-Fe system are postulated to be relevant to such phenomena as the gaseous embrittlement of steels [3].

The results of this investigation indicate that chemisorption in the H₂-Fe system occurs via a precursor state of molecularly adsorbed H₂ similar to the process previously found for the H₂-Ni system [4]. Reported here are the first measurements of the activation energy for desorption from the precursor state and estimates of the values of the absolute rate constants connecting the precursor and chemisorbed state at ~300°K. Adsorption into the precursor state does not appear to be an activated process. However, the intermediate step, going from the precursor state to the chemisorbed state, was observed to be rate limiting under certain circumstances. This observation suggests that the results of Porter and Tompkins [1] and of Bradley and Stickney [2] are not necessarily in disagreement, since their measurements were conducted under different conditions. The influence of contamination of the surface from unknown impurities in the gas phase is evidenced in this work as affecting (1) the number of available adsorption sites, and (2) modifying the prefactor for the absolute desorption rate constant for the precursor state.

The general experimental technique and procedures have been reported elsewhere [4]; however, for continuity pertinent points will be mentioned briefly while emphasizing specific procedures relevant to this particular work. The kinetic measurements were made by observing the change in the resistance of thin Fe films produced by the chemisorption process. At low coverages, the change in the film's resistance, δR , is directly proportional to the concentration of chemisorbed adatoms [5]. Isotherms, obtained from the resistance changes measured in this study, are consistent with the dissociation of molecular hydrogen into an atomic species in the chemisorbed state. Assuming that the resistance change responds instantaneously with the chemisorption process, then the resistance change reflects directly the temporal behavior of the average surface concentration of chemisorbed adatoms during the various kinetic processes under study [6].

Iron films were produced by sublimation onto glass substrates from high purity (99.998%) Fe wire; typical film dimensions are $25 \times 3 \text{ mm}^2$. Some films were evaporated onto substrates heated to 200°C and subsequently annealed at 250°C for one hour to stabilize the resistance for measurements at various temperatures below the annealing temperature. Other films were evaporated onto substrates at room temperature (21°C) with no anneal. The resistance of these latter films was sufficiently stable at room temperature that they could be utilized shortly after evaporation for room temperature adsorption studies on fresh surfaces. With regard to the kinetic measurements, no significant difference was noted between films prepared by the two different procedures. Values of film thickness, d , presented here are estimates based on the value of the film's room temperature resistance with corrections for finite size effects, assuming entirely diffuse scattering of the electrons at the film surface.

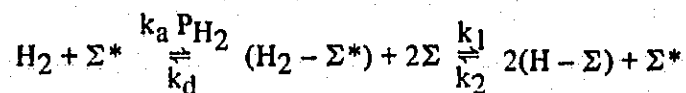
The base pressure in the vacuum system after bakeout was typically in the range between $6.7 \times 10^{-8} \text{ Nm}^{-2}$ and $1.3 \times 10^{-7} \text{ Nm}^{-2}$. During the period of measurement, the total pressure of residual gases other than hydrogen is estimated to have been below $1.3 \times 10^{-8} \text{ Nm}^{-2}$, based on previous experience with the apparatus. The total pressure rose to a typical maximum of $\sim 5 \times 10^{-7} \text{ Nm}^{-2}$ during the initial part of the evaporation process, dropping significantly during the evaporation as the Fe-film deposited on the chamber walls gettered residual gases.

