

NASA CR-166,327

NASA CONTRACTOR REPORT 166327

NASA-CR-166327
19820017492

An Investigation of the Kinetics
of Hydrogen Chemisorption on Iron
Metal Surfaces

Mickey R. Shanabarger
University of California - Santa Barbara

FOR REFERENCE

NOT TO BE TAKEN FROM THIS ROOM

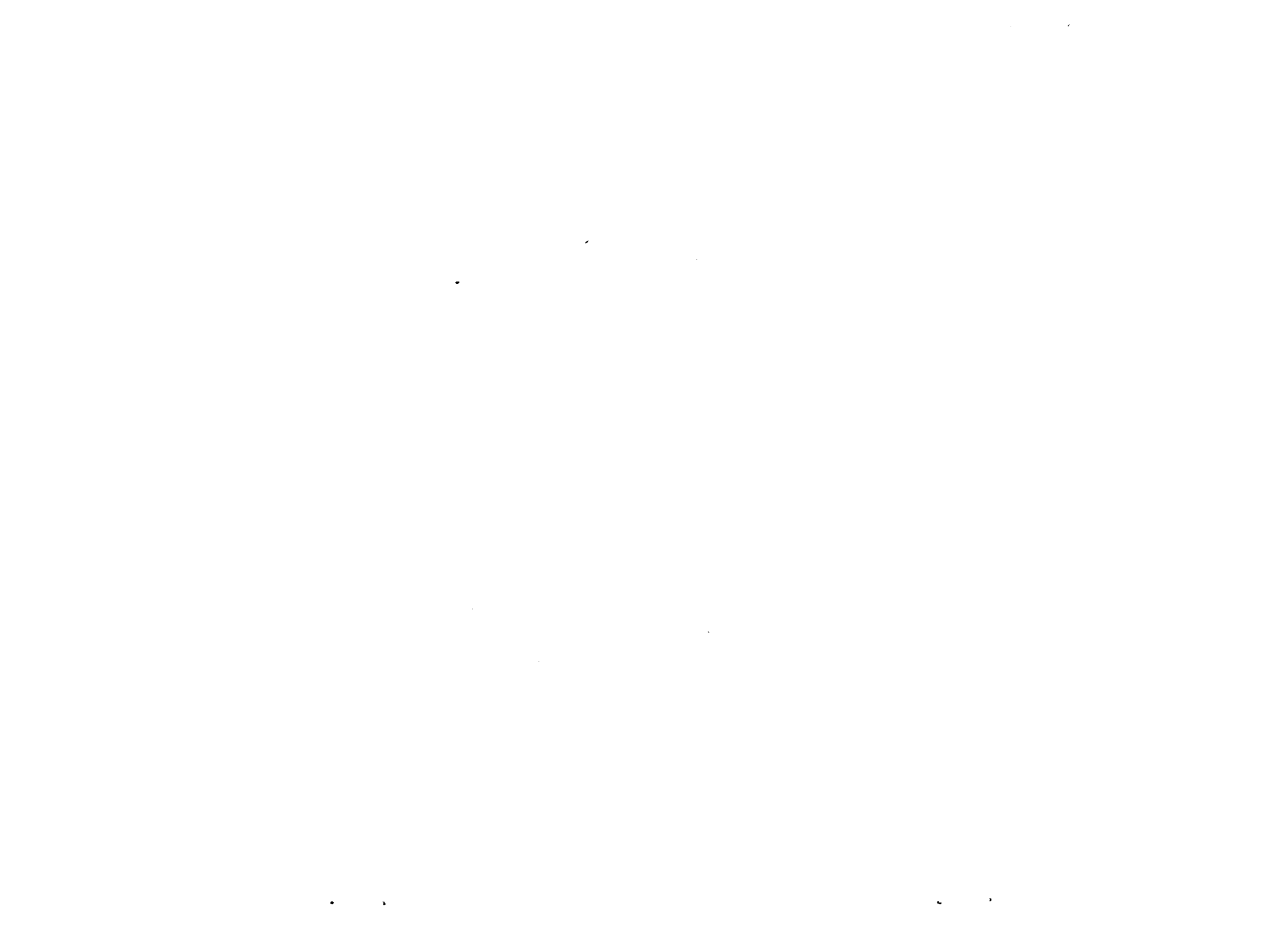
LIBRARY COPY

JUN 4 1982

LANGLEY RESEARCH CENTER
LIBRARY, NASA
HAMPTON, VIRGINIA

CONTRACT NSG-2222
April 1982





NASA CONTRACTOR REPORT 166327

An Investigation of the Kinetics
of Hydrogen Chemisorption on Iron
Metal Surfaces

Mickey R. Shanabarger
Quantum Institute
University of California - Santa Barbara
Santa Barbara, California 93106

Prepared for
Ames Research Center
under NASA Contract NSG-2222

NASA

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

NSG-25368 #

TABLE OF CONTENTS

Introduction.	1
Discussion of Results	4
Experimental Details.	4
H ₂ /Fe Chemisorption Kinetics.	5
H ₂ S/Fe Chemisorption Kinetics	7
O ₂ /Fe Chemisorption Kinetics.	9
Origin of the Chemisorption-Induced Resistance Change.12
Conclusions13
References and Footnotes.14
Bibliography/Reports.15
Papers (published and unpublished)	
Talks Presented (contributed and invited)	
Appendix A.17

INTRODUCTION

This report deals primarily with a study of the kinetics of hydrogen (H_2) and hydrogen sulfide (H_2S) chemisorption onto iron (Fe) films. It was established in another study of the kinetics of H_2 chemisorption onto Fe films that intermediate between the molecular gas phase and the dissociated chemisorbed state is an adsorbed molecular species (1). Under certain conditions of temperature and pressure the adsorbed molecular species acts as a thermally activated rate limiting step for hydrogen chemisorption. The goal of the present study was to develop a qualitative and quantitative understanding of the chemisorption kinetics of the H_2/Fe and H_2S/Fe systems so that they could be compared and related to kinetic mechanisms for the environmental degradation of steels caused by H_2 and H_2S .

The interaction of H_2 and H_2S with steels results in the environmental degradation of the structural characteristics of the steel via processes such as hydrogen embrittlement, corrosion and hydrogen attack. The degradation process associated with H-embrittlement is postulated to be rate limited by the initial chemisorption of molecular hydrogen at the gas-metal interface as indicated in the work of Nelson, et al (2). The H-embrittlement process is significantly accelerated over that due to a pure H_2 environment if H_2S is added to the environment. Dissolved protonic hydrogen in the iron lattice is believed to be the casual species which induces H-embrittlement. The most expedient explanation for the H_2S -accelerated-embrittlement is that the rate of absorption of protonic hydrogen is greater from H_2S than from H_2 ; where the initial step in the H-absorption process is chemisorption.

An accelerated chemisorption of H_2S compared with H_2 could result from either the absence of a molecular precursor for chemisorption or if one is present, the kinetic rate between the precursor and the dissociated chemisorbed state may be significantly faster for H_2S compared with H_2 . The answers to such questions were addressed in this work.

To investigate the chemisorption kinetics, a quasi-isothermal approach was employed; the coverage of chemisorbed hydrogen or chemisorbed sulfur was observed as a function of time for fixed conditions of substrate temperature and gas phase pressure. The measurements are considered to be quasi-isothermal because the gas phase temperature is constant at room temperature (about 295 K) while the substrate temperature is varied. Auger Electron Spectroscopy (AES) was used to observe the chemisorbed sulfur. To observe the chemisorbed hydrogen it was necessary to employ a much different technique since hydrogen is insensitive to many surface analysis procedures. The technique employed to monitor the hydrogen coverage was the chemisorption-induced resistance change. This is a phenomenon whereby the resistance of a thin conducting substrate changes due to chemisorption occurring on the surface. The phenomena of the chemisorption-induced resistance change and the techniques developed for the hydrogen chemisorption studies are discussed in detail in ref. 3, which is included in this report as Appendix A.

To compare the results obtained from studying kinetics by the two different techniques, namely by AES and the chemisorption-induced resistance change, a study was made of the kinetics of oxygen (O_2) chemisorption onto Fe films.

Although the chemisorption-induced resistance change is a phenomena which has been known for some 25 years, there is still controversy over

the physical mechanism for the phenomena. Several studies were made to clarify this situation for H_2 , H_2S and O_2 chemisorbed onto Fe films.

Finally, the reaction model utilized to interpret the H_2/Fe chemisorption kinetics was applied to data from an earlier study on the desorption kinetics for H_2 chemisorbed onto nickel (Ni) films in the vicinity of the Curie temperature of the film. This analysis permitted a separation of the gross desorption process into individual components so that the influence of the magnetic phase transition on the rate constants could be determined. The details of this work will not be discussed in this report as they tend to fall outside the general theme of the study. The reader is referred to ref. 4 for a discussion of this study.

Discussion of Results

In this report only major results and conclusions will be presented. Details of the various aspects of this study can be found in the open-literature publications listed in the Bibliography and in the previous semi-annual reports for this grant. The Discussion of Results will be divided into the following subject divisions: (1) Experimental Details, (2) H₂/Fe Chemisorption Kinetics, (3) H₂S/Fe Chemisorption Kinetics, (4) O₂/Fe Chemisorption Kinetics, and (5) Origin of Chemisorption-Induced Resistance Change.

