THE DECOMPOSITION OF HYDROGEN SULFIDE

WITH TUNGSTEN CATALYST

By

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CHAPTER I

INTRODUCTION

The feasibility of a process to catalytically decompose hydrogen

sulfide into the elemental constituents, hydrogen and sulfur, has been

the subject of only a modest amount of research. Currently, the most

sophisticated processes recover only sulfur while oxidizing the hydrogen

to water by methods such as the Claus process. An improved process was

the topic of a thesis by Singh (9). Singh explored the use of a

molybdenum catalyst with moderate gas temperatures to produce molecular

hydrogen and unconfirmed elemental sulfur. The sulfur was presumed to

have been condensed from the gaseous phase in the horizontal reactor.

The gas temperature and the superficial gas velocity through the re-

actor were too low to drive the sulfur from the reactor. The sulfur,

which then contacted the tube wall, reacted with the nickel that was

present in the stainless steel to form nickel sulfide.

From the considerations of previous experiments and current pro-

cesses, the following objectives were formulated for this work:

1. Determine if sulfur from a catalytic decomposition could be

    recovered by an improved reactor design.

2. Test tungsten for catalyst feasibility.

3. Obtain kinetic data and establish a model for the data obtained

    in the new reactor.

The purpose of this work is to provide useful information concerning

the feasibility of establishing such a system under industrial con-
ditions.

In order to avoid some of the previous difficulties, the reactor
system was redesigned to facilitate removal of the elemental sulfur.
A vertical flow reactor was developed and installed in a temperature-
controlled muffle furnace. The reactor was modified to permit the re-
moval of the sulfur vapor by a downflow passage of the reactant gas.

The usefulness of a process of this nature has been emphasized by
recent governmental pressure on industry concerning the disposition of
waste gases and new restrictions on product specifications. Since the
advent of several industrially feasible processes for the decomposition
of hydrogen sulfide with the subsequent production of sulfur, the main
value of the process in this work is the production of hydrogen in
addition to the sulfur. Hydrogen, as is commonly known, is of stra-
tegic importance to our aerospace program as well as being of great use
in the chemical industry as a raw material. Therefore, the production
of hydrogen from this process would be of financial significance to
industry as a whole while removing a pollution menace.

CHAPTER II

LITERATURE SURVEY

Since the inception of the modern petroleum and natural gas pro-
cessing plants, processes to convert a noxious waste gas such as hydro-
gen sulfide into a money making product have been many and varied. Some
processes depend on the specific reaction of hydrogen sulfide to form a
sulfur compound such that the reactant is capable of being regenerated
by oxidation, such as the iron oxide process. Other processes depend
on the absorption reaction of hydrogen sulfide with an alkaline solu-
tion, such as the caustic soda process which proceed at the loss of the
reagent or dependency on secondary means for sulfur recovery.

The most widespread process in industry today, however, is the
Claus process. From a stream of hydrogen sulfide, one third is drawn
off and oxidized to sulfur dioxide. The sulfur dioxide is then remixed
with the original stream and burned over a bauxite catalyst to produce
water and elemental sulfur. The advantages of the Claus system are
clear in terms of catalyst economy; however, much work has been done on
other approaches including catalytic processes. Opel (8) and Singh (9)
have described the details of most of the related processes in their
work.

Considering for a moment that no catalyst is suitable for the pro-
cess in question, Darwent and Roberts (4) worked on the effects of
thermal and photochemical decompositions of hydrogen sulfide. Although,

in terms of this work, the Darwent and Roberts paper is chiefly of
interest due to the mechanism study, some of the qualitative effects of
temperature and pressure are also relevant. Photochemical studies sug-
gest the formation of hydrosulfide radicals (HS). Spectroscopic evi-
dence determined the existence of a strong diatomic sulfur (S_2) band.
From this information, the reaction mechanism scheme was proposed:

$$H_2S \rightleftharpoons H + HS$$

$$H + H_2S \rightleftharpoons H_2 + HS$$

$$2HS \rightleftharpoons H_2 + S_2$$

$$2HS \rightleftharpoons H_2S + S$$
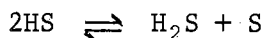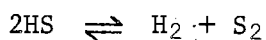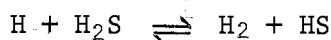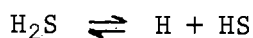
This reaction scheme is based on the photolytic effect of 2288 $\overset{o}{A}$ light
striking the molecule to provide the energy of activation required to
form the hydrosulfide radicals. The thermal decomposition also studied
in the paper, resulted in a simple bimolecular decomposition as follows:

$$2H_2S \rightleftharpoons 2H_2 + 2S$$

One should note that the energy requirement of 26 Kcal/mole favors a
two molecule mechanism over a monomolecular mechanism requiring
58 Kcal/mole. The thermal mechanism is anticipated to be related to
the catalytic mechanism of this work in the sense that spectroscopic
investigations by others in the catalytic field reveal the absence of
hydrosulfide radicals. Additionally, in the process of thermal work,
Darwent and Roberts made isothermal and isobaric studies. For a given
isotherm, an increase in pressure produced an increase in conversion
which would seem to contradict Le Chatelier's principle. This informa-
tion seems to imply that either the reverse reaction rate constants for

the reaction are small for the system or the sulfur condensed from the system as formation occurred. Under isobaric conditions, the reaction rate increases rapidly with temperature. Since the basic postulate for the thermal decomposition mechanism was collisional in nature, the kinetic theory of gases would support the increased reaction rate on a increased collision basis. The irregularity Darwent and Roberts found in temperature effects may be assigned to the activation threshold requirements of the system. The thermal decomposition studies provide an insight into the catalytic studies presented in the following paragraphs.

Among the pioneers in catalytic decomposition of hydrogen sulfide are Taylor and Pickett (10). While searching for purely unimolecular reactions, Taylor and Pickett decomposed hydrogen sulfide over a platinum filament catalyst. Their work contains the description of the catalytic behavior of hydrogen sulfide decomposition. Some conclusions were made about the mechanisms of catalytic decomposition and contamination of the platinum catalyst. The hydrogen sulfide was passed into the chamber and adsorbed by the heated platinum filament at about 1000 °C. The adsorption takes place with the sulfur atom oriented adjacent to the platinum. The decomposition takes place by means of a transition metal coordination of the outer orbital electrons of the sulfur atom, thus freeing the electrons of the attached hydrogen atoms. The hydrogen atoms are then released and immediately upon impact form diatomic hydrogen. The sulfur, due to the high temperature of the filaments, is then vaporized almost immediately to form a thin vapor over the filament. Noteworthy at this point is the fact that part of the sulfur is not revaporized but instead forms a stable complex with the

platinum. When such a stable complex is formed, the catalyst is slowly
deactivated or poisoned. Since the vast majority of the sulfur is re-
vaporized, Taylor and Pickett considered the consequences of the stag-
nant film about the filament. The sulfur film creates problems for the
hydrogen sulfide approaching the filament. First, the hydrogen sulfide
must go through a slow diffusion process to reach the catalyst surface.
Secondly, the high concentration of sulfur above the catalyst surface
served to promote the reverse reaction, thus lowering the conversion.
The data taken in the course of this experiment by Taylor and Pickett
provided a partial solution to the sulfur film. If the flow rate of
hydrogen sulfide across the filament is increasing, then the stagnant
film decreased. Increasing the flow rate provides a reverse effect also
in terms of increased conversion forming more sulfur. Yet the highest
overall conversions were obtained at the higher flow rate. At higher
temperatures the film caused less difficulty due to improved diffusion
at a higher temperature. The per cent conversions, nonetheless, drop-
ped from about twenty to fifteen per cent with increasing flow rates.
Further, Taylor and Pickett calculated an activation energy of
11,750 cal/gm mole.