The main experimental data consist of the following: (1) measurements of the isothermal kinetics of adsorption from the gas phase to the chemisorbed state, and (2) measurements of the isothermal kinetics of desorption from the chemisorbed state to the gas phase. The adsorption kinetics were obtained by observing δR as equilibrium was approached following an increase in P_{H_2} , the hydrogen gas phase pressure, from a low value where adsorption was negligible ($\sim 7 \times 10^{-7} \text{ Nm}^{-2}$) to a higher value where adsorption was enhanced. A characteristic adsorption curve is presented in fig. 1. Analysis of this type of adsorption data for a variety of hydrogen pressures shows an exponential approach to equilibrium with a characteristic rate constant, τ_a^{-1} . τ_a^{-1} is observed to be linearly proportional to P_{H_2} at low pressures and extrapolates to nonzero values at $P_{\text{H}_2} = 0$ [7]. The value of the zero pressure intercept was found to be in reasonable numerical agreement with the value obtained for the isothermal rate of desorption, when measured under comparable circumstances. The relationship between the rate, τ_a^{-1} , and P_{H_2} deviates from linearity at higher values of P_{H_2} and shows signs of saturating; an example of this is presented later.

The initial sticking coefficient, s_0 , for adsorption was estimated for low pressures (linear region) by dividing the measured value of τ_a^{-1} by the flux of molecules per adsorption site. In estimating the flux of molecules per adsorption site, the value of 1.2×10^{15} sites/cm² was employed [8]. The variation in s_0 measured as a function of film age at 294°K is shown in fig. 2. Attempts to estimate s_0 at higher temperatures for freshly evaporated films were not successful as significant measurement problems arise from the instability of the film's resistance due to thermally activated annealing. A few measurements on older surfaces (films greater than 10 hours old) over the temperature range from 20°C to 60°C did not reveal any significant variation in s_0 with temperature when compared with anticipated experimental fluctuations.

Data on the desorption kinetics were obtained by observing the decay of δR after rapidly evacuating the gas phase H_2 to a pressure where readsorption was negligible. Analysis of the data is consistent with an exponential decay for δR with a temperature dependent decay rate denoted by τ_d^{-1} . Within experimental fluctuations, τ_d^{-1} , as well as the functional form of the decay, is independent of both film thickness and the initial surface concentration of chemisorbed adatoms, Θ , for $\Theta \leq 0.4$ (Θ was estimated from the resistance isotherm [4]). Variations of τ_d^{-1} with temperature are presented in fig. 3 for relatively "new" films (approximately 2 to 6 hours old) with a few measurements on "older" films to indicate the effect of aging.

The general features of the data, namely, 1st-order adsorption-desorption kinetics (exponential behavior) for a dissociative chemisorption process and a small activation energy for desorption compared to the heat of adsorption [9], suggest that chemisorption is occurring via a precursor state as demonstrated for the H_2 -Ni system [4]. In this model, the chemisorption of hydrogen is schematically represented by the following reaction:



Here, $k_a P_{H_2}$ and k_d are, respectively, the absolute rate of adsorption and desorption between the gas phase H_2 and the precursor state of molecularly adsorbed hydrogen ($H_2 - \Sigma^*$); k_1 and k_2 are absolute rates connecting the precursor state with the chemisorbed state of dissociated adsorbed hydrogen ($H - \Sigma$); and Σ^* and Σ are physically distinct adsorption sites for the precursor and chemisorbed state. The solutions to the coupled differential equations which describe the kinetics of this model have been shown to be [10] exponential in nature (1st order) if the fractional coverage in the chemisorbed state, Θ , and the physisorbed state, Θ^* , is small compared with unity so that

it is possible to linearize the equations by neglecting quadratic and cross terms. Assuming further that there is a rate limiting step between the precursor state and the gas phase, i.e., $k_a P_{H_2}$, $k_d \ll k_1, k_2$, then the slow kinetic rate is given by

$$\tau^{-1} = k_a P_{H_2} + k_d \quad (1)$$

where a small systematic correction has been neglected [4]. Since $P_{H_2} \approx 0$ when measuring the desorption kinetics, the measured net desorption rate τ_d^{-1} is interpreted as being equal to k_d , the rate for desorption from the precursor state to the gas phase. The measured adsorption rate τ_a^{-1} is interpreted as being equal to τ^{-1} . The measured form of τ_a^{-1} at low pressures is in agreement with this relationship.