Experimental Details

Utilized throughout this study were thin Fe film substrates. The Fe films were prepared by sublimation from high purity Fe wire filaments onto either glass substrates for the H₂, H₂S and O₂ studies or onto Si(111) monocrystals for additional H₂S and O₂ studies on epitaxially grown Fe films. Great care was taken in cleaning the evaporation substrates, primarily by thermal outgassing. The evaporated films were either annealed at elevated temperature to stabilize their resistance for use at elevated temperatures or were allowed to self-anneal for use at room temperature. The major effect of annealing the film was to change the roughness of the film, thereby changing the number of adsorption sites per unit geometrical area of the film. No attempt was made to characterize the morphology of the polycrystalline films; the structure of the epitaxially grown films was characterized with Low Energy Electron Diffraction (LEED). The exposed surface of the epitaxially grown Fe films had a [111] orientation. The chemical purity of the surfaces was checked with AES. Except for a maximum of about 3-5% of a monolayer of oxygen, the film surfaces were free of contaminants. It was concluded that the oxygen originated from

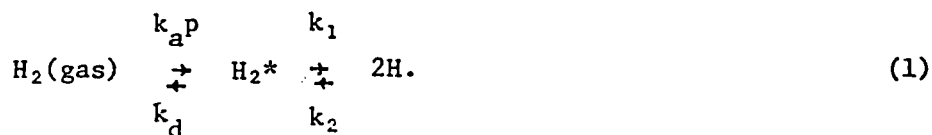
the evaporation filament and not from gas phase adsorption. The films utilized in the study varied in thickness with a minimum thickness of about 5 nm. Films thinner than 5 nm showed signs of being patchy. The thickness of the films was established from the effective resistivity of the film.

The films were made and the measurements performed in an ultra-high-vacuum (UHV) apparatus with a base pressure of about $2.7 \times 10^{-8} \text{ N/m}^2$. Considerable effort was spent to insure that the film surfaces were not contaminated by residual gas impurities and that spurious impurity gas generation in the UHV apparatus was minimized.

H₂/Fe Chemisorption Kinetics

The kinetics of H₂ chemisorption onto polycrystalline Fe films was extensively studied over a gas phase pressure range of 10^{-7} to 10^{-2} N/m^2 and a temperature range of 290 K to 500 K. For this study the chemisorption-induced resistance change was utilized to monitor the coverage of chemisorbed hydrogen in response to variations of the gas phase hydrogen pressure at various constant substrate temperatures. The principal kinetic measurements used in the H₂/Fe study were: (1) (gross) adsorption, (2) (gross) desorption and (3) p-j (pressure-jump) relaxation measurement. In addition an equilibrium measurement of the resistance change isotherm was made. A detailed discussion of the procedures used in the H₂/Fe kinetic measurements is presented in Appendix A under the section entitled, "Kinetic Measurements".

The results of the H₂/Fe study can be summarized as follows: molecular hydrogen dissociately chemisorbs on Fe via an adsorbed molecular species. The reaction path is schematically illustrated as follows:



In this model, molecular hydrogen adsorbs into the molecular state H_2^* , with a rate given by $k_a p$. The constant k_a is equal to $\alpha/\bar{n}\sqrt{2\pi mk_B T}$, where α is the probability for adsorption into an empty molecular site, \bar{n} is the average number of molecular adsorption sites per unit area, m is the mass of the hydrogen molecule, k_B is Boltzmann's constant and T is the gas temperature. Chemisorption occurs when the adsorbed molecular species proceeds into the dissociated chemisorbed state, H , with rate k_1 . For desorption, the atoms in the chemisorbed state recombine and go to the molecular state at rate k_2 . The adsorbed molecular species then desorbs into the gas phase with a rate k_d . The rate constants k_1 , k_2 and k_d are temperature dependent with various activation energies. The schematic model presented in Eq. (1) is mathematically described as follows:

$$d\theta^*/dt = k_a p (1-\theta^*) - k_d \theta^* - 1/2 d\theta/dt, \quad (2a)$$

$$1/2 d\theta/dt = k_1 \theta^* (1-\theta)^2 - k_2 \theta^2 (1-\theta^*), \quad (2b)$$

where θ^* is the coverage of the adsorbed molecular state and θ is the coverage of the dissociated chemisorbed state. At equilibrium the solution for θ reduces to the Langmuir isotherm for dissociative adsorption, $\bar{\theta} = \sqrt{Kp} / \sqrt{1 + Kp}$, where $K = (k_a \cdot k_1)/(k_d \cdot k_2)$. From measurements of $\bar{\theta}$ at various temperatures and pressures, the isothermic heat of adsorption was determined to be 82.1 kJ/mole for $\bar{\theta} < 0.1$. This is in agreement with the heat of adsorption determined from the temperature dependence of K . This value is, also, in good agreement with a recent study of H_2 chemisorption on oriented Fe surfaces (5). In general the rate constants and K were found to be independent of θ up to coverages of about 0.8.

The rate constants for the reaction were obtained from an extensive analysis of the data and comparisons of the data with approximate and exact numerical solutions of the model. The rate constants for H_2/Fe chemisorption

are summarized in Table I for measurements conducted over the pressure range of 10^{-7} to 10^{-2} N/m² and the temperature range 290 K to 500 K.

Table I. Rate Constants for H₂/Fe Chemisorption Reactions

Rate Constants	H ₂ /Fe
$k_a, (\text{Nm}^{-2} \text{sec})^{-1}$	6×10^2 (at 300 K), $\alpha = 0.2$ (6)
k_d, sec^{-1}	$11T \exp(-28.9/RT)$
k_1, sec^{-1}	$604T \exp(-34.7/RT)$
k_2, sec^{-1}	$3.45 \times 10^{13} T \exp(-87.9/RT)$

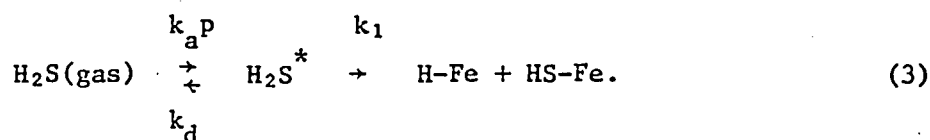
R is in units of kJ/mole K and T is in degrees Kelvin.

H₂S/Fe Chemisorption Kinetics

The study of the kinetics of H₂S chemisorption onto polycrystalline as well as [111] oriented epitaxially grown Fe films was studied only at 300 K and over a gas phase pressure of 10^{-7} to 10^{-5} N/m². In the study the chemisorption-induced resistance change as well as AES was utilized to monitor the coverage of chemisorbed sulfur. It was possible to observe only (gross) adsorption kinetics with H₂S since sulfur does not desorb from Fe at 300 K.

The results discussed herein relate to measurements made on the [111] oriented epitaxially grown Fe films. Observations with LEED during adsorption show the growth in intensity of a ($\sqrt{3} \times \sqrt{3}$) R 30° pattern with exposure to H₂S up to saturation coverage. This suggests that at saturation coverage 1/3 of the available adsorption sites are filled with sulfur atoms.

The adsorption kinetics for H₂S/Fe are modeled in a similar fashion as H₂/Fe. Assuming that the dissociation products are H and HS, then schematically, the adsorption of H₂S onto Fe is given by:



The rate constants have the same definition as for H₂ adsorption. Note, however, that for H₂S/Fe, k₂ is zero since sulfur does not desorb at 300 K. The dissociation products for H₂S have not been clearly established, but there is evidence for the presence of H and HS on the surface. The adsorption model can be written mathematically as:

$$d\theta^*/dt = k_a p (1-\theta^*) - k_d \theta^* - 1/2 d\theta/dt \quad (4a)$$

$$1/2 d\theta/dt = k_1 \theta^* (1-\theta/\theta_{sat})^2 \quad (4b)$$

where $\theta_{sat} = 2/3$.

An analytical solution to the model was obtained in the steady-state approximation ($d\theta^*/dt = 0$) and compared with the data. From an analysis of the pressure dependence of the adsorption rate and the general kinetics it was possible to obtain estimates of all the rate constants. The rate constants for H₂S/Fe(111) chemisorption are summarized in Table II for measurements conducted at 300 K over the pressure range 10^{-7} to 10^{-5} N/m². The H₂S/Fe(111) rate constants are also compared with corresponding values for H₂/Fe at 300 K in Table II.

Table II. Rate Constants for H₂S/Fe(111) Chemisorption Reaction

Rate Constant	H ₂ S (at 300 K)	H ₂ (at 300 K)
k _a , (Nm ⁻² sec) ⁻¹	1.2 x 10 ³ , α = 0.4	6 x 10 ²
k _d , sec ⁻¹	0.05	0.03
k ₁ , sec ⁻¹	0.22	0.16

Although the values in Table II relate to adsorption onto an oriented iron surface, they are also representative of adsorption onto polycrystalline Fe films. The primary difference in the two measurements is the uncertainty in

knowing the number of adsorption sites per unit area which directly affects k_a , but not k_d or k_1 . This particular ambiguity is removed by using oriented surfaces.

O₂/Fe Chemisorption Kinetics

A study was carried out of the kinetics of O₂ chemisorption onto polycrystalline Fe films at 300 K. The study employed both the chemisorption-induced resistance change and AES to monitor the coverage of chemisorbed oxygen. Since dissociated chemisorbed oxygen does not desorb from Fe, only (gross) adsorption measurements were possible. The objective of this short study was to compare the kinetics measured by these two techniques.

We find no significant difference in the form of the adsorption kinetics as measured by AES or the chemisorption-induced resistance change. A model in which chemisorption occurs via an adsorbed molecular specie was compared with the data. Schematically the model is similar to that presented for H₂S chemisorption, Eq. (3) and is given by,



where O₂^{*} is the adsorbed molecular specie and 2O is the dissociated chemisorbed state. The definition for the rate constants is as for H₂ adsorption. A limiting form for the model, obtained when $(k_a p + k_d)/k_1 > 5$, is an excellent fit to the data over an exposure range from about 0.5 to 2000 L. The limiting form to this adsorption model is, however, mathematically equivalent to another model where dissociative chemisorption occurs directly from the gas phase and does not involve a precursor. The data at 295 K cannot distinguish between the two models, but other data at 80 K supports the model with the adsorbed molecular specie. We conclude that oxygen chemisorption onto iron occurs via a mobile-adsorbed molecular specie.