After Taylor and Pickett, Kingman (5) explored the same type of
reaction using hydrogen sulfide and water with a molybdenum filament
catalyst. In Kingman's experiment, the test gas was passed into a
chamber containing a filament which ran the length of a cylindrical
Pyrex tube. The filament was maintained at a constant temperature while
the various residence times were examined. By measuring the pressure
of the entering hydrogen sulfide and freezing out the residual hydrogen
sulfide from the completed run, the conversion was recorded based on

the percentage change in hydrogen sulfide pressure. Plotting the logarithm of hydrogen sulfide pressure versus residence time in the reactor vessel, Kingman confirmed the reaction to be first order and monomolecular. A conversion on the order of seventy per cent for a one hour residence time at 685°C was reported. Kingman further confirmed the presence of hydrogen and elemental sulfur while noting that no molybdenum sulfide had been formed. A value for the activation energy for the reaction was calculated to be 25,000 cal/gm mole. During the decomposition of water vapor experiment, an oxide coating formed on the filament reducing the reaction rate to a negligible value. The fact infers that molybdenum sulfide formation might indeed be a problem under different conditions in the hydrogen sulfide process.

More recently, Blanchard and LeGoff (2) made a study of the decomposition of various chemical species on a pure tungsten and carburized tungsten ribbon. Among the materials studied was hydrogen sulfide which was observed between 1500°K and 2100°K. The results of the catalysis were determined by means of a mass spectrometer and only ion intensities were reported. One of the primary objectives was to discover if the hydrosulfide radical played any part in the mechanism of the catalysis. The location of the small hydrosulfide peak found just above the hydrogen sulfide peak was disclaimed by Blanchard and LeGoff as purely experimental error. The following reaction scheme was then proposed:

$$H_2S \xrightarrow[\text{ribbon}]{\text{pure W}} H_2 + S$$

$$2S \xrightarrow{\text{wall}} S_2$$
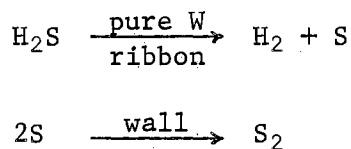
The ribbon was electrically heated with the walls remaining at an

ambient temperature. The procedure allowed the elemental sulfur to contact the surface, form diatomic sulfur unmolested on the wall, and reenter the vapor phase due to the low system pressure. The internal pressure of the system was recorded to be .00001 mm. of Hg which places a severe restriction on the operating conditions under ordinary circumstances. The importance of the transition metal catalyst was underscored in the second phase of the experiment with hydrogen sulfide. For the carburized tungsten, the following reaction mechanism was proposed:

$$H_2S + C \xrightarrow{\text{W-C ribbon}} H_2 + CS$$

$$2CS \rightleftharpoons CS_2 + C$$
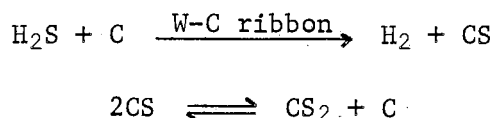
Although the reaction proceded quite readily on the carburized tungsten catalyst, no decomposition could be detected as high as 2100°K on pure carbon surfaces.

With a substantial portion of the possible catalysts proposed, Singh (9) set about the conversion of this idea into a useful industrial type experiment. Using ambient pressures, temperatures in the gas phase were increased to 350°F. Actual tube wall temperatures in the reactor were speculated to be about 1400°F. Under these conditions, Singh attempted to make useful application of a catalytic process. The apparatus consisted of a horizontal reactor made of 316 stainless steel pipe one half inch in diameter and forty inches long. Molybdenum foil catalyst was randomly dispersed in the reactor. Hydrogen sulfide was passed through a catalyst bed at between 500 and 1500 cc/min. Singh obtained a maximum conversion of 85.6 per cent at an interfurnace gas temperature of 350°F with 75.49 grams of catalyst. The thermocouples were set in the space between the electrically heated furnaces.

However, severe problems arose during the operation of the apparatus as the reactor tube became plugged repeatedly. Upon examining one of the tubes, large quantities of molybdenum sulfide were found. While inspecting a portion of the stainless steel reactor pipe, a metal sulfide was found to have destroyed approximately half the thickness of the tube. This metal sulfide, according to Mantell (7), was postulated to be nickel sulfide which is readily formed when 316 stainless steel is exposed to hot hydrogen sulfide. The conclusion drawn from this was the 1400°F internal reactor temperature had aided in the breakdown of the tube wall.

Although Singh's conversion was quite high, elemental sulfur was never obtained from the apparatus. Of the many authors discussed in this section, only Blanchard and LeGoff actually experimentally confirmed the presence of elemental sulfur but they did not obtain a quantitative appraisal of sulfur production. In order to improve upon some future apparatus, Singh suggested that the reactor should be in a vertical position with down flow to aid in the removal of sulfur vapor. The basic experiment that Singh performed did, however, provide the first pilot scale test for such a process, and despite imprecisions in the procedure, an activation energy of 23,050 cal/gm mole was obtained. Kingman calculated 25,000 cal/gm mole for the activation energy on a molybdenum filament.

One of Singh's difficulties was in the analytical procedure when assaying how much hydrogen sulfide had been converted in the reactor. Singh claimed a sensivity of .0000001 for the analytical balance which he used to measure conversion. This procedure, of course, cast some doubt on the quality of this portion of that data.

After being discouraged from a number of sources on the use of gas chromatography with hydrogen sulfide systems, an article by Adams and Koppe (1) stated that such an analysis had been accomplished when determining the composition of a corrosive paper pulp effluent gas mixture. The chromatograph provided another means of comparing the material balance closure properties with the effluent gas mixture.

In summary, little has been written and proposed about the problem of catalysis of hydrogen sulfide by a transition metal, and an industrial type process has not yet been elucidated. The use of heated filaments and ribbons or even foil does not represent a large scale, useful process. The fact that elemental sulfur has not been collected in sufficient quantities to make a macroscopic qualitative chemical analysis possible does not begin to meet the detailed data needs for scaling up such a process. The calculation of a fouling factor or possible techniques in the regeneration of a catalyst have as yet been neglected in the studies as mentioned. Therefore, much work is still to be done in this area.

