1959


Lester Deurelle Hulett Jr
Louisiana State University and Agricultural & Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_disstheses

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_disstheses/562

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Historical Dissertations and Theses by an authorized administrator of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
KINETICS OF THE IRON-HYDROGEN SULFIDE REACTION AT HIGH TEMPERATURES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Lester D. Hulett, Jr.
B.S., Louisiana State University, 1955
M.S., Louisiana State University, 1958
August, 1959
ACKNOWLEDGEMENT

The author wishes to express his deep gratitude to Dr. Paul Delahay under whose direction this work was done. The author profited greatly by assisting Dr. Fritz Hügli, Dr. C. M. Hudgins, and Dr. H. Arm in the initial phase of this work. These men are primarily responsible for the development of the experimental techniques, and I am very grateful for their guidance. The author's immediate colleague in this work was Dr. M. M. Qureshi. His help and advice are deeply appreciated. Mr. E. G. Smith and Dr. G. F. Mathes of the Mechanical Engineering Department, Louisiana State University, provided equipment and guidance in the microphotographic studies; the author is very grateful for their help.

Throughout the course of our research, several conferences were held with members of the American Petroleum Institute Subcommittee on Corrosion. Private conferences with Dr. A. Dravnieks and Dr. E. W. Haycock were also held. Many useful suggestions came from these conferences.

The financial support of the American Petroleum Institute, which made this work possible, is gratefully acknowledged.
TABLE OF CONTENTS

I. SCOPE OF INVESTIGATION 1
   1. Purpose of Study 1
   2. Previous Work 1
   3. Methods of Attack 3

II. EXPERIMENTAL METHODS 5
   1. Attack in Hydrogen Sulfide and Hydrogen Sulfide-Hydrogen or Hydrogen Sulfide-Helium Mixtures 5
   2. Mixed Attack 6
   4. Diffusion of Hydrogen in Iron and Iron Sulfide Scale 10
   5. Scale Thickness Studies 12

III. THE MECHANISM OF THE IRON-HYDROGEN SULFIDE REACTION 14
   1. Postulated Mechanism 14
   2. General Characteristics and Effect of Temperature 15
   4. Mixed Attack 22
   5. Influence of Diffusing Hydrogen on Sulfur Vapor Attack 24
   6. Recrystallization of the Scale 31

IV. CONCLUSION 33

V. SELECTED BIBLIOGRAPHY 34

VI. VITA 35
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A.</td>
<td>Apparatus for Reaction of Iron with Hydrogen Sulfide and Mixtures of Hydrogen Sulfide and Hydrogen or Hydrogen Sulfide and Helium</td>
<td>6</td>
</tr>
<tr>
<td>1B.</td>
<td>Apparatus for Mixed Attack Experiments and for Hydrogen Diffusion Experiments</td>
<td>6</td>
</tr>
<tr>
<td>2A.</td>
<td>Apparatus for Measuring Rates of Hydrogen Diffusion through Iron and Iron Sulfide</td>
<td>11</td>
</tr>
<tr>
<td>2B.</td>
<td>Apparatus for Scale Studies</td>
<td>11</td>
</tr>
<tr>
<td>3.</td>
<td>Weight Gain of Iron Against Time for Reaction in Hydrogen Sulfide at 1 Atmosphere at Different Temperatures</td>
<td>16</td>
</tr>
<tr>
<td>4.</td>
<td>Microphotograph of Section of Specimen after 60 min. Exposure to Hydrogen Sulfide at 1 Atmosphere and 649°C</td>
<td>17</td>
</tr>
<tr>
<td>5.</td>
<td>Arrhenius Plots of the Rate Constant for Attack in Hydrogen Sulfide and in Hydrogen-Hydrogen Sulfide Mixture</td>
<td>18</td>
</tr>
<tr>
<td>6.</td>
<td>Rate of Attack at 649°C Against Volume Per Cent of Hydrogen Sulfide for Mixtures of Hydrogen Sulfide with Hydrogen or Helium</td>
<td>20</td>
</tr>
<tr>
<td>7.</td>
<td>A Verification of Equation (3) for the Data in Fig. 6</td>
<td>23</td>
</tr>
<tr>
<td>8.</td>
<td>Increase of Weight Against Time for Specimens Previously Attacked in Sulfur Vapor</td>
<td>25</td>
</tr>
<tr>
<td>9.</td>
<td>Microphotograph of Specimen Subjected to Mixed Attack by Sulfur Vapor and Hydrogen Sulfide</td>
<td>26</td>
</tr>
<tr>
<td>10.</td>
<td>Plots of the Square of the Weight Gain for Iron Cartridge during Attack by Sulfur Vapor</td>
<td>28</td>
</tr>
</tbody>
</table>
11. Data for Hydrogen Diffusion through Iron or Iron Coated with Iron Sulfide Scale
LIST OF TABLES