For the limiting form to the adsorption model, Eq. 4, the effective initial adsorption rate is given as

$$K_{\text{eff}} = 2k_a p \cdot k_1 / \theta_{\text{sat}} (k_a p + k_d)$$

(Note that this result is identical to that for H₂S adsorption).

There is no obvious pressure dependence to K_{eff} for p < 10⁻⁴ N/m², so in this low pressure regime

$$K_{\text{eff}} = \frac{2k_a p}{\theta_{\text{sat}}} \left(\frac{k_1}{k_d} \right).$$

By comparing values of K_{eff} at 295 K and 80 K, an activation energy of -5.2 kJ/mole is calculated for (k₁/k_d). There is no obvious coverage dependence to the rate constants, since an excellent fit to the data is possible with coverage independent parameters. Some variation is found in K_{eff} as measured by AES and by the chemisorption-induced resistance change. These variations appear to be related to the AES measurement technique. Similar problems are not encountered in the resistance-change measurement because of its passive nature.

Measurements have also been made of a current noise which occurs when O₂ chemisorbs to saturation to polycrystalline iron films. The current noise is assumed to arise from a reversible reaction between two different adsorbed oxygen states on the surface, where thermodynamic forces produce fluctuations in the number of adatoms in a particular state. The number fluctuations are coupled to the current via the chemisorption-induced resistance change. The exact nature of the oxygen states has not been established. The simple proposed model for the noise is qualitatively and quantitatively in agreement with the data. The model assumes only a single correlation time for the autocorrelation function implying that surface heterogeneity is not important to this reaction process. An understanding of this noise process

may have important implications for understanding noise sources in conductors as well as offering a new technique to investigate reaction kinetics under passive-ambient conditions.

Origin of the Chemisorption-Induced Resistance Changes

Since the application of the chemisorption-induced resistance change was a technique utilized throughout this work, it was considered important to investigate the origin of the phenomena for the H_2/Fe , H_2S/Fe and O_2/Fe adsorption systems.

There are three models for the origin of the resistance change. The first assumes that the change results from a reduction in the conducting thickness of the film. The second model assumes that the scattering properties of the conduction electrons at the surface are modified by adsorption. It can be shown for both of these models that the magnitude of the fractional resistance change due to chemisorption will be temperature dependent and have very specific thickness dependence for very thin films. Experimentally we have shown that there is no temperature dependence to the fractional resistance change and that the thickness dependence follows a simple inverse thickness relationship down to films as thin as 2 nm. These observations are in contradiction to the predictions of the two models discussed above. A third model, originally proposed by Suhrmann, assumes that the density of states for the conduction electrons is changed by chemisorption at the surface. The predictions of this model are in good agreement with the observations for H_2/Fe , O_2/Fe , and H_2S/Fe . Additional details of this study can be found in Appendix A.

Conclusions

There are several conclusions to be drawn from this study. The first is that the chemisorption-induced resistance change is a viable technique for use in isothermal kinetic studies. With regard to the chemisorption induced resistance, the origin of the phenomena for H_2/Fe , H_2S/Fe and O_2/Fe chemisorption systems is related to modification in the adsorption substrate's conduction electron bulk density of states.

For the H_2/Fe , H_2S/Fe and O_2/Fe chemisorption systems, the kinetics of chemisorption are best described by a model where dissociative chemisorption occurs via an adsorbed molecular specie. The primary difference in the kinetics for these three systems is that chemisorption for H_2/Fe is reversible on a reasonable time scale at temperatures above 250 K, whereas for H_2S/Fe and O_2/Fe chemisorption is irreversible. These studies also suggest that the rate parameters involved in the chemisorption reaction are coverage independent which is surprising since coverage dependent effects are often observed in other types of chemisorption studies.

For both the H_2/Fe and the H_2S/Fe chemisorption systems, the step between the adsorbed molecular specie and the dissociated chemisorbed state can act as a rate limiting step for chemisorption. From our measurements we can conclude that at 300 K the adsorption rate at high pressures in the rate limited regime, is essentially identical for H_2 and H_2S . At low pressures where adsorption is dominated by adsorption from the gas phase into the adsorbed molecular specie, the adsorption rate for H_2S will be about twice that for H_2 .

References and Footnotes

1. M. R. Shanabarger, Surface Sci. 52 (1975) 689.
2. Howard G. Nelson, Dell P. Williams and Alan S. Tetelman, Metal. Trans. 2 (1971) 953.
3. M. R. Shanabarger, "The Chemisorption-Induced Resistance Change and its Application to Determining H₂/Fe Chemisorption Kinetics," to be published in Advanced Techniques for the Characterization of Hydrogen in Metals, N. Fiore and B. Berkowitz, eds., The Metallurgical Society of AIME (Warrendale, PA).
4. M. R. Shanabarger, Phys. Rev. Letters 43 (1979) 1964.
5. F. Bozso, G. Ertl, M. Grunze and M. Weiss, Applications of Surface Sci. 1 (1977) 103.
6. The value of α obtained from this study is in agreement with the initial sticking coefficient observed in other studies, e.g. see ref. 5.

Bibliography

Papers/Reports (published and unpublished)

- H₂/Fe: M. R. Shanabarger, "Temperature Dependence of the Adsorption Kinetics for Hydrogen Chemisorbed onto Evaporated Fe Films" in Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces, R. Dobrozemoky, ed., Vienna, 1977.
- H₂/Ni: M. R. Shanabarger, "Isothermal-Desorption-Rate Measurements in the Vicinity of the Curie Temperature for H₂ Chemisorbed on Nickel Films", Physical Review Letters 43 (1979) 1964.
- H₂S/Fe: M. R. Shanabarger, "Kinetics of H₂S Adsorption onto Fe Films", in Proceedings of the Fourth International Conference on Solid Surfaces and the Third European Conference on Surface Science, Cannes, 1980, Supplement a la Revue LeVide, les Couches Minces, No. 201.
- H₂ & H₂S/Fe: M. R. Shanabarger, "A Comparison of Adsorption Kinetics on Iron of H₂ and H₂S" in Hydrogen Effects in Metals, I. M. Bernstein and A. W. Thompson, eds; The Metallurgical Society of AIME (Warrendale, PA, 1981).
- O₂/Fe: M. R. Shanabarger and Jo Wilcox, "Origin of the Chemisorption-Induced Resistance Change for O₂ Adsorbed onto Fe" in Proceedings of the Eighth International Vacuum Congress, Cannes, 1980. Supplement a la Revue LeVide, les Couches Minces, No. 201.
- M. R. Shanabarger, Jo Wilcox and H. G. Nelson, "Summary Abstract: Observation of an Excess Current Noise Resulting from Oxygen Adsorption onto Iron Films" to be published in Journal of Vacuum Science and Technology, March/April, 1982.
- M. R. Shanabarger and R. D. Moorhead, The Kinetics of Oxygen Adsorption onto Polycrystalline Iron Films, unpublished.
- Other: M. R. Shanabarger, "The Chemisorption-Induced Resistance Change and Its Application to Determining H₂/Fe Chemisorption Kinetics", to appear in Advanced Techniques for the Characterization of Hydrogen in Metals, N. Fiore and B. Berkowitz, eds.; The Metallurgical Society of AIME (Warrendale, PA).

Talks Presented (contributed and invited)

1. M. R. Shanabarger, "Atom-Adsorbate Charge Transfer when O₂ Chemisorbs on Fe Films", contributed paper, March Meeting of the American Physical Society, San Diego, California (1977).
2. M. R. Shanabarger, "Temperature Dependence of the Adsorption Kinetics for Hydrogen Chemisorbed onto Evaporated Fe Films", contributed paper, 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces, Vienna, Austria (1977).
3. M. R. Shanabarger, "Chemisorption Kinetics in the H₂/Fe System", contributed paper, AIME Annual Meeting, New Orleans, Louisiana (1979).
4. M. R. Shanabarger, "Kinetics for Hydrogen Sulfide Adsorption onto Evaporated Iron Films", contributed paper, Spring Meeting of the California Catalysis Society, Stanford, California (1979).
5. M. R. Shanabarger, "Fluctuation Spectroscopy - A Technique to Measure Fast Chemisorption Kinetic Processes", contributed paper, Fall Meeting of the California Catalysis Society, Irvine, California (1979).
6. M. R. Shanabarger, "A Comparison of Adsorption Kinetics on Iron of H₂ and H₂S", contributed paper, Third International Conference on the Effect of Hydrogen on Behavior of Materials, Jackson Lake Lodge, Wyoming (1980).
7. M. R. Shanabarger, "Adsorption of H₂S onto (111) Oriented Fe Films at 300 K", contributed paper, 8th International Vacuum Congress, 4th International Conference on Solid Surfaces, and the 3rd European Conference on Surface Science, Cannes, France (1980).
8. M. R. Shanabarger, "Origin of the Chemisorption-Induced Resistance Change for O₂ and H₂S Adsorbed onto Fe Films" (with Jo Wilcox), contributed paper, 8th International Vacuum Congress, 4th International Conference on Solid Surfaces, and 3rd European Conference on Surface Science, Cannes, France (1980).
9. M. R. Shanabarger, "Adsorption of H₂S onto (111) Oriented Fe Films at 300 K", University of Munich, Munich, Germany (1980).
10. M. R. Shanabarger, "Changes in the Desorption Rate Near the Curie Temperature for H₂ Chemisorbed onto Ni Films", Institut für Grenzflächenforschung und Vakuumphysik der Kernforschungsanlage Jülich GmbH, Jülich, Germany (1980).