Data Analysis For a Plug Flow Reactor

Since the actual size of the reactor is prescribed by several variables, a discussion of design variables is presented here as described by Levenspiel (6). A steady state plug flow reactor may be analyzed in terms of an elementary material balance of an irreversible reaction in order to yield the basic equation for residence time, t.

$$t = C_{A}o \int_{o}^{X_A} (1/k(C_A)^n) dX_A$$

Of course, any reaction may be considered irreversible if the reverse

reaction rate is small enough to include in an effective overall reaction rate. The expansion of the fluid is assumed to be proportional to conversion. For irreversible first order reactions, the residence time equation may be integrated to give:

$$kt = (1 + z_A)\log_e(1/(1 - X_A)) - z_A X_A$$

By the definition of residence time, the volume of the reactor and the volumetric flow rate may be substituted:

$$t = Ve_A/v_o$$

The rate constant for the reaction system may then be obtained.

$$k = (v_o/V)(1 + z_A)\log_e(1/(1 - X_A)) - z_A X_A$$

A disagreement arises between authors on the method of computing residence time. For this reason, Singh (9) used the residence time units of mass flow rate normalized over the amount of catalyst present. Other authors insist that only the residence time calculated on volumetric flow rate through the reactor can yield meaningful data. The above equation requires a volumetric flow type residence time. The above equation may be used in the design and scale up of processes of this nature barring other restrictions.

The temperature dependence of a reacting system is represented by the Arrhenius Law:

$$k = k_o(e^{-E/RT})$$

In order to remove the frequency factor dependency, the difference form of the above equation is often used.

$$\log_e(k_1) - \log_e(k_2) = -E(1/RT_1 - 1/RT_2)$$

To prove that the Arrhenius Law is applicable, a plot of the natural logarithm of the rate constant versus the reciprocal temperature must be constructed. Linearity indicates that the Arrhenius Law is applicable for the reaction in question. Of course, the lower the activation energy, the more quickly the reaction will proceed. Since the activation energy is dependent upon the catalyst involved, the information is then used to select the optimum catalyst. Alternately, the Arrhenius Law may be tested by means of a nonlinear curve fit which will examine all the data while testing the hypothesis.

Consideration of the thermodynamic equilibrium described by Blanchard and LeGoff leads to the conclusion that the value of the fractional volume change on a reaction, z_A, must lie between .5 to 1.0. This equilibrium condition is further complicated by the formation of allotropic forms of sulfur, such as S_4, S_6, and S_8. In addition, condensation occurred to some extent in the reactor. Consideration of these factors led to the arbitrary assumption of a value of .62 for z_A to be used in the Levenspiel design equation.

CHAPTER III

APPARATUS

Design Considerations

The system of hydrogen sulfide at elevated temperatures is one of the most difficult species one can deal with in the chemical world. First, since hydrogen sulfide is poisonous, the apparatus must be leak free, and the laboratory must be well ventilated. The apparatus accordingly was constructed from stainless steel. A large fan was installed in the room to aid ventilation while experimental runs were under way. Secondly, hydrogen sulfide is extremely corrosive to most metal systems. The problem was compounded by the fact that 1500°F was considered the minimum design temperature for the reactor system. According to the data available in Mantell (7), type 446 stainless steel was selected on the basis of low nickle content and excellent thermal strength properties. However, due to the lack of availability of 446 stainless steel and expedience, the system was constructed of 316 stainless steel which was more subject to corrosion than 446 due to a higher nickle content. The 316 stainless steel was, nonetheless, suitable for a small scale project such as this experiment. The remainder of the apparatus was constructed of Tygon tubing which conducted the cool effluent mixture to the absorber system.

System Component Descriptions

The numbers behind the process elements refer to Figure 1. An additional view of the reactor cell is shown in Figure 2.

Hydrogen Sulfide Source

The source consisted of a cylinder (1) of 98.5% hydrogen sulfide Matheson number EJ-3639, which had been used in previous work. To couple the tank to the system, a stainless steel Matheson regulator (2) was used. The regulator was further fitted with a stainless steel needle valve to control the flow rate.

Rotameter

A Brooks Brothers "Sho rate" rotameter (4) with tube size R-2-15-D was employed to measure the flow rate of hydrogen sulfide from the tank. The standard air curve which accompanied the rotameter was corrected for system pressure and hydrogen sulfide density. The final calibration curve is shown in Figure 8.

Pressure Gauge

The pressure gauge measured the pressure of the gas going into the reactor. If the pressure was not ambient, an obstruction was indicated. The apparatus was then shut down, and the obstruction was cleared. The gauge was a Crosby gauge which contained a stainless steel Bourden tube pressure sensing element. The gauge was calibrated against a Budinberg dead weight tester which is accurate to .05% (9). The calibration table is shown as Table 4.

Thermocouples

The three thermocouples (10, 11, and 12) were Con-o-clad type with 316 stainless steel sheathing for protection from the hydrogen sulfide. Using the design temperature of 1500°F, the Iron-Constantan type of thermocouple was selected. The thermocouples were placed just before the furnace, in the catalyst bed, and just after the furnace. Calibration was achieved by a secondary calibration from a Leeds and Northrup platinum resistance thermometer which is accurate to ±.0001°C. The calibration was accomplished in the muffle furnace of the experiment. Calibration curves are presented in Figures 9 and 10.

Muffle Furnace

The reactor (7), also see Figure 2, was contained in a Leco model 540-231-331 muffle furnace (6). This 230 volt furnace featured a temperature controller that could hold the reactor temperature ±5°F of the controller setting. The power rating of the furnace was 4600 watts and could operate as high as 3000°F. A small correction was necessary between the catalyst bed temperature and the controller setting due to internal heat transfer resistance.

Reactor

The reactor consisted of a two inch tube of schedule 80, 3/4 inch diameter, 316 stainless steel pipe welded between two plates. In the two plates were 1/32 inch diameter holes on the top plate to diffuse the gas and 1/16 inch diameter holes in the bottom plate to support the catalyst. The reactor was sealed by means of asbestos gaskets coated with Form-a-gasket sealing compound.

Catalyst

The catalyst originally was to have been molybdenum metal, but three factors altered the choice to tungsten. First, the use of other catalysts in the literature caused some interest in testing if Singh's (9) results were reproduceable in terms of another catalyst. Secondly, the melting point of tungsten is 3370°C as opposed to 2620° for molybdenum. Using this periodicity of elements, the melting point difference implies that sulfide formation for tungsten would take place at a higher temperature and thus provide greater catalyst stability. Finally, the availability of molybdenum metal is less than that of tungsten. Due to cost and availability considerations, 1/8 inch diameter tungsten welding rods that were two per cent thoriated were used for this study. Thorium dioxide is a stable compound used for improving the strength properties of the rods. The rods were broken up into cylinders approximately 3/8 inch long and randomly placed in the reactor tube.

Absorbers and Gas Measuring

The absorber section (8) consisted of three Pyrex bottles in which the gas was bubbled through concentrated (400 gram/liter) sodium hydroxide to remove the residual hydrogen sulfide left after the completion of the reaction. The gas measuring mechanism at the end of the system consisted of a water bath and an inverted graduated cylinder (9) in which the gas was collected and measured at ambient conditions. The collected gas was then analyzed.