The initial sticking coefficient, s_0 , presented in fig. 2 represents the sticking coefficient associated with the precursor state. The nearly unity value of s_0 for new films may be fortuitous and could be in error by at most a factor of two; the correct value depends critically upon the actual average number of adsorption sites per unit area. The fact that s_0 is so large for new films strongly suggests that adsorption into the precursor state is not activated, since an activation energy of any significance would greatly reduce s_0 (at 300°K an activation energy of only 7×10^{-21} J/molecule would reduce s_0 from unity to a value of ~ 0.2).

Assuming the variation of s_0 with film age to be due to contamination of the surface by adsorption to an equilibrium coverage of residual impurities, the variation of s_0 with time was fit to an exponential decay as shown by the solid line in fig. 2. From the decay constant the estimated pressure of the impurities (based on O_2) is approximately $2.7 \times 10^{-8} \text{ Nm}^{-2}$. This value is somewhat higher than anticipated, but is not unreasonable considering the typical residual base pressures observed during the course of these measurements. Since there was no obvious temperature dependence associated with s_0 for older films, we conclude that the reduction of s_0 represents a loss of available chemisorption sites rather than the development of an activation barrier.

Deviations from linearity in τ_a^{-1} as a function of P_{H_2} would be expected as $k_a P_{H_2}$ is increased to the point where it is large compared with k_1 ; k_1 would then become the rate limiting step for adsorption. This behavior can be observed in fig. 4 where, for an aged film with s_0 essentially constant, the difference $(\tau_a^{-1} - k_d)$ is plotted against P_{H_2} . At high incident fluxes (large $k_a P_{H_2}$), the precursor state is rapidly occupied, while the chemisorbed state is, comparatively, more slowly occupied. Assuming that the backflow from the chemisorbed state to the precursor can be neglected (the chemisorbed state is initially unoccupied) and that steady state conditions

exist with regard to the precursor state, then

$$\tau_a^{-1} \approx k_1 \left[\frac{k_a P_{H_2}}{k_1 + k_d + k_a P_{H_2}} \right] + k_d$$

This approximation for the net adsorption rate for the coupled system reduces to the limit expressed by eq (1) when the rate limiting step is between the gas phase and the precursor state. The solid line in fig. 4 is a least means square fit of the above expression to the data where k_a is required to be consistent with the low pressure data for τ_a^{-1} . The value for k_1 which gives the best fit is $k_1 \approx 0.15 \text{ sec}^{-1}$ at 294°K . From the resistance isotherm, the quantity k_1/k_2 can be evaluated [4] and, in this instance, was found to be approximately 0.034 at 294°K . Based on the value for k_1 and the ratio k_1/k_2 , k_2 is computed to be $\sim 4.4 \text{ sec}^{-1}$ at 294°K . Although there are no other estimates for k_2 , the value obtained here is not unreasonable when compared with similar values obtained for the $\text{H}_2\text{-Ni}$ system where fluctuation spectroscopy was employed to observe the fast process [11]. The values for k_1 and k_2 should only be considered as representative since the presence of nearby chemisorbed impurities may alter these rates.

The activation energy for desorption from the precursor state, ϵ_d , was obtained from the data for τ_d^{-1} presented in fig. 3. The low value of $\epsilon_d = 5.3 \times 10^{-20} \text{ J/molecule}$ suggests that the precursor state corresponds to a physisorbed state of molecular hydrogen. For comparison, the value of ϵ_d for the $\text{H}_2\text{-Fe}$ system is only slightly larger than for the $\text{H}_2\text{-Ni}$ system ($\epsilon_d = 4 \times 10^{-20} \text{ J/molecule}$), but the prefactor for k_d ($\approx \tau_d^{-1}$) is larger for the $\text{H}_2\text{-Fe}$ system by more than two orders of magnitude [4].

As will be noted in fig. 3, the principal effect of the contaminated surface on k_d is to decrease the magnitude of the prefactor without significantly modifying the activation energy. The chemisorbed impurities may modify the shape of the potential for the precursor state without significantly modifying the binding energy. This may not be unreasonable, assuming the precursor state to be that of an essentially physisorbed molecule, where the dominant force giving rise to the binding energy is an electrostatic interaction between the adsorbed molecule and the adsorbate.