APPENDIX A

THE CHEMISORPTION-INDUCED RESISTANCE CHANGE AND
ITS APPLICATION TO DETERMINING H₂/Fe CHEMISORPTION KINETICS*

M. R. Shanabarger

Quantum Institute, University of California
Santa Barbara, California 93106

Abstract

Hydrogen adsorbed on a surface is difficult to detect because it is effectively invisible to most of the modern surface analysis techniques developed to detect surface species. One of the few techniques which is sensitive to adsorbed hydrogen is the chemisorption-induced resistance change. The chemisorption-induced resistance change is a phenomenon where the resistance of a metal film substrate is changed due to chemisorption on its surface. For hydrogen this phenomenon provides a sensitive and, because of its passive nature, unique technique to monitor the coverage of chemisorbed hydrogen. The principles, advantages and limitations of the technique are reviewed. A specific application to the determination of the hydrogen-iron chemisorption kinetics is presented.

* This work supported in part by NASA NCC-2-63 and NASA NSG-2222.

Introduction

The characterization of hydrogen adsorbed on metal surfaces is relevant to a large class of materials and materials related problems. For example, because hydrogen adsorbed on nickel and iron is chemically reactive, these metals are often used as catalysts. Adsorbed hydrogen can alter the electronic nature of silicon surfaces and cause the surface structure of tungsten to reconstruct relative to the bulk structure. The surface is also the boundary through which hydrogen enters or exits the interior of the metal. The kinetics of this boundary passage are important to our understanding of the mechanisms of gaseous hydrogen embrittlement.

There are a number of techniques available to study adsorbed species on surfaces, one of which is the chemisorption-induced resistance change. The major advantages of this technique are that it can indicate the chemisorption of virtually any species including hydrogen and it is non-intrusive in that the measurement does not interfere with the phenomenon being measured. In the present review I will first consider hydrogen-metal adsorption and available measurement techniques in some detail. The emphasis when discussing the measurement techniques will be on their usefulness for kinetic studies. I will next focus on the chemisorption-induced resistance change technique and discuss its origin and characteristics including its advantages and limitations. Finally, an example will be given of the chemisorption-induced resistance change technique applied to the determination of the isothermal kinetics of hydrogen chemisorption on iron films.

Adsorbed States of Hydrogen

On or near a metal surface there are several different adsorbed states in which hydrogen can exist. Fig. 1 is a simplified schematic of the potential energy curve of a hydrogen molecule as it approaches a metal surface from free space along an appropriate reaction coordinate showing the principal adsorbed states. The hydrogen molecule first encounters a shallow potential minimum (typically less than 21 kJ/mole (5 kcal/mole)) about 0.4 nm from the surface. This is the physisorbed state which for simplicity is not indicated separately in Fig. 1. The weak binding of the physisorbed state is due to Van der Waals (electrostatic) forces (1). Because of the weak binding, the physisorbed state will be occupied only at very low temperatures. After the physisorbed state, the hydrogen molecule next encounters a less understood state which is referred to as an adsorbed molecular state or molecular precursor (2). The location of the precursor with regard to the surface is not known nor is the nature of the forces binding the molecule in this state. It has been suggested that the precursor may be the physisorbed state (2b). More likely the precursor lies closer to the surface than the physisorbed state and the binding forces involve weak chemical bonds with the surface (2c). Typical binding energies for the precursor are 25-42 kJ/mole (6-10 kcal/mole). It is known that the precursor is vital in mediating the adsorption-desorption reaction between the gas phase and the chemisorbed state. The chemisorbed state is 0.1-0.2 nm from the surface (3). In the chemisorbed state the molecular hydrogen is dissociated into atomic hydrogen. The

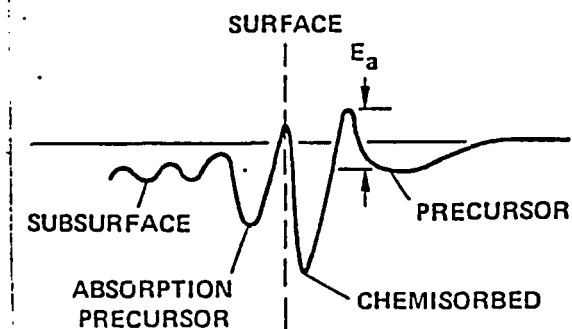


Fig. 1 - Simplified potential energy curve showing the principal adsorbed states of hydrogen in the vicinity of a metal surface for molecular hydrogen adsorption.

It is known that the precursor is vital in mediating the adsorption-desorption reaction between the gas phase and the chemisorbed state. The chemisorbed state is 0.1-0.2 nm from the surface (3). In the chemisorbed state the molecular hydrogen is dissociated into atomic hydrogen. The

chemisorbed state involves covalent bonding (electron transfer) between the adatoms and the atoms of the substrate with adatom binding energies of about 170 kJ/mole (40 kcal/mole).

Between the molecular precursor and the chemisorbed state is an activation barrier of height E_a which the hydrogen molecule must overcome to be chemisorbed. For many metals (e.g. Fe, Ni, Pd and W) this activation barrier is small and chemisorption occurs readily at moderate temperatures, 300K. For other metals (e.g. Ag, Au, Cu, Al and Mg) E_a is large (greater than 40 kJ/mole) and chemisorption is inhibited except at elevated temperatures.

From the chemisorbed state hydrogen can enter the bulk. It has recently been suggested that for hydrogen, intermediate between the chemisorbed state and the subsurface-dissolved protonic hydrogen is an intermediate subsurface hydrogen state, see Fig. 1 (4). This intermediate state acts to some degree as an atomic absorption precursor between the chemisorbed hydrogen and the subsurface-dissolved hydrogen.

Hydrogen Measurement Techniques

The characterization of hydrogen in the chemisorbed state involves the investigation of a large number of properties of the hydrogen-metal complex. These properties can be placed in either of two broad categories; static or dynamic (kinetic). The static properties include examples such as the structure of the chemisorbed overlayer with regard to the substrate; the occupancy and energy of the electronic levels of the hydrogen-metal complex and the binding energy of the chemisorbed hydrogen (5, 6). Examples of the dynamic (kinetic) processes are; the adsorption-desorption kinetics between the gas phase and the chemisorbed hydrogen (7, 8); diffusion of chemisorbed hydrogen along the surface (9); kinetic processes between the various adsorbed hydrogen states (8) and adsorption-desorption between the chemisorbed hydrogen and the subsurface-dissolved protonic hydrogen.

To observe the dynamic processes associated with the chemisorbed state, it is necessary to monitor directly the chemisorbed hydrogen coverage (concentration). There are many adatom specific techniques, but the majority are either insensitive or simply don't work for hydrogen (6, 10). For example, all techniques based on the excitation of electronic core levels of the adatom (the most common of which is Auger Electron Spectroscopy) do not work with chemisorbed hydrogen because it is a one-electron atom (6). These techniques do work for certain applications involving hydrogen-bearing molecules, such as hydrogen sulfide, where the multielectron atom, sulfur, can be observed. There are other techniques such as, Ion Scattering Spectroscopy (ISS) (10), Electron-Ion Desorption (EID) (11, 12) and Secondary Ion Mass Spectroscopy (SIMS) (10, 13), which require considerable experimental care for their application and interpretation. SIMS, for example, is a very sensitive technique. It has been found however, to be difficult in practice to discriminate hydrogen on the surface from hydrogen below the surface (13).

Two techniques to monitor the chemisorbed hydrogen coverage which are relatively straightforward to utilize and are adatom specific are Ultraviolet Photoelectron Spectroscopy (UPS) (6) and Thermal Programmed Desorption (TPD) (11). In UPS, energy levels of the hydrogen-metal complex are probed; the integrated spectral intensity of the excitation due to hydrogen is proportional to the coverage of hydrogen. Although UPS can detect hydrogen coverage as low as about 0.1 monolayers, the technique has limited application to dynamic studies since it requires fairly long data accumulation and processing times. Thermal Programmed Desorption is perhaps the oldest surface analysis technique in common use. After adsorbing hydrogen onto the

surface, the surface is heated in a programmed fashion causing the hydrogen to desorb. The desorbing hydrogen is monitored with a mass spectrometer. The thermally integrated hydrogen signal is proportional to the initial coverage of adsorbed hydrogen. Although TPD does not monitor the surface coverage directly, it is an extremely sensitive technique with some application to kinetic studies (14).

There are several techniques to monitor chemisorbed hydrogen which are non-atom specific. Techniques, such as surface potential measurement, magnetization changes and the chemisorption-induced resistance change are very sensitive with detectability limits on the order or below 0.01 monolayers. Consider first the surface potential measurement. When hydrogen chemisorbs onto a metal surface it changes the work function of the surface. The work function change is the surface potential (6). The surface potential can be a complicated function of the coverage, but for most hydrogen-metal systems it is linearly related to the coverage at coverages less than 0.2 monolayers. The surface potential measurement has been used in isothermal kinetic studies (15). If the metal substrate is magnetic, then chemisorption can change the magnetic moment of the surface atoms (16). The magnetization changes have been used to study hydrogen adsorption onto iron (17). The use of large magnets required to carry out the magnetization measurements places restrictions on the arrangement of the experimental apparatus and the concurrent use of additional analytical surface techniques. Finally, the simplest and perhaps most experimentally straightforward technique to monitor the coverage of chemisorbed hydrogen is the chemisorption-induced resistance change (18). Very simply, the resistance of thin metal substrates change when hydrogen chemisorbs on the surface. As will be seen, this technique has the sensitivity and measurement response time necessary to carryout comprehensive studies of isothermal kinetics not possible with other techniques (19, 20).