Table                                                                                         Page
I. Thicknesses of the Dense Layer of Iron Sulfide
    Produced by Attack by a 4:1 Hydrogen-Hydrogen Sulfide Mixture at 575 °C                  32
ABSTRACT

The mechanism of the iron-hydrogen sulfide reaction was studied in the 500-760°C temperature range for a total gas pressure of one atmosphere. The rate of attack was essentially constant (linear law), and the corrosion scale was composed of two layers: a thin dense layer adjacent to the metal and a porous layer with a coarse crystalline structure. These two features which differentiate this reaction from the iron-sulfur vapor reaction are interpreted on the basis of two main effects: (a) partial blocking of reaction sites by hydrogen produced during attack, and occurrence of a reaction at a constant number of reaction sites; and (b) continuous recrystallization of the dense scale into a porous scale offering no barrier to transport of reactants. This mechanism is self-regulating.

The following evidence is presented: (a) linear Arrhenius plots were obtained; (b) essentially the same rate of attack was observed for hydrogen-hydrogen sulfide and helium-hydrogen sulfide mixtures having the same partial pressure of hydrogen sulfide; and the dependence of rate on hydrogen sulfide pressure was accounted for; (c) the attack rate was not affected by the coating of specimen with a dense layer of varying thickness obtained by preliminary attack in sulfur vapor; (d) the iron-sulfur reaction,
which obeys the parabolic law of attack, was inhibited by hydrogen diffusing from the back of the specimen surface; (e) recrystallization of the dense layer into the porous one was observed for specimens aged in helium.

Discussion of experimental methods covers the following points: (a) measurements of the rate of attack with a quartz spring balance in hydrogen-hydrogen sulfide and helium-hydrogen sulfide mixtures; (b) techniques for attack in sulfur vapor followed by hydrogen sulfide attack; (c) use of a mild steel cartridge containing lithium aluminum hydride in the hydrogen diffusion studies; (d) scale thickness studies.
CHAPTER I

SCOPE OF INVESTIGATION

1. PURPOSE OF STUDY

The iron-hydrogen sulfide reaction at elevated temperatures has two unusual features which distinguish it from most other metal-gas reactions with solid scale formation: (a) the rate of attack becomes constant after a short time (a few minutes above 500°C), i.e., the attack follows a linear law, and (b) a scale composed of two layers is formed, the layer adjacent to the metal having a fine crystalline structure and the outer layer being of a porous and coarse structure. In contrast, the iron-sulfur reaction, according to Hauffe and Rahmel (1), follows the normal parabolic law of attack (corresponding to a diffusion controlled process) with formation of a single homogeneous scale having a fine crystalline structure. The same product of attack, iron sulfide, is obtained in both reactions, and yet the kinetics are very different. It is the purpose of this dissertation to account for these differences.

2. PREVIOUS WORK

The two fundamental characteristics of the iron-hydrogen sulfide reaction -- linear law and a two-layer scale -- were well established in earlier work. This material was reviewed by
Hudgins (2) and by Dravnieks and Samans (3). Initial work by Hügli and Hudgins in this laboratory indicated that the kinetics was accounted for by a modified Wagner model (reaction with diffusion control) but subsequent work by these authors and the writer disproved this explanation. Recent kinetic investigations of this problem were also made by Dravnieks and Samans (3) and by Haycock (4). The manuscript of the former authors was available at the onset of our work while Haycock's manuscript became available in the fall of 1958.

Dravnieks and Samans postulate a mechanism controlled by a surface reaction which they assume to be the dissociation of hydrogen sulfide at the scale surface. They account for the two-layer scale by assuming two different processes, namely diffusion of sulfide ions in the dense layer and diffusion of ferrous ions in the coarse layer.

Haycock (4) postulates mixed control by diffusion of sulfide ions across the dense layer and recrystallization of the dense layer into the porous layer. A linear law is observed when the dense layer reaches a constant thickness. Continuous recrystallization is greatly accelerated by hydrogen produced in the iron-hydrogen sulfide reaction. Haycock also believes, by analogy with other cases (5), that hydrogen is trapped in the cation vacancies of the lattice with the formation of what he calls "E-centers". These E-centers greatly decrease the rate of diffusion of ferrous ions and, according to him, sulfide ions therefore must be the
diffusing species.