In conclusion, we find that the chemisorption process for the $\text{H}_2\text{-Fe}$ system proceeds via a precursor state of molecularly adsorbed hydrogen; the low activation energy for desorption from this state suggests that it corresponds to a physisorbed state. Adsorption into the precursor state is not activated, whereas the step from the precursor state to the chemisorbed state may be activated and can, under certain circumstances, be the rate limiting adsorption step. Additional work will

reveal more about the kinetics between the precursor and chemisorbed states; in particular, the determination of the activation energies for k_1 and k_2 should be useful in establishing potential energy curves for the states involved.

References and Footnotes

- [1] A. S. Porter and F. C. Tompkins, Proc. Roy. Soc. (London) A217 (1953) 529.
- [2] T. L. Bradley and R. E. Stickney, Surface Sci. 38 (1973) 313.
- [3] Howard G. Nelson, Dell P. Williams, and Alan S. Tetelman, Met. Trans. 2 (1971) 953; and Dell P. Williams and Howard G. Nelson, Met. Trans. 1 (1970) 63.
- [4] M. R. Shanabarger, Solid State Commun. 14 (1974) 1015.
- [5] P. Zweitering, H. L. T. Koks, and C. Van Heerden, J. Phys. Chem. Solids 11 (1959) 18.
- [6] This is a reasonable assumption, since the chemisorption rates are quite small compared with any relevant electronic relaxation times associated with the resistance process in the film.
- [7] This behavior is similar to that shown in fig. 2 of ref. 4.
- [8] This value is a simple average of the number of sites per unit area for the three principal directions, (100), (110), and (111).
- [9] A. S. Porter and F. C. Tompkins, Proc. Roy. Soc. (London) A217 (1953) 544.
- [10] With regard to the net desorption process, a more complete solution to the coupled equations describing the model can be found in M. R. Shanabarger, Surface Sci. 44 (1974) 297.
- [11] M. R. Shanabarger, Bull. Am. Phys. Soc. 18 (1973) 1589.