The Chemisorption-Induced Resistance Change

The chemisorption-induced resistance change is the change in resistance of a metal substrate resulting from chemisorption occurring on the surface. This is schematically shown in Fig. 2, where the resistance change of a thin substrate is changing as species adsorb from the gas phase. The resistance change, $\delta R = R(\theta) - R(0)$, is the difference between the resistance at coverage θ and the resistance at $\theta = 0$. The coverage θ is the ratio of the number of

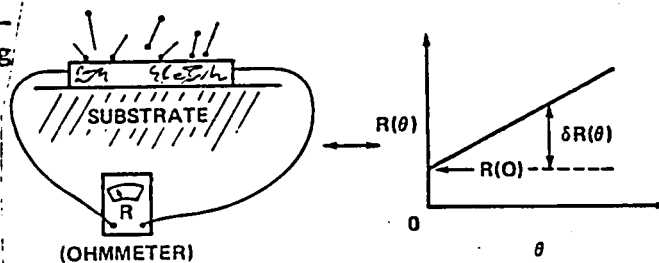


Fig. 2 - Schematic illustration of the chemisorption-induced resistance change.

chemisorbed adspecies to the number of surface atoms, where $\theta=1$ is referred to as monolayer coverage. Resistance change data will be presented as the fractional resistance change, $\delta R/R (= \delta R/R(0))$, as this facilitates comparison of the data for different chemisorption systems.

Characteristics of the Resistance Change

The chemisorption-induced resistance change is a well established phenomenon for many chemisorption systems (18, 21) and was a very early technique used to study the chemisorption process (22). A typical example of the type of information that can be obtained with this technique is illustrated in Fig. 3. Presented here is a typical resistance change isotherm for hydro-

gen adsorbed onto a Ni film at 295 K. A resistance change isotherm is the variation of the equilibrium resistance change with gas phase pressure for a constant temperature. At low pressures, the equilibrium resistance change shown in Fig. 3 is proportional to \sqrt{p} . This indicates that molecular hydrogen is dissociated into atomic hydrogen when chemisorbed onto Ni. The solid line in Fig. 3 is a fit of the data to a particular coverage isotherm for dissociative adsorption (2b). In fitting the data to the coverage isotherm, it was assumed that $\delta R/R = A\theta$, where A is the magnitude of the fractional resistance change at monolayer coverage and θ is given by the coverage isotherm. In addition to obtaining an estimate of the coverage of the chemisorbed state, the heat of chemisorption can be obtained from determinations of the isotherms at various temperatures (20).

The general characteristics of the chemisorption-induced resistance change have been established from observations on a number of systems (21). The principal characteristics are; (1) the sign of the resistance change, (2) variation with coverage and (3) magnitude of the resistance change and its variation with film thickness and temperature. The sign of the resistance change has already been indicated in Fig. 3, namely the resistance change for hydrogen chemisorption is positive ($\delta R/R > 0$). The initial resistance change at low coverage is positive for all chemisorption systems studied to date which involve covalent bonding between the adspecies and the surface atoms (21). A negative resistance change ($\delta R/R < 0$) for hydrogen is reported to result from adsorption on a contaminated surface (23)

The hydrogen-metal systems which have been studied show at low coverage ($\theta < 0.2$) a linear relationship between the resistance change and the coverage of adsorbed hydrogen (21, 24). This linear relationship is not necessarily observed at higher coverages. The methods used to determine the coverage of chemisorbed hydrogen in these studies are, however, questionable because they are based on volumetric determinations of the total amount of adsorbed hydrogen. The adsorbed hydrogen is distributed among the various adsorption states (see Fig. 1) and does not necessarily reside only in the chemisorbed state, hence a non-linear behavior might be expected. Variation of the fractional resistance change with coverage for the O_2/Fe system is shown in Fig. 4. Here the relative coverage of chemisorbed oxygen was determined directly with Auger Electron Spectroscopy (AES). As can be seen, the resistance change for O_2/Fe is linearly related to the coverage up to saturation. The data for H_2/Ni in Fig. 3 suggests that the resistance change for this system is linearly related to the coverage up to saturation. A similar result has also been obtained for H_2/Fe (20) based on analysis of the resistance isotherm and not on the measurement of the total amount of adsorbed hydrogen.

Another characteristic of the resistance change is that the magnitude is inversely proportional to film thickness. This is demonstrated in Fig. 5 for

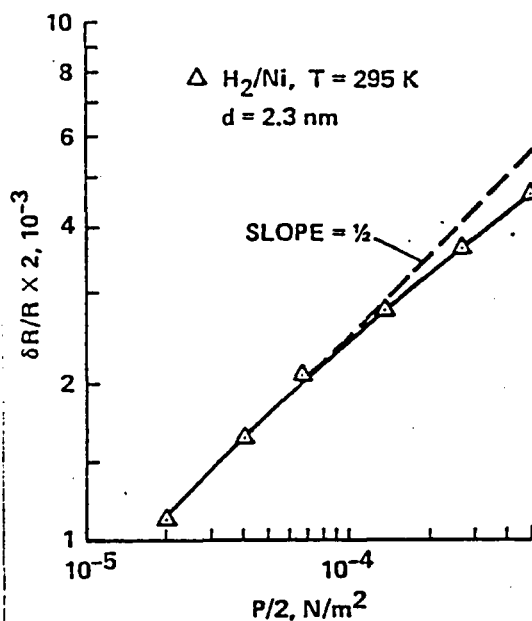


Fig. 3 - Typical resistance change isotherm for H_2 adsorbed onto a Ni film. The solid line is a fit of the data to a Langmuir isotherm for dissociative adsorption.

H_2/Fe , H_2/Ni , H_2S/Fe and O_2/Fe , where the magnitude of the fractional resistance change at estimated monolayer coverage, A , is shown as a function of film thickness, d . The inverse thickness dependence is a manifestation of the fact that the resistance change is a phenomenon whose magnitude is directly related to the surface-to-volume ratio of the substrate. The magnitude of A for different species has been shown to be related to the adsorption heat of adsorption (25). On this basis the magnitude of the resistance change which might be associated with adsorption into an adsorbed molecular state is negligibly small compared with the resistance change from the chemisorbed state. Finally, studies indicate that A is independent of temperature. This has been reported for O_2/Fe (26) and H_2S/Fe (27). The temperature dependence of A for H_2/Fe is presented in Fig. 6. As can be seen, within experimental error, A is constant with temperature over the temperature range of from 320 K to 420 K.

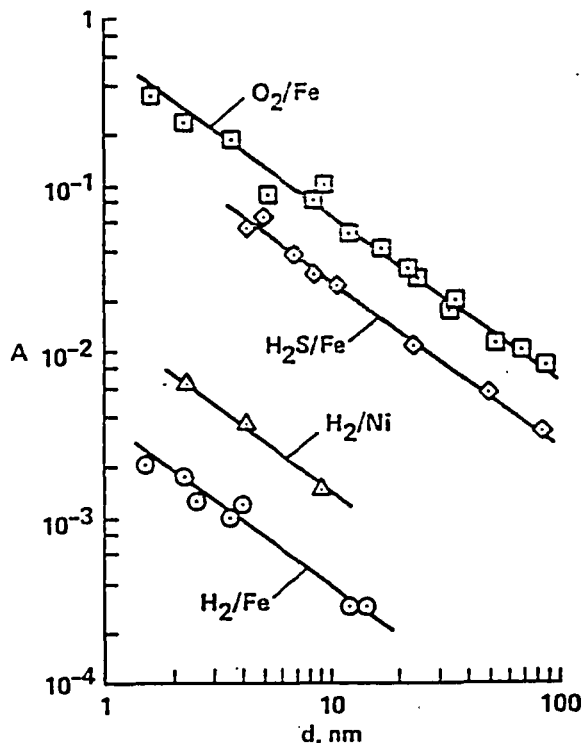


Fig. 5 - Variation of the amplitude of the fractional resistance change at estimated monolayer coverage, A , as a function of film thickness, d . The solid lines have slope of -1 .

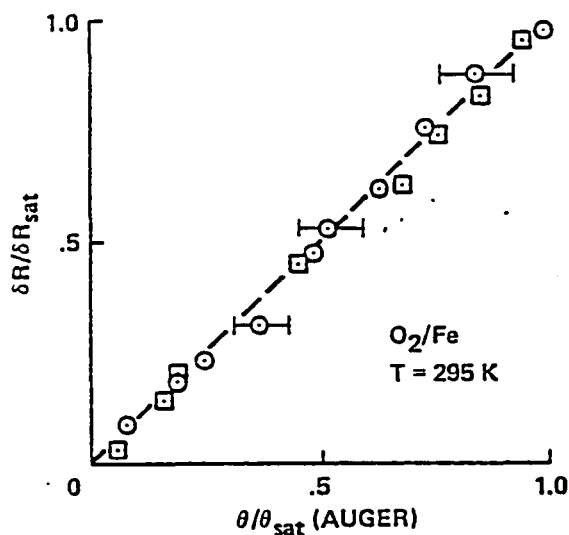


Fig. 4 - The chemisorption-induced resistance change normalized by its saturation value for O_2 chemisorbed into iron films as a function of the relative coverage of chemisorbed oxygen. The oxygen coverage was determined with Auger Electron Spectroscopy. The data is from measurements on two different films.

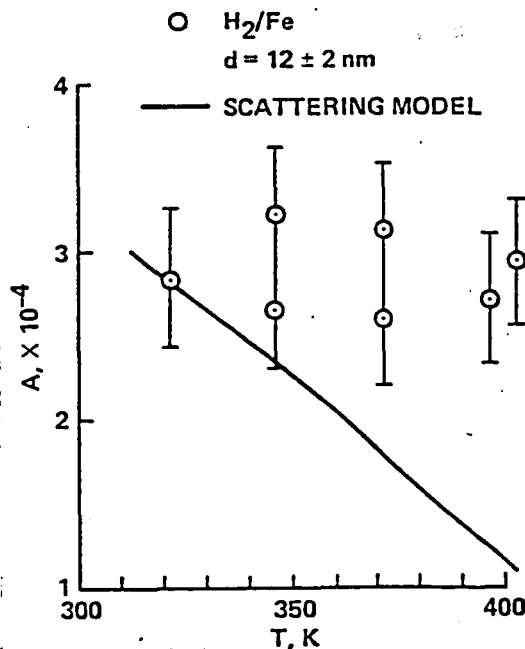


Fig. 6 - Temperature dependence of the amplitude of the fractional resistance change as estimated monolayer coverage, A , for H_2 adsorbed onto Fe films. The data is from measurements on two comparable films. The solid line is the temperature dependence calculated from the scattering model (29).