3. METHODS OF ATTACK

Our purpose was to design experiments to discriminate as unambiguously as possible between control by a surface reaction and that by a diffusion process and to determine the role of hydrogen in recrystallization of the dense layer into a coarse layer (not observed when hydrogen is not present). The following studies were made:

(a) Confirmation of the linear law at different temperatures and determination of the heat of activation.

(b) Attack in mixtures of hydrogen sulfide and hydrogen or helium

(c) Attack of iron in sulfur vapor followed by hydrogen sulfide attack.

(d) Study of the effect of hydrogen on the iron-sulfur vapor reaction, hydrogen being supplied by diffusion through the iron from the unexposed face of the corroding specimen.

(e) Determination of the scale thicknesses and effect of aging on the two-layer scale.

Experiment (a) would give an indication of mixed control by two processes having different heats of activation if a non-linear Arrhenius plot were obtained. The combination of experiments (b), (c), and (d) should allow discrimination between
control by a surface reaction and by diffusion. Experiment (e) should provide direct evidence of recrystallization.
CHAPTER II

EXPERIMENTAL METHODS

1. ATTACK IN HYDROGEN SULFIDE AND HYDROGEN SULFIDE-HYDROGEN
OR HYDROGEN SULFIDE-HELIUM MIXTURES

Rates of attack were determined from the increase in specimen weight. The specimen in the lower, Vycor made reaction chamber (Fig. 1A) was suspended on a fine Vycor fiber attached to a quartz spring (obtained from Worden Laboratories, Houston, Texas). The quartz spring extended only in the upper, Pyrex made, chamber and was essentially at room temperature; i.e., no temperature correction in the calibration was necessary. The elongation of the spring was measured with a cathetometer (Gaertner, Chicago) with an error not exceeding 0.05 mg. for specimens weighing approximately 0.5 g.

The chamber with its gas preheater coil was connected to a gas mixing system which could supply hydrogen and mixtures of hydrogen sulfide with either hydrogen or helium. Traces of oxygen in the electrolytic grade hydrogen (Matheson) were removed by passing the gas through a "Deoxo" catalyst cartridge (obtained from Engelhard Industries, Inc., Newark, N.J.). Hydrogen sulfide and helium were used as supplied in tanks (Matheson). The composition of the gas mixtures was constantly controlled (a) from the individual flow rates, as measured with differential pressure.
**Fig. 1A** - Apparatus for the study of the reaction of iron with hydrogen sulfide and mixtures of hydrogen sulfide and hydrogen or hydrogen sulfide and helium. F - specimen; S - quartz spring; P - gas preheater coil.

**Fig. 1B** - Apparatus for mixed attack experiments and for hydrogen diffusion experiments. F - iron cartridge or other specimen; S - quartz spring; E - sulfur pool; P - gas preheater coil; M - platinum wire marker.
manometers, in the determination of the heat of activation, and (b) by a sensitive thermal conductivity cell in the comparison of attack rates for hydrogen-hydrogen sulfide and helium-hydrogen sulfide mixtures. A gas reservoir with twice the capacity of the reaction chamber was inserted between the chamber and the mixing system. The gas reservoir was used in the initiation of the reaction. The reaction chamber was bypassed during the adjustment of the gas mixture composition.

Specimens were made of spectroscopically-pure iron sheets, for which the suppliers (Jarrell Ash Co., Newtonville, Massachusetts) gave the following analysis: 4ppm Mn; 2ppm Ni, Si, Mg; 1ppm Cu, Ag, Na, Li; other metals were not detected spectroscopically. The specimen dimensions of approximately 0.05 x 0.7 x 1.4 cm. were determined accurately with a micrometer. Specimens were washed in petroleum ether and acetone before use.

After introduction of the specimen in the reaction chamber the entire flow system was evacuated to a pressure below 1 mm. The absence of leaks was ascertained, and the system was repeatedly flushed with hydrogen and finally evacuated again. Hydrogen was then passed through at a rate of approximately 200 ml. per minute, and the furnace was brought to the desired temperature. Reduction of traces of oxide on the specimen followed for two hours at 500°C or a higher temperature. After removal of hydrogen by evacuation, the gas mixture was passed through the chamber at the rate of 200 ml. per minute, and the attack was followed as
described above.