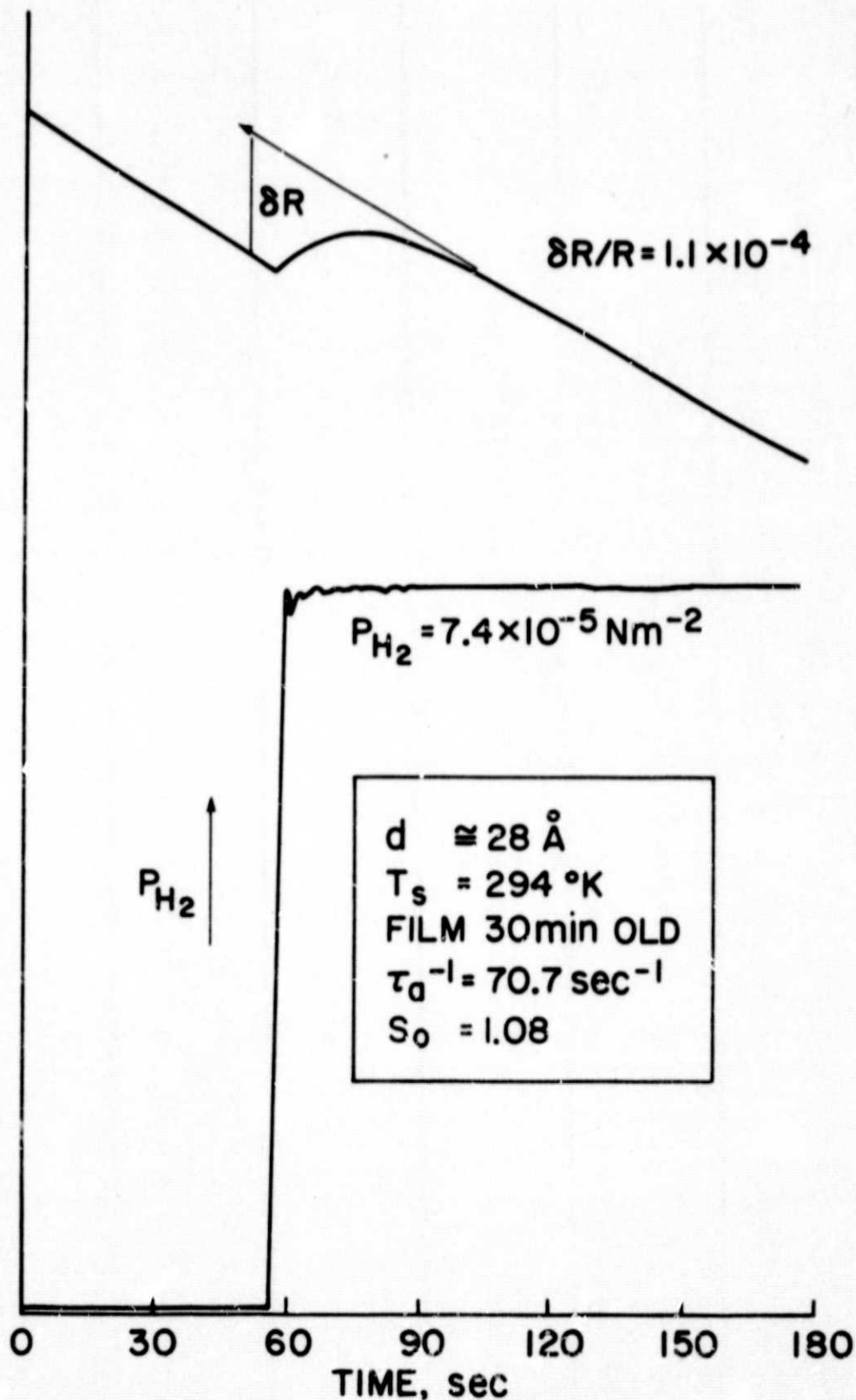


Fig. 1. Tracing of a typical recording of the change in resistance, δR , of a thin Fe film due to the dissociative chemisorption of H_2 . The data were taken on a two-channel recorder with the hydrogen pressure, P_{H_2} , presented simultaneously with the resistance change. The baseline drift is due to self-annealing of the film. The film substrate temperature is indicated as T_s and d is the estimated film thickness.