Gas Chromatograph

The gas chromatograph was a Model GG 2500R Microtek with a thermal conductivity detector. Helium was used as the carrier gass. The column was a six foot, fifteen per cent Triton, X-305, 80-100 mesh prepared by the F&M Company. The column was maintained at 100°C while in operation. The chromatograph was frequently recalibrated during the course of a run. The thermal conductivity cell temperature averaged about 37°C during operation.

Heating Tape

Since the exit tube from the reactor was continually becoming plugged with solid elemental sulfur during the course of operation, two feet of one half inch wide doubly insulated heating tape (13) was installed to aliviate the nuisance. The tape was operated at ninty volts supplied by a Powerstat rheostat. The sulfur was then permitted to condense a section of Tygon tubing which was replaced as necessary.

Testing the Apparatus

The apparatus, as mentioned, was examined under ten pounds per square inch gauge pressure of helium. A soap solution was painted around all jointed surfaces to test for leakage. The asbestos gasketing material around the reactor was found to leak at pressures above ten pounds. Since the reactor would be under only ambient pressure, the system was considered satisfactory. As an additional precaution against leakage, all internal gasket surfaces were coated with Form-a-gasket sealing compound.

1. H₂S CYLINDER
2. H₂S REGULATOR
3. PRESSURE GAUGE
4. ROTAMETER
5. TEMPERATURE CONTROLLER
6. FURNACE
7. REACTOR CELL
8. NaOH ABSORBER
9. GAS COLLECTION DEVICE
10. PREFURNACE THERMOCOUPLE 1
11. REACTOR THERMOCOUPLE 2
12. POSTFURNACE THERMOCOUPLE 3
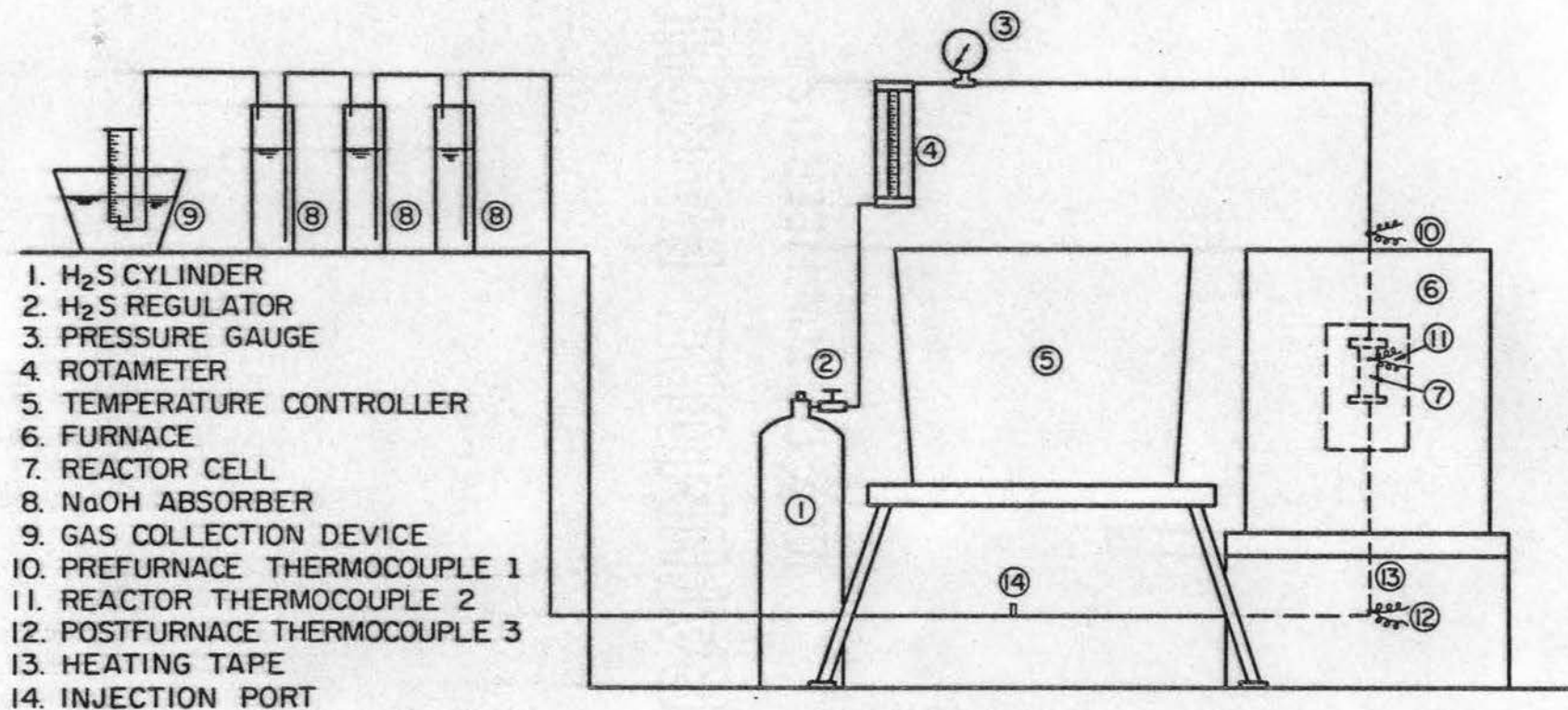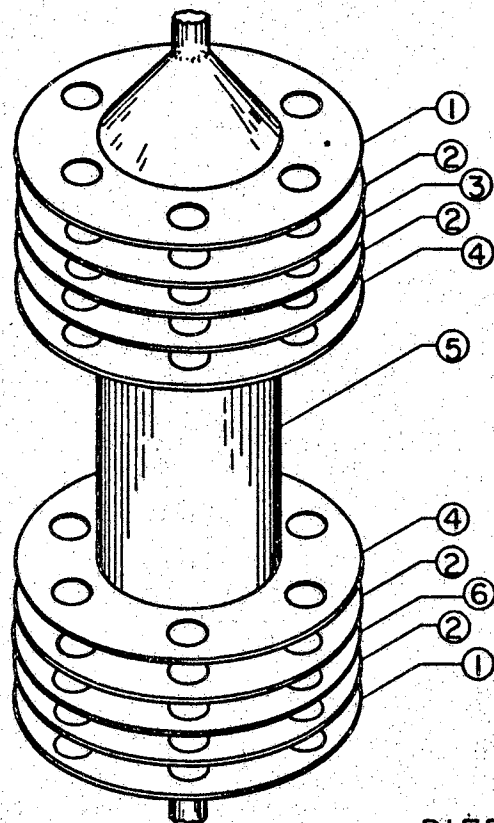13. HEATING TAPE
14. INJECTION PORT

Figure 1.   Apparatus

1. REACTOR HEAD
2. ASBESTOS GASKET
3. TOP DIFFUSER PLATE
4. CONSTRAINING PLATE
5. REACTOR TUBE
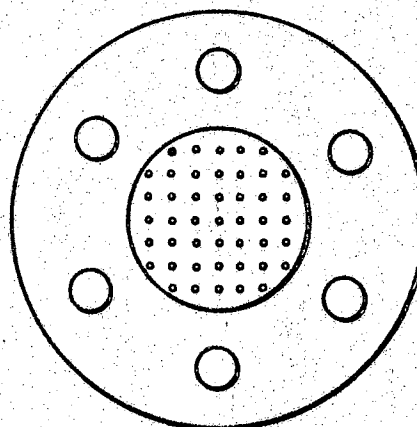6. BOTTOM DIFFUSER PLATE

DIFFUSER PLATE

Figure 2. Reactor Cell

The Process

The process generally consists of passing gaseous hydrogen sulfide over a fixed metal catalyst bed contained in the reactor. The reactor was maintained at a constant elevated temperature throughout a given run. The effluent gas was analyzed for composition to determine the amount of hydrogen sulfide catalysis in the reactor.