2. **MIXED ATTACK**

Experiments in which attack by sulfur vapor was followed by hydrogen sulfide attack involved one difficulty, namely that, to avoid condensation, no part of the apparatus could be colder than the vessel in which sulfur was vaporized. The Pyrex chamber of Fig. 1B, which was designed by E. Arm in this laboratory, was constructed with the upper end open. Sulfur was introduced, and the specimen, suspended on a quartz spring, was hung on an inverted U-rod. The top of the chamber then was sealed. Procedures for the purging and reduction were the same as for the hydrogen sulfide attack. After reduction of the specimen, the chamber was filled with helium and sealed at the constricted sections of the side arms, the upper part of the chamber being maintained all the time at 575°C. The lower furnace was raised around the sulfur reservoir and heated to 230°C. Vaporized sulfur condensed in the section of the chamber (between the two furnaces), approximately 2 inches in length, which remained cool during the warm-up of the lower furnace. Heater sleeves were slipped over the side arms to avoid sulfur condensation. After the lower furnace reached 230°C, a heater clamp was placed around the exposed midsection, and attack of the specimen was initiated. This method reduced the uncertainty of the zero time to a few minutes.

After the desired increase in weight, as followed by the
cathetometer, had been reached, sulfur attack was stopped by removal of the lower furnace, the upper furnace remaining at 575°C. The heater sleeves were removed and the gas flow system, discussed above, was connected to the sidearms with thick-walled Tygon tubing. The system was then evacuated and purged with hydrogen. The H₂S-H₂ mixture of previously adjusted composition, was introduced in the chamber by the snapping of the sidearm tips inside the Tygon tubing at the inlet and outlet. Rates of attack were determined from cathetometer readings for a gas flow rate of 200 ml. per minute.

3. INFLUENCE OF DIFFUSING HYDROGEN ON THE IRON-SULFUR REACTION

The effect of hydrogen diffusing from the back of the specimen surface during attack in sulfur vapor was studied. The specimen was a mild carbon steel cartridge, 4 x 20 mm. with a bore of 2 mm. diameter, containing 20 mg. of lithium aluminum hydride. The air in the cartridge was flushed with helium while the mouth was crimped together. The cartridge was immediately sealed with an acetylene torch, the lower part of the cartridge being kept cold in water. A platinum wire was attached to the top of the cartridge for suspension purposes, and the wire and sealed portion of the cartridge were masked with a porcelain cement (Saureisen). The cement was allowed to harden in air for at least 24 hours before the cartridge was used. Immediately before use, the cartridge was polished with Behr-Manning 400A sandpaper and jeweler's rouge cloth and then washed with acetone and
petroleum ether.

The cartridge and a long platinum wire were suspended on a quartz spring inside a Pyrex tube whose bottom had been filled previously with sulfur (Fig. 1B). This Pyrex tube was provided with an inlet and outlet for hydrogen. The tube was then sealed at the top and placed in a furnace. The cartridge was reduced for two hours in a stream of hydrogen, the lower part of the reaction tube remaining at room temperature. After reduction, the furnace was cooled and the tube was removed. The hydrogen remaining in the tube was replaced with helium, and the gas inlet and outlet were sealed off and shortened so that they would not protrude outside the furnace. Sulfur attack followed according to the procedure described in the previous section.

In some experiments with blank cartridges, i.e., without lithium aluminum hydride, the reaction tube was evacuated after hydrogen reduction and kept at a pressure of 0.02 mm. for eight hours to remove the hydrogen which had diffused into the metal.

4. DIFFUSION OF HYDROGEN IN IRON AND IRON SULFIDE SCALE

Rates of hydrogen diffusion through iron with or without ferrous sulfide scale were obtained with the chamber of Fig. 2A. The initial steps were the same as in the preceding section. After reduction, hydrogen was replaced by helium in the chamber. The side arm on the left was sealed off close to the wall of the chamber, and the small sidearm protruding from the U-tube was sealed off at the constriction. Condensation of sulfur was
Fig. 2A - Apparatus for measuring rates of hydrogen diffusion through iron and iron sulfide. S - quartz spring; F - cartridge; E - sulfur pool; M - platinum wire marker; H - differential pressure manometer; Q - tube containing the reference volume of gas at the same temperature as the cartridge.

Fig. 2B - Apparatus for scale studies. F - specimens; W - chromel wires; T - thermocouple; C - detachable casting tubes containing sulfur; D - rubber stoppers; R - cooler.
prevented by a specially shaped heater. Sulfur vapor attack was carried out at 500°C all the time. The U-tube was connected, after removal of its heater, to a vacuum system with a thick wall Tygon tube. A small glass bulb containing 5 ml. of mercury was also connected near the U-tube and in parallel with the vacuum system. The tip of the sidearm in the Tygon tube was snapped and the reaction chamber was evacuated with the fore-pump. The sulfur reservoir was sealed off to eliminate subsequent errors in pressure measurements as a result of gas release from the sulfur. Evacuation to 1 micron was continued with an oil diffusion pump. Mercury from the small reservoir was poured through the sidearm and into the U-tube, and the sidearm was sealed. An all glass, completely sealed system with a built-in differential pressure manometer was thus obtained. The pressure variations in the reaction chamber resulting from hydrogen diffusion through the cartridge wall were measured with a cathetometer.