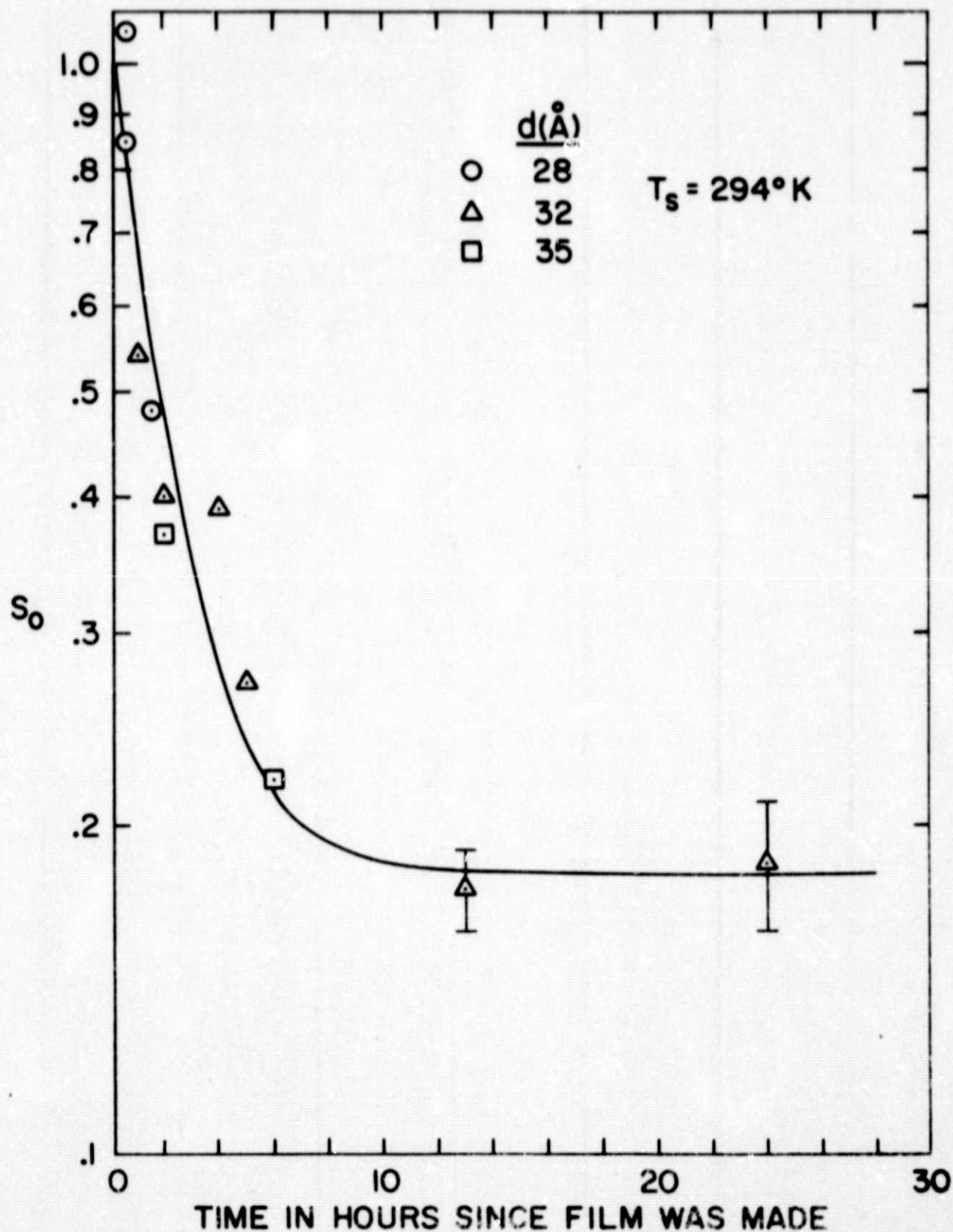


Fig. 2. The variation with film age of the initial sticking coefficient, s_0 , for a series of films measured at room temperature ($T_s = 294^\circ\text{K}$). The values for s_0 were calculated from the measured values of the adsorption rate τ_a^{-1} and the gas phase hydrogen pressure, PH_2 . The solid curve represents an empirical fit to the data of the form: $s_0 = 0.18 + 0.82 e^{-\alpha t}$, where $\alpha = 0.533 \text{ hr}^{-1}$.