The specific flow of the reactor system is given as follows. The hydrogen sulfide is released from the storage tank (1) at ambient pressure. The gas then is permitted to pass to the rotameter (4) where the flow rate is manually adjusted and controlled. The pressure gauge (3) also served as a check against obstructions in the reactor system. Positive system pressure indicated a plugged tube. The gas is then conducted to the muffle furnace (6) where the temperature is checked at the inlet by thermocouple 1 (10). The reactor cell (7) in which the tungsten catalyst cylinders are suspended is contained in the muffle furnace. Thermocouple 2 (11) measures the temperature of the catalyst bed. Exiting from the muffle furnace, the gas remains at an elevated temperature due to the after heater (13) which consists of an electrical heating tape coiled around the exit tube. The tape prevents the sulfur fron condensing and solidifying in the tube from the furnace prior to reaching the cool Tygon tube. From the sulfur condensation point, the stream next passes the injection port (14) where chromatographic samples are extracted for analysis. Finally, the effluent gas arrives at the absorber chain (8) in which the residual hydrogen sulfide is purged from the system by a solution of concentrated sodium hydroxide. The remainder of the effluent gas is collected in an inverted graduated cylinder over water in order to ascertain the volume flow of the

hydrogen product gas for a measured increment of time. The final exit gas was then qualitatively tested for hydrogen content by combustion.

CHAPTER IV

PROCEDURE

The procedure consisted of passing hydrogen sulfide at ambient pressure over a heated tungsten catalyst bed. Subsequently, the effluent gas was analyzed by gas chromatography and by hydrogen gas collection over water. Experimental runs were conducted at four different temperatures and at five different flow rates.

The actual procedure for the operation of the system was as follows:

1. In preparation for a run, the thermocontroller on the furnace was set to a predetermined point to provide temperatures consistant with previous runs. The muffle furnace was then allowed a minimum of three hours to equilibrate at that temperature. Additionally, the heating tape was adjusted to 90 volts and maintained at this level throughout all runs.

2. The hydrogen sulfide absorbers were filled with fresh, concentrated sodium hydroxide. The sodium hydroxide concentration was arbitrarily set at 400 grams per liter of solution.

3. The helium carrier gas for the gas chromatograph was turned on and adjusted to 25 pounds per square inch gauge. The column rotameter was adjusted to the five centimeter mark. The power was then switched on, and the column allowed to warm up to 100°C. Next, the bridge current was turned on and adjusted to

400 milliamperes. When the cell temperature reached 37°C the chromatograph recorder was activated and was in readiness for a run.

4. Just prior to the run, the potentiometer was standardized against solution of distilled water and ice. Then the internal temperature of the reactor cell was checked for the correct temperature.

5. The hydrogen sulfide was turned on and adjusted to the first flow rate as indicated by the rotameter. The system was operated at five flow rates, repeating each once during a run.

6. After an equilibration period at least five minutes the analytic operations were begun.

   a. The tube exiting from the absorber chain was fitted with a copper "U" tube to facilitate gas collections. The effluent gas was collected in an inverted 100 milliliter graduated cylinder which had been filled with water and placed in a trough. When the copper tube was inserted beneath the graduated cylinder, a stopwatch was started simultaneously. After about five minutes, the stopwatch was stopped, and the volume of collected gas was noted. The quality of the gas was periodically checked by filling the graduated cylinder with effluent and igniting the gas as a qualitative test for hydrogen.

   b. While the effluent gas was being collected, samples were drawn from the system just prior to the absorber chains. Standard samples were withdrawn from a point adjacent to the source tank. The injection procedure included two

standards and two samples per datum point. Usually the
results of the injections were consistent enough to make
further repetition unnecessary. The chart paper was then
removed from the recorder and labeled.

7. The flow rate was then adjusted to the next level and the pro-
cedure was repeated.

8. The reactor temperature was continuously checked throughout
the period of the run and was found to range $\pm5^\circ$F from the re-
ported value. Further, the flow rate of hydrogen sulfide
through the system was continuously observed and corrected
when necessary in an effort to insure the consistency of the
data points. Since the system was run at ambient conditions,
any pressure recorded on the pressure gauge indicated a plug-
ged tube. The hydrogen sulfide was immediately turned off and
the tube was replaced. The system was checked for residual
conversion by making some preliminary runs on an empty reactor
tube. The catalyst was then randomly placed in the reactor,
and runs with 152 grams and 140 grams of tungsten, were made.
Further, in an effort to learn how the catalyst deteriorates
with exposure to hydrogen sulfide, a 72 hour run was conducted
with six hour sampling intervals. The actual operation was
the same as mentioned except the flow rate was altered as
little as possible during the run.

At the termination of each run, the absorber system was rinsed,
and fresh sodium hydroxide was placed in the absorber chain. The
chromatograph was turned off and the thermal conductivity cell was per-
mitted to cool in preparation for the next run. The pressure on the

regulator of the hydrogen sulfide tank was carefully discharged to eliminate the possibility of seepage. Then the laboratory was thoroughly ventilated prior to leaving the apparatus.

CHAPTER   V

RESULTS AND DISCUSSION

Qualitative   Results

The objective of prime importance in this project was the recovery

of elemental sulfur. Additionally, the collection of kinetic data on

the tungsten catalyst system and the formulation of a model for the

kinetic data were also to be accomplished. Finally, the stated objec-

tives were to be achieved using catalyst particles similarly shaped to

those used in industry.

The recovery of about five grams of crystalline sulfur was achieved

after many alterations of the system. The system became frequently

plugged with solid sulfur, and after many subsequent modifications, the

sulfur was collected. Although many changes were employed in the sys-

tem design, only a small amount of sulfur could be collected for quan-

titative measurement.

In the following paragraph the results of the experiment are sum-

marized. A more complete discussion is contained later in this chapter.

A total of 120 data points were taken to use in kinetic analysis. These

data are presented in Tables V and VI. These points were averaged for

the two catalyst bed weights and presented in Tables I and II. The

hydrogen flow rate was used as the basis for calculating conversion.