5. **SCALE THICKNESS STUDIES**

A special reaction vessel was designed for scale thickness studies to allow rapid casting of specimens in molten sulfur. Five specimens (only three shown in Fig. 2B) were suspended on chromel wire by means of insulating glass hooks. The wires were strung through rubber stoppers. The casting tubes were filled with sulfur chips which were melted with a clamp heater just before the casting of a specimen. After attack in a hydrogen sulfide-hydrogen mixture, the specimen was lowered into the
molten sulfur, and the casting tube was allowed to cool. The five specimens could be cast at different times. The reduction in hydrogen before attack and the attack were conducted as above.

The tendency of the scale to peel off as a result of the temperature change was minimized by the use of curved specimens as suggested by Haycock (4). The scale remained quite adherent on the concave side.

Mounted specimens were cut with a high-speed, glass-cutter's saw. The cross section was polished with graded emery cloths and levigated alumina on a metallographic polishing wheel. A Bausch and Lomb metallographic microscope was used for examination and photography.

Specimens obtained in mixed attack and cartridges from experiments with hydrogen diffusion were mounted in an EPON resin. The procedure was as follows: Add 9 parts EPON 828 to 1 part curing agent (DTA); mix well; pour into mold around the specimen; allow the EPON to cure for 24 hours at room temperature.

---

1 Courtesy of Dr. E. W. Haycock, Shell Development Co., Emeryville, California. Information about EPON resins can be obtained from the Shell Development Co.
CHAPTER III
THE MECHANISM OF THE IRON-HYDROGEN SULFIDE REACTION

1. POSTULATED MECHANISM

The results of attack in helium-hydrogen sulfide mixtures and mixed attack experiments led us to postulate a mechanism for the iron-hydrogen sulfide reaction which was further confirmed by experiments on sulfur attack with hydrogen diffusion and experiments on aging of the scale. The mechanism is as follows:

Hydrogen produced by the iron-hydrogen sulfide reaction remains in large part adsorbed (or associated in some other fashion) with iron sulfide. The number of reaction sites available for attack by hydrogen sulfide is considerably decreased as a result of hydrogen adsorption, and attack occurs at an essentially constant number of reaction sites, i.e., a linear law of attack is observed. Furthermore, diffusion is not rate controlling (at least at sufficiently high temperatures, i.e., above 500°C approximately) because of continuous recrystallization of the scale into a coarse layer which offers no diffusion barrier. The thickness of the thin layer is not sufficient to result in diffusion control.

This mechanism is self-regulating in that a decrease (or increase) in rate would result in a decrease (or increase) in the
rate of hydrogen production and, consequently, in an increase (or decrease) in the number of reaction sites. The latter effect then would compensate the initial decrease (or increase) in rate that caused it.

Supporting evidence will now be presented.

2. GENERAL CHARACTERISTICS AND EFFECT OF TEMPERATURE

The two essential characteristics of the iron-hydrogen sul­fide reaction -- linear law of attack and formation of a two-layer scale -- are apparent from the results of Hugli and Hudgins (2) in Figures 3 and 4. The slope of the log-log plot in Figure 3 is quite close to unity, i.e., the law of attack is linear. In the early stage of attack (5 - 15 minutes) the rate is somewhat larger than the constant rate observed afterwards. This effect causes the slope of the log-log plot in Figure 3 to be somewhat smaller than unity. The initial high rate possibly results from the difference in the metal and scale surfaces and the initial absence of adsorbed hydrogen.

At temperatures below 500°C, plots of the increase in specimen weight versus time exhibit a marked curvature (cf. Dravnieks and Samans (3) and Haycock (4) which is probably due to partial diffusion control.

Arrhenius plots for the data on Figure 3 and similar data obtained by the writer for $H_2S - H_2$ mixtures are linear (Fig. 5). The corresponding heat of activation is 30 Kcal./mole, as compared to 20 Kcal./mole according to Dravnieks and Samans (3) and 12 Kcal./mole according to Haycock (4). No explanation is offered
Fig. 5 - Weight gain of iron against time for reaction in hydrogen sulfide at 1 atmosphere at different temperatures.
Fig. 4 - Microphotograph of section of specimen after 60 min. exposure to hydrogen sulfide at 1 atmosphere and 649°C. (magnification, 200).
Fig. 5 - Arrhenius plots of the rate constant for attack in hydrogen sulfide and in hydrogen - hydrogen sulfide mixture.
for the discrepancy among these data.