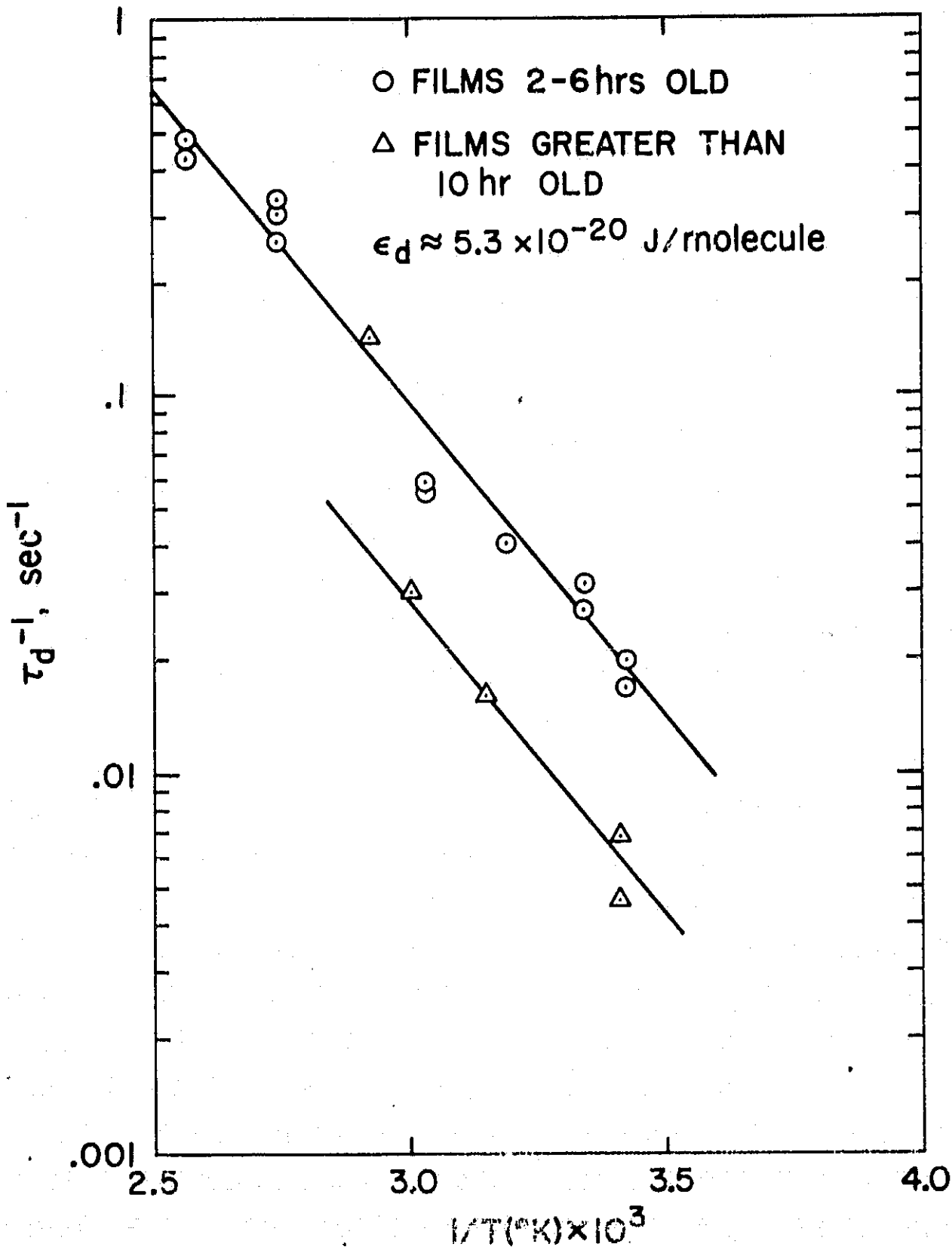


Fig. 3. Arrhenius plot of the desorption rate, τ_d^{-1} , as a function of reciprocal temperature for relatively new films (uncontaminated surface) and older film (contaminated surface). The activation energy for desorption, $\epsilon_d = 5.3 \times 10^{-20}$ J/molecule, was obtained from the slope of the indicated straight line. Within small systematic errors, τ_d^{-1} equals k_d , the absolute rate of desorption from the precursor state. A reasonable fit to the data is described by

$$k_d \approx (9.42 \times 10^3) e^{-\epsilon_d/k_B T} \text{ (sec}^{-1}\text{)}.$$