Chromatographic evidence served only to initially confirm the hydrogen

flow rate measurements. Since the hydrogen sulfide peak heights were

±1% in error, accurate chromatography measurements were impossible. The conversion ranged from 9.61% at 910°F. On the 68 hour run, which served to test the effect of catalyst fouling on the conversion rate as a function of time, the conversion ranged as high as 8.70% at 690°F. An unexpected variation in the conversion of the 140 and 152 gram catalyst beds was encountered.

Data Analysis

The kinetic model of Levenspiel (6) was selected to calculate the rate constants from the conversion data.

$$k = ((1 + z_A)\log_e(1/(1 - X_A)) - z_A X_A)/t$$

The results of this analysis are presented in Tables I and II with the conversion data. The deviations in the rate constant for an isotherm leads to the conclusion that additional effects must be included in the Arrhenius model.

$$k = k_o \exp(-E/RT)$$

Taylor and Pickett (10) proposed the existence of a sulfur diffusion barrier. The sulfur film surrounding the catalyst particle retards the conversion. Due to the fact that the vapor pressure of sulfur at these conditions is less than the partial pressure of sulfur around the catalyst cylinders, a greater stream velocity should cause a greater rate constant by sweeping away a greater portion of the dense sulfur film. By this reasoning, the amount of film swept away should be proportional to the lost work of passing through the reactor and thereby the drag coefficient. The model takes on a slightly different form.

TABLE I

RESULTS FROM 152 GRAM BED

Temperature ($^\circ$F)	Flow Rate (cc H_2S/min)	Residence Time (min)	Conversion (%)	Rate Constant (min^{-1})	Model Rate Constant (min^{-1})	Percent Difference
450	138	.03576	5.05	1.4721	1.6390	11.35
450	309	.01575	2.55	1.6534	1.8025	9.04
450	458	.01060	1.76	1.6836	1.8836	11.91
450	575	.00845	1.58	1.8938	1.9298	1.95
450	665	.00731	1.34	1.8536	1.9590	5.66
615	138	.03027	7.34	2.5766	2.5828	.23
615	309	.01333	3.82	2.9567	2.8432	-3.85
615	458	.00898	2.55	2.9004	2.9753	2.53
615	575	.00715	2.13	3.0296	3.0491	.63
615	665	.00619	1.92	3.1525	3.0960	-1.78
770	138	.02646	9.36	3.8211	3.5661	-6.77
770	309	.01165	4.72	4.2114	3.9277	-.673
770	458	.00785	3.31	4.3346	4.1094	-5.20
770	575	.00625	2.66	4.3480	4.2155	-3.05
770	666	.00541	2.41	4.5459	4.2828	-5.79
910	138	.02375	9.61	4.3830	4.4854	2.34
910	309	.01046	4.75	4.7218	4.9416	4.65
910	458	.00704	3.47	5.0681	5.1725	2.06
910	575	.00561	2.75	5.0104	5.3068	5.92
910	665	.00485	2.57	5.4068	5.3930	-.25
						AVG = 4.59

Model Coefficients: k_o = 13.55   E = 2532 cal/gm mole C_1 = .1215 C_2 = 421.41 C_3 = -7.78

TABLE II

RESULTS FROM 140 GRAM BED

Temperature ($^{\circ}$F)	Flow Rate (cc H_2S/min)	Residence Time (min	Conversion (%)	Rate Constant (min^{-1})	Model Rate Constant (min^{-1})	Percent Difference
450	138	.03294	3.00	.9335	.7530	-19.03
450	309	.01450	1.50	1.0469	.9456	-9.07
450	458	.00977	1.10	1.1362	1.0630	-5.93
450	575	.00778	.95	1.2298	1.1392	-6.62
450	665	.00673	.85	1.2715	1.1911	-6.36
615	138	.02788	3.30	1.2274	1.1755	-4.20
615	309	.01228	1.72	1.4206	1.4657	3.15
615	458	.00827	1.29	1.5766	1.6438	4.23
615	575	.00659	1.13	1.7308	1.7590	1.62
615	665	.00570	1.00	1.7692	1.8380	3.90
770	138	.02437	3.80	1.6088	1.6184	.58
770	309	.01073	1.98	1.8752	2.0093	5.75
770	458	.00723	1.50	2.1013	2.2491	7.10
770	575	.00576	1.30	2.2813	2.4050	5.48
770	665	.00498	1.14	2.3104	2.5122	8.75
910	138	.02188	4.20	1.9871	2.0337	2.35
910	309	.00963	2.32	2.4540	2.5160	-1.10
910	458	.00649	1.85	2.8948	2.8121	-2.86
910	575	.00517	1.61	3.1589	3.0050	-4.85
910	665	.00447	1.46	3.3047	3.1376	-5.04
						AVG = 5.40

Model Coefficients: k_o = 8.545   E = 2458 cal/gm. mole C_1 = .1644 C_2 = 15.61 C_3 = 10.07

TABLE III

72 HOUR RUN

(150 Gram Bed)