**Mixed control of kinetics by two processes having rather different heats of activation** is ruled out by the linear plot of Fig. 5.

3. **ATTACK IN HYDROGEN SULFIDE-HYDROGEN AND HYDROGEN SULFIDE-HELIUM MIXTURES**

It is well established that the rate of attack of iron in hydrogen-hydrogen sulfide mixtures depends on the partial pressure of the gases (cf. Dravnieks and Samans (3) and references therein). The effect can be accounted for by thermodynamics, and there is little doubt that near equilibrium a thermodynamic interpretation holds. Hydrogen, however, might act primarily as a diluent in hydrogen-hydrogen sulfide mixtures with partial pressures corresponding to concentrations not near equilibrium. Essentially the same rate of attack should then be obtained with hydrogen-hydrogen sulfide and helium-hydrogen sulfide mixtures having the same partial pressures of hydrogen sulfide. This seems to be the case according to the data obtained by Hügli, Hudgins, and the writer (Fig. 6).

These observations preclude interpretation based on a Wagner model (2) for the kinetics of attack, since such a model presupposes equilibrium attainment at the metal-scale and gas-scale interfaces. Very different rates of attack would be obtained for a reaction obeying a Wagner model when hydrogen is replaced by helium, especially for low partial pressures of hydrogen sulfide.
Fig. 6 - Rate of attack at 649°C against volume per cent of hydrogen sulfide for mixtures of hydrogen sulfide with hydrogen or helium.
The data of Fig. 6 do not eliminate diffusion as a partial or total rate-controlling factor, but it can be concluded from them that equilibrium is not reached at the metal-scale and/or scale-gas interfaces. Of course, departure from equilibrium does not necessarily imply control by a surface reaction since the surface reaction might be too fast to be rate controlling.

Data of Fig. 6 can be interpreted on the basis of the postulated mechanism. It is assumed (a) that the attack rate is proportional to the partial pressure of hydrogen sulfide and (b) that the rate is proportional to the number of reaction sites, i.e., the "free area". Thus,

\[ v = kp(1 - \theta) \]  

(1)

where \( v \) is the attack rate, \( k \) a proportionality constant, \( \theta \) the "coverage" by hydrogen, and \( p \) the partial pressure of hydrogen sulfide. The coverage by hydrogen, \( \theta \), increases with the rate of production of hydrogen, i.e., with \( v \). A rigorous relationship between \( v \) and \( \theta \) would be complicated because it would include the adsorption isotherms for hydrogen and hydrogen sulfide, or kinetic terms corresponding to these isotherms, and possibly other considerations for the interaction between hydrogen and the scale (Haycock's E-centers (4)). It will suffice for the present purpose to assume without any claim to rigor that:

\[ \theta = k'v \]  

(2)

By elimination of \( \theta \) from equation (1) and (2) there follows an equation in the form of a Langmuir isotherm (but it should be
noted that the similarity ends with the form of the equation:

\[ v = \frac{kp}{1+k'p} \]  

(3)

It follows from eq. (3) that a plot of \( p/v \) against \( p \) should be linear. This is the case (Fig. 7) for the data of Fig. 6. Values of \( k \) and \( k' \) were not calculated in view of the approximation in eq. (2).

Dravnieks and Samans (3) also noted that the dependence of attack on pressure obeys a Langmuir isotherm type of equation, and, in fact, they reported linear plots of \( p/v \) against \( p \). Their explanation, however, is different from the one offered here.

4. MIXED ATTACK

Rather conclusive proof of the absence of diffusion control was obtained from mixed attack experiments. Data for attack in hydrogen-hydrogen sulfide mixtures (4:1) are given in Fig. 8 for specimens with different initial thicknesses of iron sulfide scale (as obtained by preliminary attack in sulfur vapor). After an initial period, which is interpreted below, the same rate of attack prevails regardless of the thickness of the initial scale of iron sulfide. This conclusion holds even when the initial scale was approximately twice as thick as the scale formed during hydrogen sulfide attack. An interpretation of the iron-hydrogen sulfide reaction based on control by diffusion in the scale is inconsistent with these observations.

It could be argued that the scale underwent some transformation during the initial hydrogen sulfide attack, and that
Fig. 7 - A verification of equation (3) for the data in Fig. 6.
the rate became constant when the thin dense layer obtained in
the usual hydrogen sulfide attack was formed. Examination of
the scale (Fig. 9) did not confirm this view. The outer scale
exposed to hydrogen sulfide was composed of large crystals, but
the bulk of the scale had remained quite compact and homogeneous.
Furthermore, the initial rate of attack in hydrogen sulfide was
higher than the constant value reached at a later stage, and yet
the initial scale (formed in sulfur vapor) had a fine crystalline
structure.