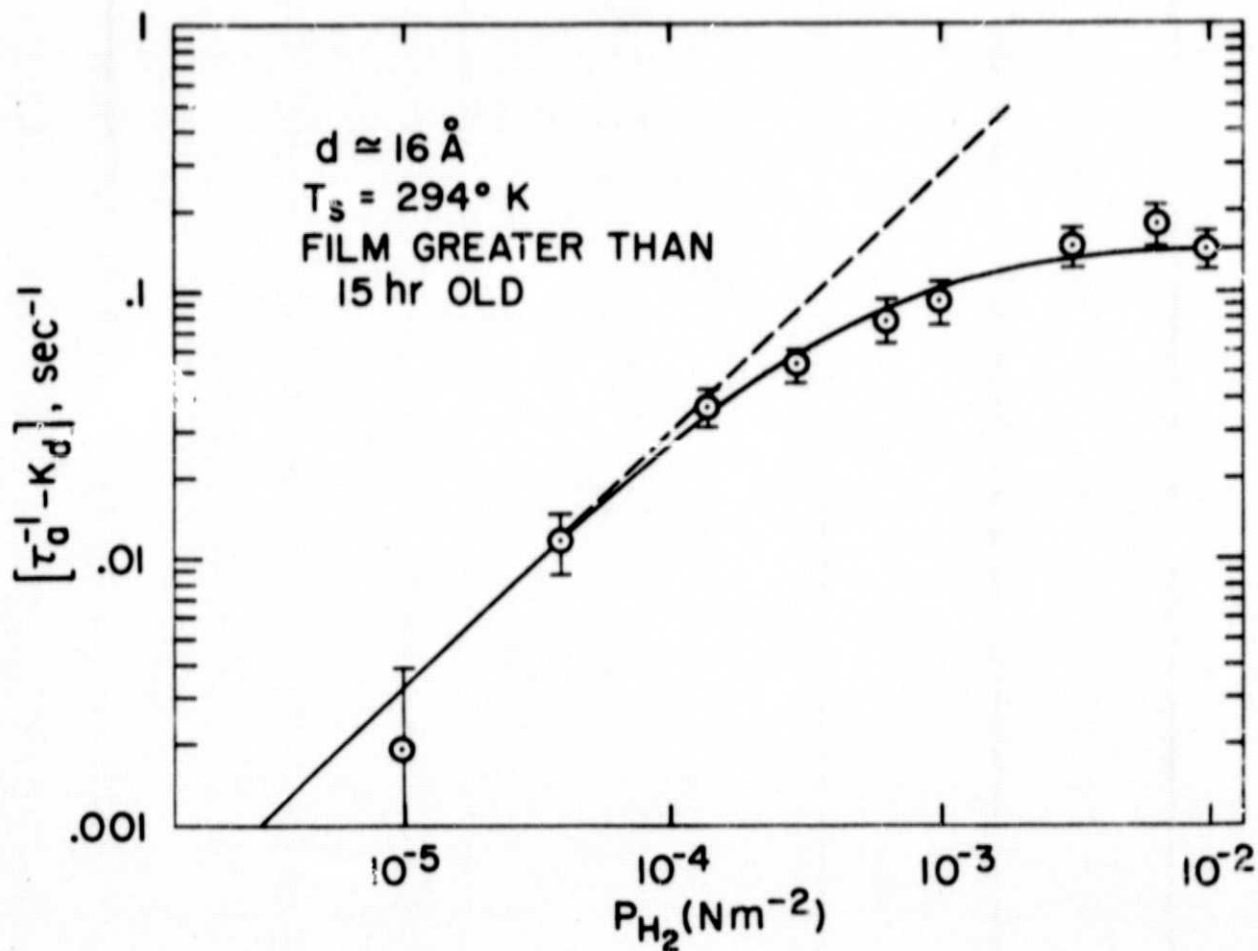


Fig. 4. Plot of the quantity $[\tau_a^{-1} - k_d]$ as a function of hydrogen gas phase pressure, P_{H_2} , demonstrating the crossover in the adsorption rate limiting step from between the gas phase and the precursor state to between the precursor and chemisorbed state. The dashed line is based on the predicted low P_{H_2} behavior, whereas the solid line is the fit of an approximate theoretical result spanning the entire pressure range. For this fit, the only adjustable parameter is the value of k_1 , the rate to go from the physisorbed state to the chemisorbed state; a least means square fit gives $k_1 \approx 0.15 \text{ sec}^{-1}$ at 294° K .