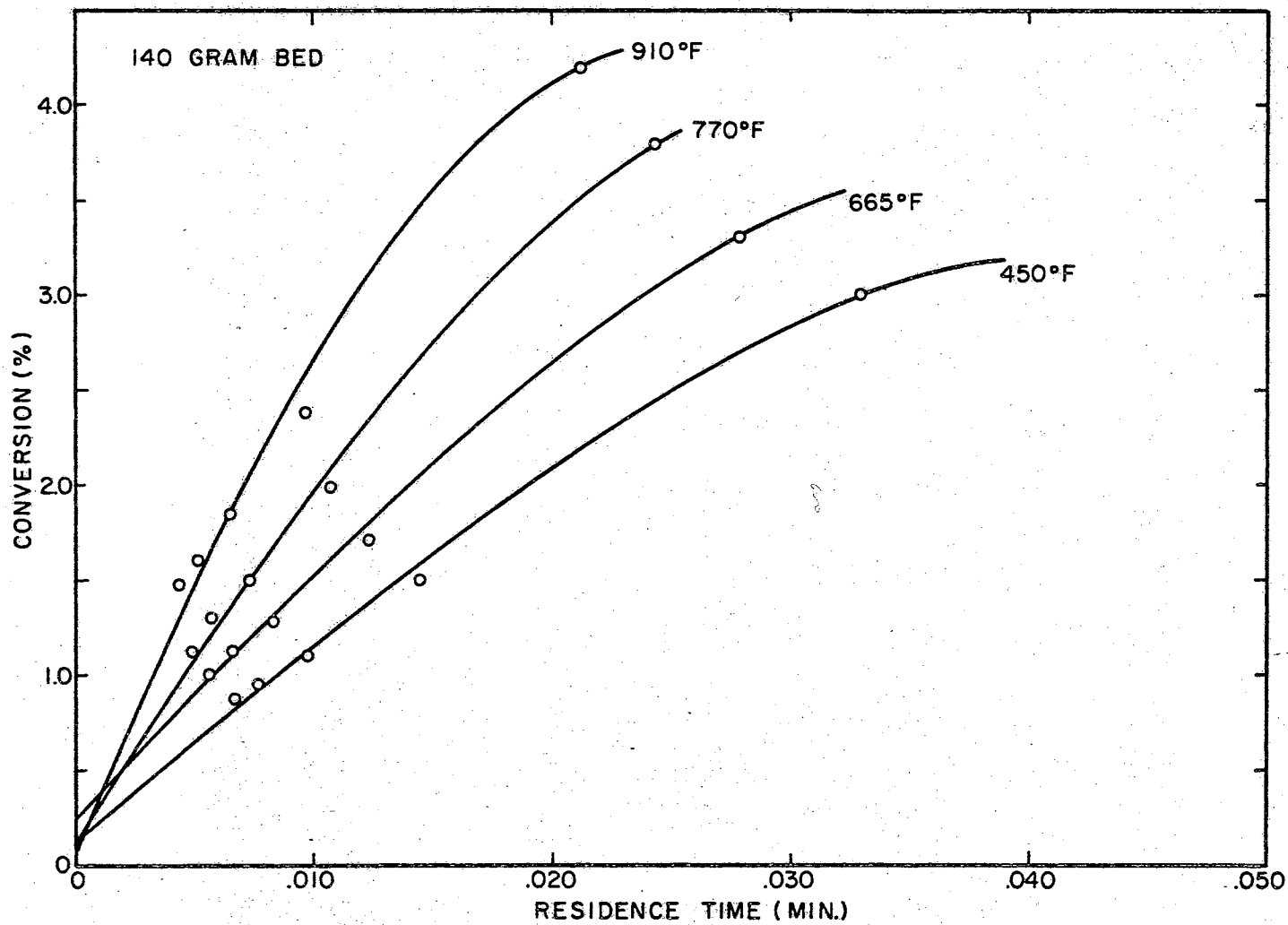| Time (Hours)	Conversion	% Decrease
0.0	8.70	0.0
3.0	7.83	10.0
9.0	7.10	18.4
14.5	7.39	15.1
18.5	7.10	18.4
21.5	7.03	19.2
25.5	7.03	19.2
28.5	6.74	22.5
35.5	6.30	27.6
40.0	6.23	28.4
44.5	6.16	29.2
51.5	6.23	28.4
59.5	6.16	29.2
63.5	6.16	29.2
67.5	6.09	30.0

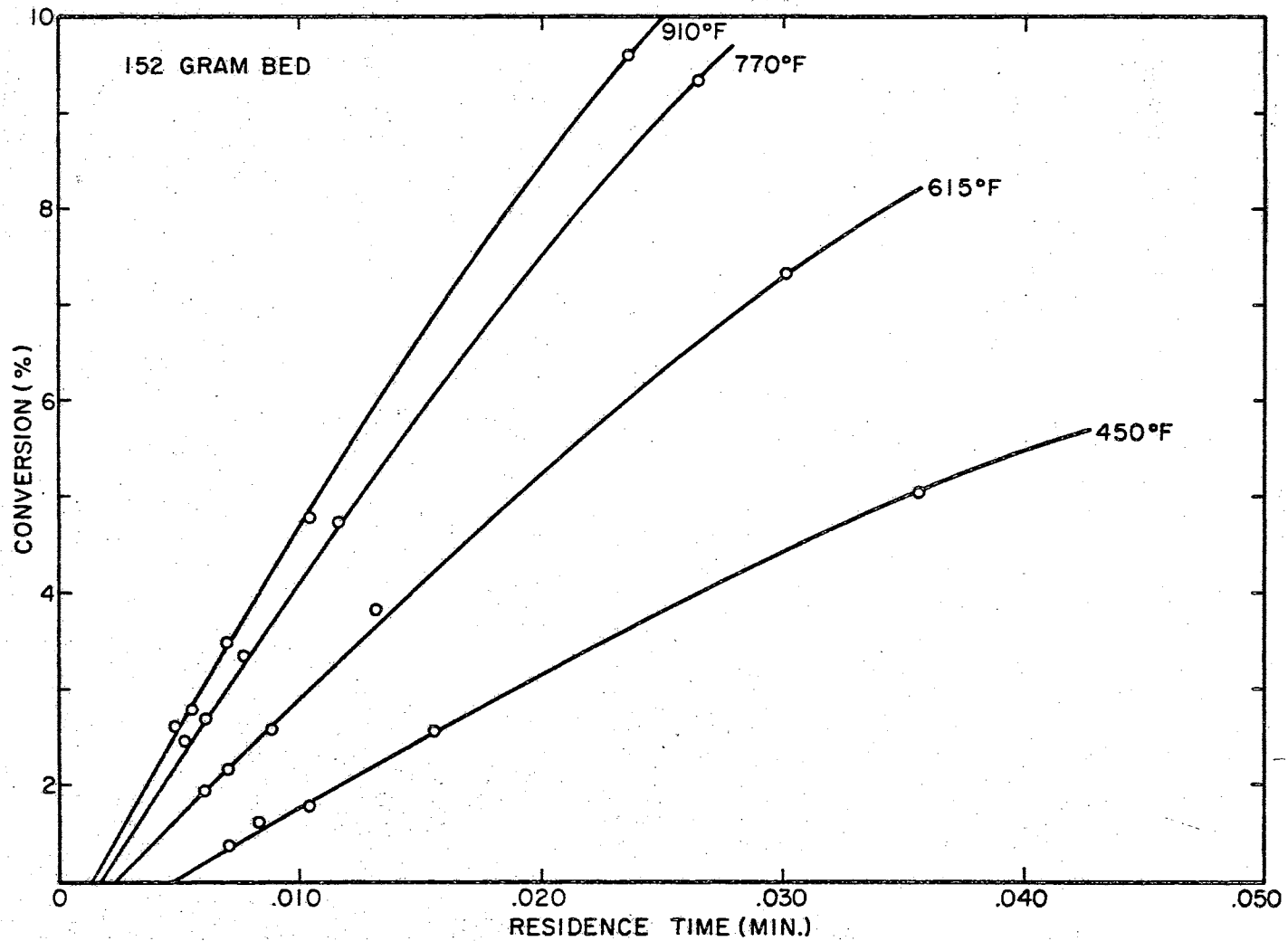Figure 3.   Conversion vs. Residence Time 140 Gram Bed