Origin of the Resistance Change

There are several models for the origin of the resistance change (21). The model which is consistent with all of the data will be briefly reviewed in this section; a more extensive discussion of the models is presented in Ref. 26.

Calculations have shown that the electrical conductivity, σ , of a film with chemisorbed species on the surface is given by

$$\sigma = \sigma_f \{1 - 3(1-p)\Lambda/8d\}, \quad (1)$$

where σ_f is the equivalent bulk conductivity of the film material; p is the probability for specular scattering of the conduction electrons at the film surface; d is the film thickness and Λ is the conduction electron mean free path (28). Assuming that the dimensions of the film are constant, then $\delta R/R = -\delta\sigma/\sigma$. The conductivity, σ , can change either by changes in the specular scattering coefficient, p , or changes in σ_f .

Adatoms on the surface can act as scattering centers for the conduction electrons producing changes in p . The degree of the adatom-conduction electron wavefunction overlap determines the amount p can change. For a given change in p it is straightforward to show from Eq. 1 that $\delta R/R$ will be temperature dependent and for very thin films ($d < \Lambda$) it will be thickness dependent (26). Both of these predictions are in disagreement with the experimental observations as is shown for H_2/Fe in Fig. 6 for the temperature dependence and in Fig. 5 for the thickness dependence. The solid line in Fig. 6 is the calculated temperature dependence for A assuming that the resistance change results from changes in p (scattering model) (29):

It is reasonable to assume that σ_f can change because of the electron transfer which occurs between the adatom and the substrate when the chemisorption bond is formed. For this situation, a simplistic interpretation suggests that the conduction electron density, n , is changed, since that fraction of the conduction electron wavefunction resonant with the bonding levels will be lost to the conduction process. As a result of n changing it can be shown that

$$\delta R/R = -\delta\sigma_f/\sigma_f = -\{2\beta n_s/3nd\}\theta = A\theta,$$

where β is the charge transferred to the conduction band per adatom per electron and n_s is the number of adsorption sites per unit area. Here, $\delta R/R$ is inversely proportional to film thickness independent of thickness and is temperature independent, assuming that β is temperature independent. This is a reasonable assumption based on the temperature independence of the heat of adsorption which should be related to β . Both of the predictions of the model (charge transfer model) are in agreement with the observations. Furthermore, for covalently bonded species charge is usually transferred from the substrate toward the adatom ($\beta < 0$) and A will be positive, also in agreement with observations.

The characteristics of the resistance change for many systems strongly suggest that the charge transfer model is the dominant mechanism for the chemisorption-induced resistance change. It is not obvious at present that this is the general situation for all systems. The correct mechanism for each system will require an individual assessment of the data for that system.

Resistance Change Measurement

A straightforward and simple procedure to measure the resistance change is to utilize a Wheatstone bridge (30). Here the film onto which adsorption is to be studied forms one arm of the bridge. The output of the bridge will be directly proportional to the resistance change if the bridge is adjusted to balance before adsorption takes place. A typical D. C. Wheatstone bridge delivering about 30 mw of power to a 1000 ohm film can resolve resistance changes on the order of $\delta R/R = 10^{-5}$. A fractional resistance change equal to 10^{-5} corresponds to coverage changes on the order of $\delta\theta = 2.5 \times 10^{-2}$ for H_2/Fe and $\delta\theta = 1.5 \times 10^{-4}$ for O_2/Fe using the data shown in Fig. 4 for $d=10$ nm.

Sensitivity can be increased by increasing the operating voltage of the bridge. This may result, however, in an excessive temperature rise of the film above that of the substrate. Reducing the film thickness will increase the sensitivity by increasing A, but this is limited by the formation of non-uniform (patchy) films. Perhaps a better way to increase the sensitivity is to utilize an A. C. excited bridge and synchronous detection techniques.

Advantages of the Resistance Change Technique

There are several advantages to the resistance change technique which have made it a useful tool in surface investigations. It can directly monitor the coverage of hydrogen chemisorbed onto metal films with good sensitivity. It is not difficult, for example, at constant temperature to resolve coverage changes on the order of 0.01 monolayers with the resistance change linearly proportional to the coverage up to $\theta = 0.8$ monolayers for the H_2/Fe and H_2/Ni systems.

The resistance change measurement has a very large temporal response range (bandwidth) for its sensitivity making it ideal for in vivo kinetic or reaction studies where the large bandwidth is beneficial.

The resistance change technique is one of the very few non-intrusive techniques in that the measurement does not interfere (in a macroscopic sense) with the phenomena being measured. Various other techniques, such as AES, ISS, EID and SIMS, modify the surface condition during the measurement unless great care is taken.

The use of evaporated films for adsorption substrates simplifies the problems associated with obtaining a clean adsorption substrate. The films can be either polycrystalline or epitaxially grown single crystal. The surface of the film can be readily characterized using standard surface analysis techniques, including Low Energy Electron Diffraction (LEED) for the oriented films.

And finally, the resistance change technique can be used for studies at high hydrogen pressures unlike most other surface analysis techniques which are limited to pressures below about 10^{-3} N/m² (10^{-5} torr). At sufficiently high pressures, however, hydrogen will absorb into the bulk. This will also produce a resistance change. In principle, the chemisorption and the bulk resistance changes can be separated either by varying the film temperature (changing the kinetic rates) or by varying the film thickness if the magnitudes of the two resistance changes are comparable. The fractional resistance change due to dissolved hydrogen should be independent of film thickness unless metal hydrides form. Depending upon how the metal hydride forms the resistance change could be difficult to interpret. Care in designing the experiment should permit separation of these effects and allow for their independent study.

Limitations of the Resistance Change Technique

There are two fairly severe restrictions in utilizing the resistance change technique. The first is that the technique is non-discriminating; any species which chemisorbs will produce a resistance change. This tends to limit the technique to studies involving a single adsorbate. Good experimental technique is also required, because impurity gases may chemisorb along with the species under study to produce an equally large resistance change. The data in Fig. 4 show, for example, that a resistance change proportional to 0.1 monolayers hydrogen chemisorption would also be produced by about 0.001 monolayers of oxygen adsorption.

The second major limitation relates to the stability of the resistance; it must be adequately constant to be able to reliably determine the chemisorption-induced resistance change. The evaporated film must be annealed before use to stabilize the resistance by relieving strains and completing film growth. Good vacuum technique is required during annealing to prohibit impurity adsorption onto the film prior to the hydrogen study. During measurements the substrate temperature must be controlled. Temperature stability usually requires some type of electronic feedback control. For a $d = 10$ nm Fe film, for example, a change of hydrogen coverage of 0.05 monolayers is equivalent to $\delta R/R = 2 \times 10^{-5}$. The temperature coefficient of resistance, $(1/R)(\Delta R/\Delta T)$, for this film is about $3 \times 10^{-3} \text{ C}^{-1}$. Therefore if temperature stability is required such that the resistance change is at least 10 times that due to thermal variations, the maximum temperature excursion must be less than $7 \times 10^{-4} \text{ C}$. Temperature stability of this level is readily available through careful experimental design and the use of feedback temperature control electronics.

The resistance change technique gives only a relative measure of the coverage of the chemisorbed state and not an absolute measure. This limitation is, however, characteristic of almost all surface analysis techniques; they also require an independent calibration. An independent calibration is very difficult to achieve for hydrogen and has only been established for the case of hydrogen adsorption onto Fe(110) (31). The coverages reported herein are estimates based on the analysis of the resistance isotherm and the assumption that at saturation coverage $\theta = 1$.

Application: Determination of the Kinetics of H₂/Fe Chemisorption

Chemisorption kinetics is important to understanding the dynamics of many materials processes. A particular example is the gaseous hydrogen embrittlement of steel where the chemisorption of hydrogen on iron is believed to play a major role in controlling the rate of embrittlement (32). A study was undertaken to quantify the kinetics of the H₂/Fe chemisorption reaction for comparison with hydrogen embrittlement models and data. The chemisorption-induced resistance change was utilized in the kinetic study. As an example of the application of the chemisorption-induced resistance change, the procedures utilized in the study of the isothermal kinetics for H₂/Fe chemisorption and the results of this study are summarized in this section. A more comprehensive discussion of this study is presented elsewhere (20).

Experimental Considerations - Film Preparation

The iron films were prepared and the measurements were carried out in an all metal ultra-high-vacuum system. The vacuum system utilized the combination of a titanium sublimation pump with a liquid nitrogen cooled cryopanel and an ion pump to achieve vacuums on the order of $6.6 \times 10^{-8} \text{ N/m}^2$ (5×10^{-10} torr) after bakeout and repeated cycling at hydrogen pressures up to 1.3×10^{-3}

N/m^2 (10^{-5} torr). The residual background at $6.6 \times 10^{-8} N/m^2$ was primarily He and H_2 . Hydrogen gas was introduced into the vacuum system during the measurements through a mechanical leak valve under flowing gas conditions to eliminate the buildup of gaseous impurities. A conductance valve between the experiment chamber and the pumping system reduced the gas load to the pumps.