The initial rapid attack can be interpreted in terms of this
postulated mechanism. Thus, the area at the gas-iron sulfide
interface before hydrogen sulfide attack was larger than for the
metallic surface corresponding to the same projected area. Hence,
rates of attack by hydrogen sulfide were initially larger than
for a metallic specimen without prior sulfur attack. However, the
self regulating mechanism soon brought the rate to a constant
value. It is important that the curves of Fig. 8 for the three
thicker scales appear to be the same, i.e., the initial process
was independent of the scale thickness once a sufficiently thick
scale had been produced.

5. INFLUENCE OF DIFFUSING HYDROGEN ON SULFUR VAPOR ATTACK

Since hydrogen, in our interpretation, is supposed to block
in part the surface for attack in the iron-hydrogen sulfide
reaction, it was thought that a similar effect might be observed
in the iron-sulfur vapor reaction if hydrogen were allowed to
diffuse from the back of the specimen surface. The data of
Fig. 8 - Increase of weight against time for specimens previously attacked in sulfur vapor. Number on each curve is weight of iron sulfide in mg./cm.² formed during sulfur vapor attack. Temperatures: molten sulfur during sulfur vapor attack, 230°C; specimen during sulfur vapor and hydrogen sulfide attacks 500°C; curves are shifted for clarity.
Fig. 9 - Microphotograph of section of specimen after attack by sulfur vapor followed by hydrogen sulfide attack. Temperature: 575°C (Magnification, 200).
Fig. 10, obtained by the cartridge technique, confirm this inference. The parabolic law was confirmed for the blank cartridges which had been left in vacuum for 8 hours after hydrogen reduction. An induction period was observed for blank cartridges which had not been vacuum treated, and an even longer induction period was observed for cartridges containing lithium aluminum hydride. In all cases, sulfur attack resumed its normal course after a sufficiently long time. The interpretation is as follows:

Hydrogen produced in the lithium aluminum hydride cartridge diffused toward the outside surface of the cartridge and greatly reduced the attack by sulfur vapor. Nevertheless, an iron sulfide scale slowly built up. The diffusion rate for hydrogen through the compact scale (no leaks!) was lower than through iron, as shown in Fig. 11, and consequently, coverage of the scale by hydrogen decreased as the scale became thicker. This resulted in a progressive increase in rate of attack until the film had become so thick that diffusion was practically stopped. Attack then resumed its normal course. It was verified that cartridges after attack still contained active lithium aluminum hydride.

The same interpretation holds for the blank cartridges which had not been vacuum treated. Hydrogen which had diffused in the metal during reduction then hindered attack in sulfur vapor until it could no longer appreciably cover the scale surface.

An alternative explanation, based on thermodynamic considerations, namely that iron attack by sulfur did not proceed in the
Fig. 10 - Plots of the square of the weight gain against time for iron cartridge during attack by sulfur vapor. Temperatures during attack: molten sulfur, 230°C; cartridge, 500°C. Curves are equally shifted at the origin by 20 mg²/cm².
Fig. 11 - Data for hydrogen diffusion through iron or iron coated with iron sulfide scale. Number on each line is the weight of iron sulfide in mg per sq. cm. Temperature: 500°C.
presence of hydrogen, is ruled out. Thus, one calculates from the data of Rosenqvist (6) that the equilibrium constant for the reaction \( \text{FeS} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{S} \) at 500°C is \( 2 \times 10^{-4} \). The amount of hydrogen sulfide formed in one of the experiments was in fact determined by passing the gas through a detection tube used in air pollution studies\(^1\). A maximum amount of \( 6 \times 10^{-6} \) mole of hydrogen sulfide was formed in the reaction chamber. This small amount of hydrogen sulfide produced shows that the retarded rate of sulfur attack is definitely not due to the reduction of iron sulfide by the diffusing hydrogen.

Another possible interpretation according to which Haycock's E-centers, resulting from the presence of hydrogen in the film, decrease diffusion by cation vacancy does not account for the resumption of attack. Thus, the scale, at least in its inner layer, retained a relatively high concentration of E-centers because of the vicinity of hydrogen supply. This layer would have offered a permanent barrier to vacancy diffusion, i.e., attack would never have resumed unless the film had cracked. The latter explanation, however is invalidated by the very low diffusion rate of hydrogen through the scale (Fig. 11). Of course, one could say that sulfide ion is the diffusing species, but the role of hydrogen remains unexplained.

\(^1\)Courtesy of Prof. P. W. West, Louisiana State University
6. **RECRYSTALLIZATION OF THE SCALE**

It is well established (see Drawnieks and Samans (3) for review of literature) that the thin dense layer reaches an essentially constant thickness. The data on Table 1 confirm this. Therefore, there must be a continuous transformation of the thin dense layer into the porous one (Fig. 4). It has been observed that aging of the two layer scale in a helium atmosphere causes a progressive disappearance of the dense layer. Since such a transformation is not observed for iron sulfide produced by the iron-sulfur vapor reaction, hydrogen must be responsible for recrystallization. Haycock (4) suggested a tentative mechanism for the recrystallization process. Haycock also showed that hydrogen greatly enhanced the sintering rate of powdered iron sulfide. Powdered ferrous sulfide with a large initial surface area did not appreciably sinter when left in a vacuum for five hours at 500°C. In the presence of hydrogen at the same temperature the surface area was reduced by half after only two hours, and the powder had visibly sintered to a porous plug.
TABLE I

THICKNESSES OF THE DENSE
LAYER OF IRON SULFIDE PRODUCED
BY ATTACK BY A 4:1 HYDROGEN-
HYDROGEN SULFIDE MIXTURE AT 575°C

<table>
<thead>
<tr>
<th>Reaction Time (min.)</th>
<th>Thickness (mm. x 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>6.5</td>
</tr>
<tr>
<td>180</td>
<td>8.9</td>
</tr>
<tr>
<td>480</td>
<td>7.7</td>
</tr>
<tr>
<td>540</td>
<td>8.9</td>
</tr>
<tr>
<td>550</td>
<td>7.7</td>
</tr>
<tr>
<td>660</td>
<td>7.7</td>
</tr>
<tr>
<td>720</td>
<td>8.9</td>
</tr>
</tbody>
</table>
CHAPTER IV

CONCLUSION

It is concluded that the linear law of attack for the iron-hydrogen sulfide reaction at elevated temperatures (above 500°C approximately) results from two main effects: (a) partial blocking at reaction sites by hydrogen produced during attack, and (b) continuous recrystallization of the dense scale into a porous one offering no barrier to the transport of reactants. Blocking by hydrogen results in a reaction occurring with a constant number of reaction sites. A linear law is then observed since recrystallization prevents the formation of a thick dense scale that would be a sufficient diffusion barrier to cause departure from the linear law. The blocking of reaction sites is self regulating and the linear law is thus obeyed.
SELECTED
BIBLIOGRAPHY

1. Hauffe, K. and Rahmel, A.
"Über Den Mechanismen der Schwefelung von Eisen, Nickel, und Nickellegierungen bei höheren Temperaturen"

2. Hudgins, C. M.
"Mechanism of the Iron-Hydrogen Sulfide Reaction at Elevated Temperatures"
Louisiana State University, 1957. 50 numb. leaves.

"Kinetics of Reaction of Steel with Hydrogen Sulfide-Hydrogen Mixtures"

4. Haycock, E. W.
"High Temperature Sulfiding of Iron Alloys in Hydrogen Sulfide-Hydrogen Mixtures"

5. Coplan, D. and Cohen, M.
"High Temperature Oxidation of Some Iron-Chromium Alloys"

6. Rosenqvist, T.
"A Thermodynamic Study of the Iron, Cobalt, and Nickel Sulfides"
J. Iron Steel Institute, 176, 37 (1954).
VITA

Lester D. Hulett, Jr., was born in DeRidder, Louisiana, on May 31, 1933. He attended the DeRidder Elementary and High Schools, graduating in 1951. This same year he entered Louisiana State University and graduated with a Bachelor of Science degree in 1955 and a Master of Science degree in 1958. He is now a candidate for the degree of Doctor of Philosophy.

Mr. Hulett has membership in the American Chemical Society, Sigma Xi research society, Omicron Delta Kappa leadership fraternity, and Alpha Chi Sigma and Phi Lambda Upsilon chemistry fraternities. He also holds a USAR commission in the Army Chemical Corps. Mr. Hulett received an American Petroleum Institute fellowship to do the work presented in this dissertation.

Mr. Hulett is married to Frankie Gayle Mock Hulett and is the father of one daughter, Lisa Dee Hulett.
EXAMINATION AND THESIS REPORT

Candidate: Lester D. Hulett, Jr.

Major Field: Chemistry

Title of Thesis: Kinetics of the Iron-Hydrogen Sulfide Reaction at High Temperatures

Approved:

[Signatures of Major Professor and Chairman, Dean of the Graduate School, and other members of the Examining Committee]

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: July 9, 1959