The polycrystalline iron films used in the study were grown by sublimation from high purity iron wire filaments onto carefully cleaned (and outgassed) glass microscope slides. The substrate temperature was about 340 K during evaporation. The films were grown at a constant rate of about 0.02 nm/sec with planar dimensions of 1×40 mm and thicknesses ranging from 2 - 50 nm. During evaporation the pressure in the vicinity of the substrate (exclusive of the iron vapor) was on the order of $1.3 \times 10^{-8} N/m^2$ (1×10^{-10} torr) and composed of He and N_2 . The N_2 was the result of outgassing from the iron filament. The surface of the film was chemically pure, as determined by AES on films with $d > 20$ nm, except for a small amount of oxygen which came from the evaporation filament. Films used for measurements at room temperature (about 295 K) were annealed for several hours at ambient temperature to stabilize their resistance. Films used for measurements at higher temperatures were annealed for 30 minutes at a temperature about 50 K higher than the highest planned measurement temperature. The substrate was pressure contacted against the substrate holder which contained an integral resistance heater. The substrate temperature was monitored by a thermocouple bonded to the substrate and the temperature maintained by suitable electronics which controlled the power to the resistance heater.

Kinetic Measurements

There is a variety of kinetic measurements possible for reversible chemisorption systems such as the H_2/Fe system. One measurement has already been discussed in an earlier section, the resistance isotherm. Although this is really an equilibrium measurement, the equilibrium constant K obtained from an analysis of the isotherm is directly related to the rate constants of the reaction process. Hence K can be used as an independent check on rate constants obtained from the kinetic measurements or as a way of obtaining an unknown rate constant. The three principal kinetic measurements used for the H_2/Fe study are; (1) (gross) adsorption, (2) (gross) desorption and (3) p-j (pressure-jump) relaxation measurement. The adsorption and p-j relaxation measurement are schematically shown in Fig. 7. An additional measurement, which will not be discussed, is fluctuation spectroscopy (28). This procedure utilizes the thermally driven coverage fluctuations at equilibrium to obtain a measure of fast kinetic processes (32).

In the adsorption measurement, illustrated in Fig. 7(a), the initial hydrogen pressure, p , is at a very low value ($< 1.3 \times 10^{-7} N/m^2$). Hydrogen adsorption at pressures below $1.3 \times 10^{-7} N/m^2$ is very slow (the adsorption rate is directly proportional to pressure) and the equi-

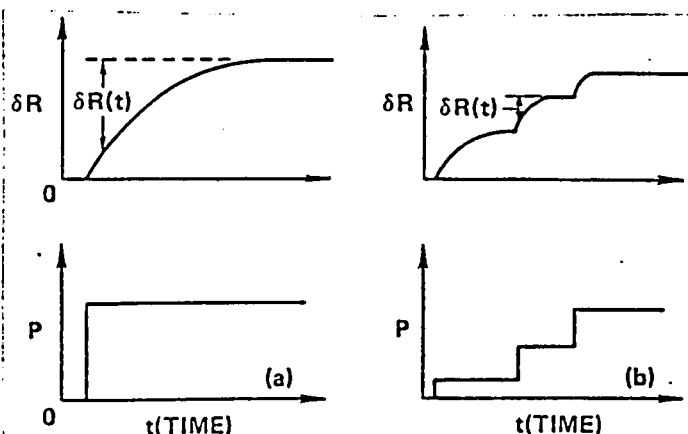


Fig. 7 - Schematic illustration of two of the principal measurements used for the H_2/Fe kinetic study; (a) adsorption measurement and (b) p-j relaxation measurement.

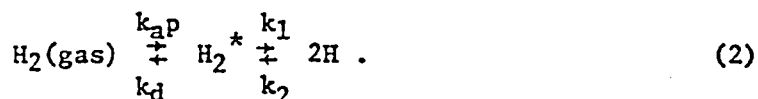
librium coverage is very small (as estimated from the resistance isotherm). The hydrogen pressure is then rapidly increased to a predetermined value while monitoring the resistance change (34). The final magnitude of the resistance change is proportional to the coverage of chemisorbed hydrogen and the initial slope of the resistance change is proportional to the initial rate of chemisorption on the clean iron surface. The entire curve of the resistance change as it approaches equilibrium describes the kinetics of adsorption. For the H₂/Fe system the approach to equilibrium follows an exponential behavior as shown in Fig. 8. The adsorption rate, τ_a^{-1} , is the decay constant of the exponential.

The desorption measurement is the opposite of adsorption. Starting from equilibrium at a hydrogen pressure p , the pressure is suddenly reduced to below 1.3×10^{-7} N/m² (1×10^{-9} torr) while observing the decay of the resistance change. For hydrogen chemisorption on iron, the resistance change is reversible on a time scale of minutes or less at temperatures above 300 K. The initial slope defines the desorption rate while the approach of the resistance change back to zero describes the overall desorption kinetics. For the H₂/Fe system the approach to equilibrium for desorption follows an exponential behavior; the desorption rate is simply defined as the decay constant of the exponential. The fastest desorption rate that can be measured depends upon the speed of the pumping system. For this work the upper limit for the desorption rate was about 2 sec⁻¹.

The p-j (pressure jump) relaxation measures the approach of the resistance change to equilibrium for small deviations in coverage away from an initial equilibrium coverage. This measurement is illustrated in Fig. 7(b), where the deviation from equilibrium is created by small step function changes in the hydrogen pressure (hence the name pressure-jump relaxation measurement) at constant temperature. The approach to the new equilibrium will always be exponential for small changes in the coverage. This is not generally true for the (gross) adsorption-desorption kinetics. The advantage of the p-j relaxation measurement is that it permits a direct measurement of the coverage dependence of the kinetic rates. A coverage dependence for the kinetic rates was not observed for the H₂/Fe system.

Chemisorption Model and Results

Measurements of the adsorption-desorption kinetics and rates give general information on the overall chemisorption process. Detailed information on the individual processes requires the use of a specific model. For H₂/Fe, the model used to analyze the data is schematically shown in Eq. 2,



In the model, molecular hydrogen adsorbs into the molecular state on the surface (precursor), H₂^{*}, with a rate given by k_{ap} . Chemisorption occurs

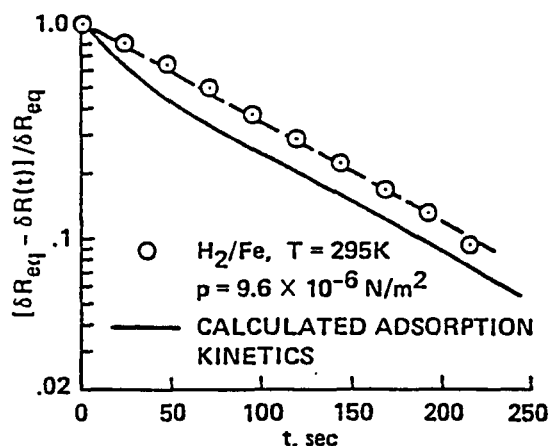


Fig. 8 - Comparison between data for the approach to equilibrium coverage for H₂ chemisorption onto an Fe film and the corresponding adsorption kinetics calculated from the adsorption model.

when the precursor goes into the dissociated chemisorbed state, H, with rate k_1 . For desorption, the atoms in the chemisorbed state recombine and go to the precursor at rate k_2 . The precursor then desorbs into the gas phase with a rate k_d . The rate constants k_1 , k_2 and k_d are temperature dependent with various activation energies. The constant k_a is equal to $\alpha/\bar{n}\sqrt{2\pi mk_B T}$, where α is the probability for adsorption into an empty precursor site, \bar{n} is the average number of precursor adsorption sites per unit area, m is the mass of a hydrogen molecule, k_B is Boltzman's constant and T the gas temperature.

The non-linear, coupled equations which describe the model were solved exactly using numerical methods (20). Estimates of the rate parameters were obtained from an analysis of all the kinetic data using approximate solutions to the model. The agreement between the exact solutions of the model and typical data for the approach to equilibrium during adsorption is demonstrated in Fig. 8. Here the deviation of the resistance change from its final equilibrium value is shown as a function of time. The exact solution reproduces the exponential behavior observed in the measurements. As indicated in Eq. 2, adsorption into the precursor from the gas phase is pressure dependent, but the step from the precursor to the dissociated chemisorbed state is pressure independent. The chemisorption rate will therefore be pressure dependent except at high pressures where it will become pressure independent. This is illustrated in Fig. 9 for data of the adsorption rate, τ_a^{-1} , as a function of pressure at 295 K. The solid line in Fig. 9 is the result of an exact solution of the model. As can be seen in Fig. 9, the agreement between the model and the data is very good. This quality of agreement is found also for the desorption kinetics and the p-j relaxation measurements. It is therefore reasonable to assume that Eq. 2 describes the process of hydrogen chemisorption on iron. The rate constants obtained from these studies are summarized in Table I.

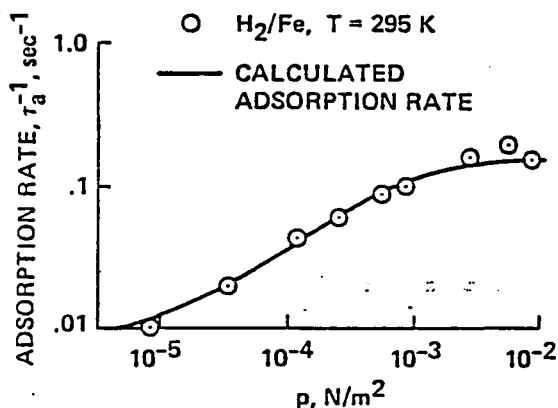


Fig. 9 - Comparison between data of the pressure dependence of the adsorption rate, τ_a^{-1} , for H_2 chemisorption onto an Fe film and the corresponding adsorption rate calculated from the adsorption model.

Table I. Rate Constants for H_2/Fe Chemisorption Reaction

Rate Constants	H_2/Fe
$k_a, (Nm^{-2}sec)^{-1}$	6×10^2 (at 300 K), $\alpha = 0.19$
k_d, sec^{-1}	$11T \exp(-28.9/RT)$
k_1, sec^{-1}	$604T \exp(-34.7/RT)$
k_2, sec^{-1}	$3.45 \times 10^{13} T \exp(-87.9/RT)$

R is in units of kJ/mole K and T is in degrees Kelvin (K).

Summary

The techniques available to easily and reliably study hydrogen chemisorption on metal surfaces are limited in number. One of the available techniques is the chemisorption-induced resistance change whereby hydrogen chemisorption on the surface of a metal film changes the film's resistance at constant temperature. The magnitude of the resistance change is directly proportional to the coverage of chemisorbed hydrogen for adsorption on iron and nickel surfaces. This technique provides a means to monitor the coverage of chemisorbed hydrogen without modifying the adatom-surface complex. It has a large temporal response range (bandwidth) and good sensitivity for hydrogen, making it an ideal technique for isothermal kinetic studies. The chemisorption-induced resistance change technique has been successfully utilized to study the chemisorption kinetics of the H₂/Fe system.

References and Footnotes

1. G. A. Somorjai, Principles of Surface Chemistry, chap. 5; Prentice-Hall, Inc., New York, 1972.
2. (a) A. Cassuto and D. A. King, Surface Sci. 102 (1981) 388 and references therein; (b) M. R. Shanabarger, Solid State Commun. 14 (1974) 1015 and (c) J. K. Norskov, A. Houmoller, P. K. Johansson and B. I. Lundquist, Phys. Rev. Letters 46 (1981) 257.
3. F. C. Tompkins in Chemistry and Physics of Solid Surfaces, vol. II, Ralf Vanselow, ed.; CRC Press, Inc., Boca Raton, Florida, 1979.
4. W. Eberhardt, F. Greuter and E. W. Plummer, Phys. Rev. Letters 46 (1981) 1035.
5. Topics in Applied Physics, vol. 4 (Interactions on Metal Surfaces), R. Gomer, ed.; Springer-Verlag, New York, 1975.
6. G. Ertl and J. Kuppers, Low Energy Electrons and Surface Chemistry; Verlag Chemie, GmbH, Weinheim, 1974.
7. D. A. King in Chemistry and Physics of Solid Surfaces, vol. II, op.cit.
8. M. R. Shanabarger, to be published in Proceedings of the 3rd International Conference on Effect of Hydrogen on Behavior of Materials (Jackson Lake Lodge, Wyoming, August 26-31, 1980).
9. R. Gomer in Chemistry and Physics of Solid Surfaces, vol. II, op. cit. and G. Ehrlich in Chemistry and Physics of Solid Surfaces, vol. III, Ralf Vanselow, ed.; CRC Press, Inc., Boca Raton, Florida, 1980.
10. Methods of Surface Analysis, A. W. Czanderna, ed.; Elsevier Scientific Publishing Co., Amsterdam, 1975.
11. D. Menzel in Topics in Applied Physics, vol. 4 (Interactions on Metal Surfaces), op. cit. and D. Lichtman in Methods of Surface Analysis, op. cit.
12. E. Bauer and H. Poppa, Surface Sci. 99 (1980) 341.
13. A. Benninghoven, P. Beckmann, D. Greifendorf, K. -H. Muller and M. Schemmer, Surface Sci. 107 (1981) 148.

14. M. R. Shanabarger, *Surface Sci.* 44 (1974) 297 and R. Gorte and L. D. Schmidt, *Surface Sci.* 76 (1978) 559.
15. (H₂/Ni) G. Ertl and D. Koppers, *Ber. Bunsenges.* 75 (1971) 1017 and (H₂/Nb) D. I. Hagen and E. E. Donaldson, *Surface Sci.* 45 (1974) 61.
16. P. W. Selwood, Adsorption and Collective Paramagnetism; Academic Press, New York, 1962 and J. K. Blum and W. Gopel, *Thin Solid Films* 42 (1977) 7.
17. (H₂/Fe) L. M. Pecore and P. J. Ficalora, *Met. Trans.* 8A (1977) 1841.
18. J. W. Ceus in Chemisorption and Reactions on Metallic Films, vol. 1, p. 327, J. R. Anderson, ed.; Academic Press, New York, 1971.
19. (H₂/Ni) M. R. Shanabarger, *Phys. Rev. Letters* 43 (1979) 1964 and M. R. Shanabarger, *Solid State Commun.* 14 (1974) 1015; (H₂S/Fe) M. R. Shanabarger in Proceedings of the Fourth International Conference on Solid Surfaces and the Third European Conference on Surface Science, September 22-26, 1980, Cannes, France (Supplement a la Revue Le Vide, les Couches Minces, no. 201); (O₂/Fe) M. R. Shanabarger and R. D. Moorhead, to be published.
20. (H₂/Fe) M. R. Shanabarger and H. G. Nelson, to be published. Elements of this work has appeared in the following; M. R. Shanabarger in Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces, R. Dobrozemsky, ed.; Vienna, 1977; M. R. Shanabarger, *Surface Sci.* 52 (1975) 689 and Ref. 8.
21. P. Wissman in Springer Tracts in Modern Physics, vol. 77, chap. 6, G. Hohler, ed.; Springer-Verlag, Berlin, 1975.
22. R. Suhrmann and K. Schulz, *Z. Phys. Chem. (Frankfurt)* 1 (1954) 69.
23. W. M. H. Sachtler, *J. Chem. Phys.* 25 (1956) 751.
24. P. Zwietering, H. L. T. Koks and C. Van Heerden, *J. Phys. Chem. Solids* 11 (1959) 18.
25. G. Wedler and P. Wissmann, *Surface Sci.* 26 (1971) 389.
26. M. R. Shanabarger and Jo Wilcox in Proceedings of the Eighth International Vacuum Congress, September 22-26, 1980, Cannes, France (Supplement a la Revue Le Vide, les Couches Minces, no. 201). Recent measurements have established that $\delta R/R$ for O₂/Fe is independent of temperature down to 220 K.
27. M. R. Shanabarger and Jo Wilcox, paper presented at The Eighth International Vacuum Congress, September 22-26, 1980, Cannes, France.
28. G. S. De and H. Suhl, *Surface Sci.* 95 (1980) 67.
29. The procedures for calculating the temperature dependence and the thickness dependence of A for the scattering model are presented in Ref. 26. The temperature dependence calculated from the scattering model was normalized to the data in Fig. 6 at 320 K.

30. G. P. Harnwell, Principles of Electricity and Electromagnetism, p. 132; McGraw-Hill Book Company, Inc., New York, 1949.
31. F. Bozso, G. Ertl, M. Grunze and M. Weiss, Applications of Surface Sci. 1 (1977) 103.
32. H. G. Nelson, D. P. Williams and A. S. Tetelman, Met. Trans. 2 (1971) 953.
33. (H₂/Ni) M. R. Shanabarger, presented at the Berkeley Meeting of the American Physical Society, December 27-29, 1973; (N₂/Fe) M. R. Shanabarger, presented at the Fall Meeting of the California Catalysis Society, November 1-2, 1979, Irvine, CA; (O₂/Fe) M. R. Shanabarger, Jo Wilcox and H. G. Nelson, to be published in The Proceedings of the 28th National Symposium of the American Vacuum Society, November 3-6, 1981, Anaheim, CA.
34. M. R. Shanabarger, Surface Sci. 52 (1975) 689, see Fig. 1 for an example of typical (gross) adsorption data.

1. Report No. NASA CR-166327	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle An Investigation of the Kinetics of Hydrogen Chemisorption on Iron Metal Surfaces		5. Report Date April 1982	6. Performing Organization Code
		8. Performing Organization Report No.	
7. Author(s) Mickey R. Shanabarger		10. Work Unit No. T-4241	
9. Performing Organization Name and Address Quantum Institute University of California - Santa Barbara Santa Barbara, CA 93106		11. Contract or Grant No. NSG-2222	
		13. Type of Report and Period Covered Contractor Report - Final April 1977 - March 1980	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration		14. Sponsoring Agency Code 505-33-21	
		15. Supplementary Notes Technical Monitor: Dr. Howard G. Nelson, Mail Stop 230-4, NASA Ames Research Center, Moffett Field, CA 94035 (415) 965-6137, FTS 448-6137	
16. Abstract A study has been made of the isothermal kinetics of H ₂ , H ₂ S, and O ₂ chemisorption onto evaporated polycrystalline Fe films and H ₂ S chemisorption onto epitaxially grown (111) oriented Fe films. The measurements were made using the techniques of (1) chemisorption-induced resistance change and (2) Auger Electron Spectroscopy (for adsorbed sulfur and oxygen). This study also established the origin of the chemisorption-induced resistance change for these systems and its applicability to kinetic measurements (by comparison with applicable AES measurements). The chemisorption kinetics were interpreted as dissociative chemisorption via an adsorbed molecular species. The applicable rate constants were established. In none of the studies were the rate constants observed to be coverage dependent. By comparing the temperature dependence of the rate constants with absolute rate theory, the binding energies and activation energies of all the kinetic processes were obtained for the H ₂ /Fe system. The initial sticking coefficient was pressure dependent for both the H ₂ /Fe and H ₂ S/Fe systems. This results from the step between the adsorbed molecular state and the dissociated chemisorbed state being the rate limiting step for adsorption at certain pressures and temperatures. Estimates were obtained for the temperature dependence of the rate constants for the O ₂ /Fe system using other data in the literature.			
17. Key Words (Suggested by Author(s)) Chemisorption, kinetics, H ₂ /Fe, H ₂ S/Fe, O ₂ /Fe, adsorption, desorption, excess current noise		18. Distribution Statement Unclassified - Unlimited STAR Category - 26	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 35	22. Price*

End of Document