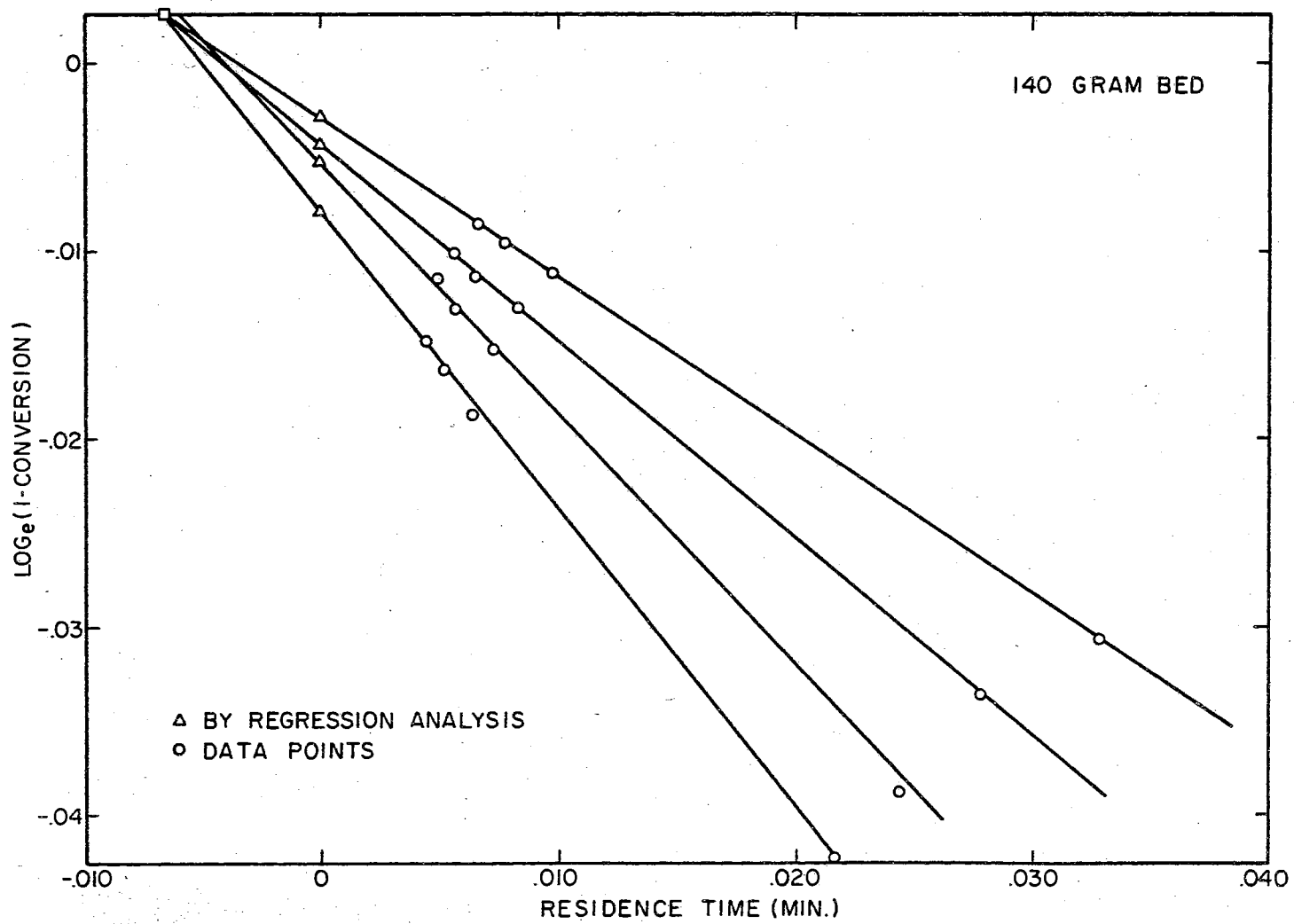Figure 4. Conversion vs. Residence Time 152 Gram Bed

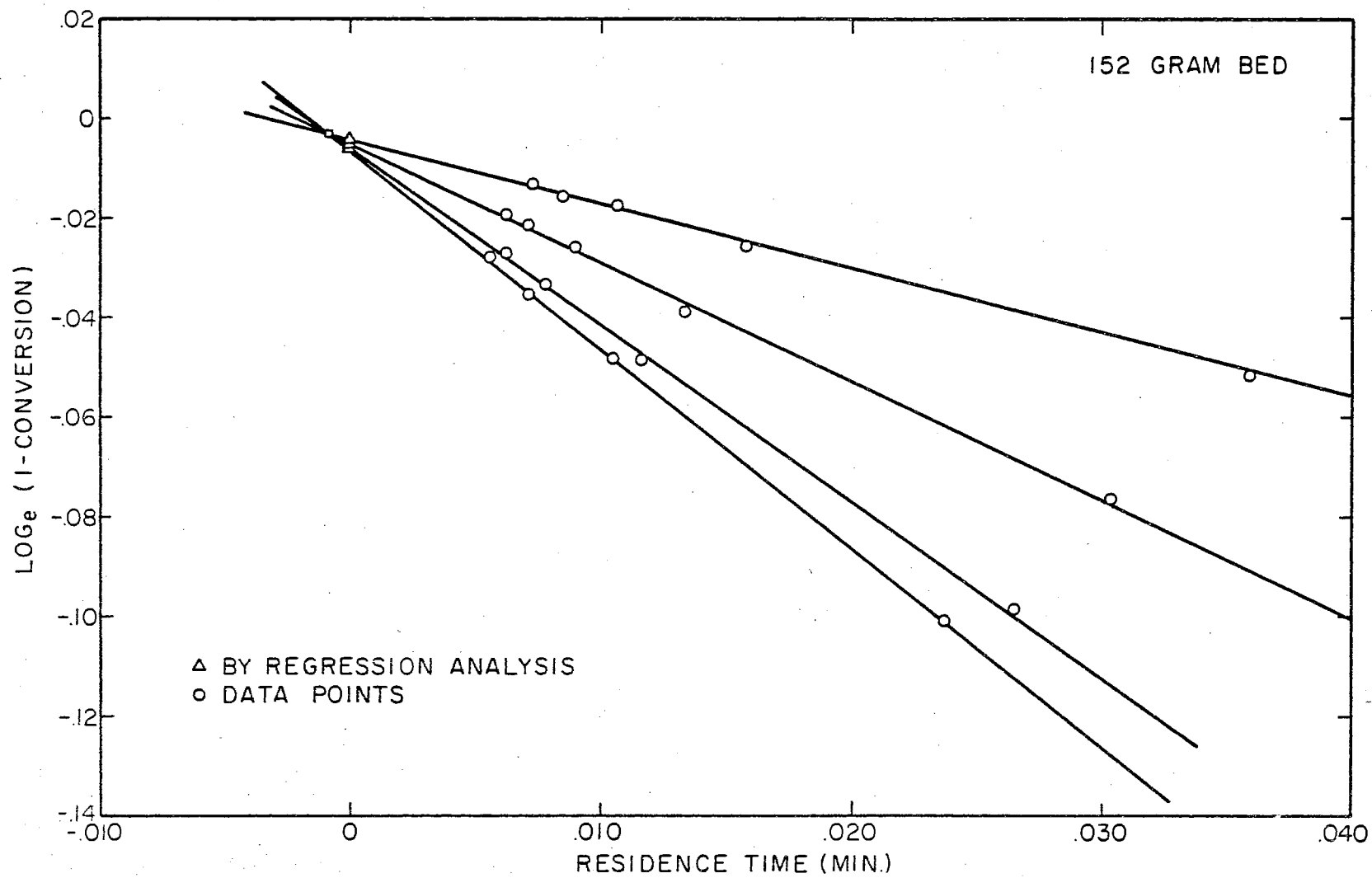Figure 5. First Order Confirmation Plot 140 Gram Bed
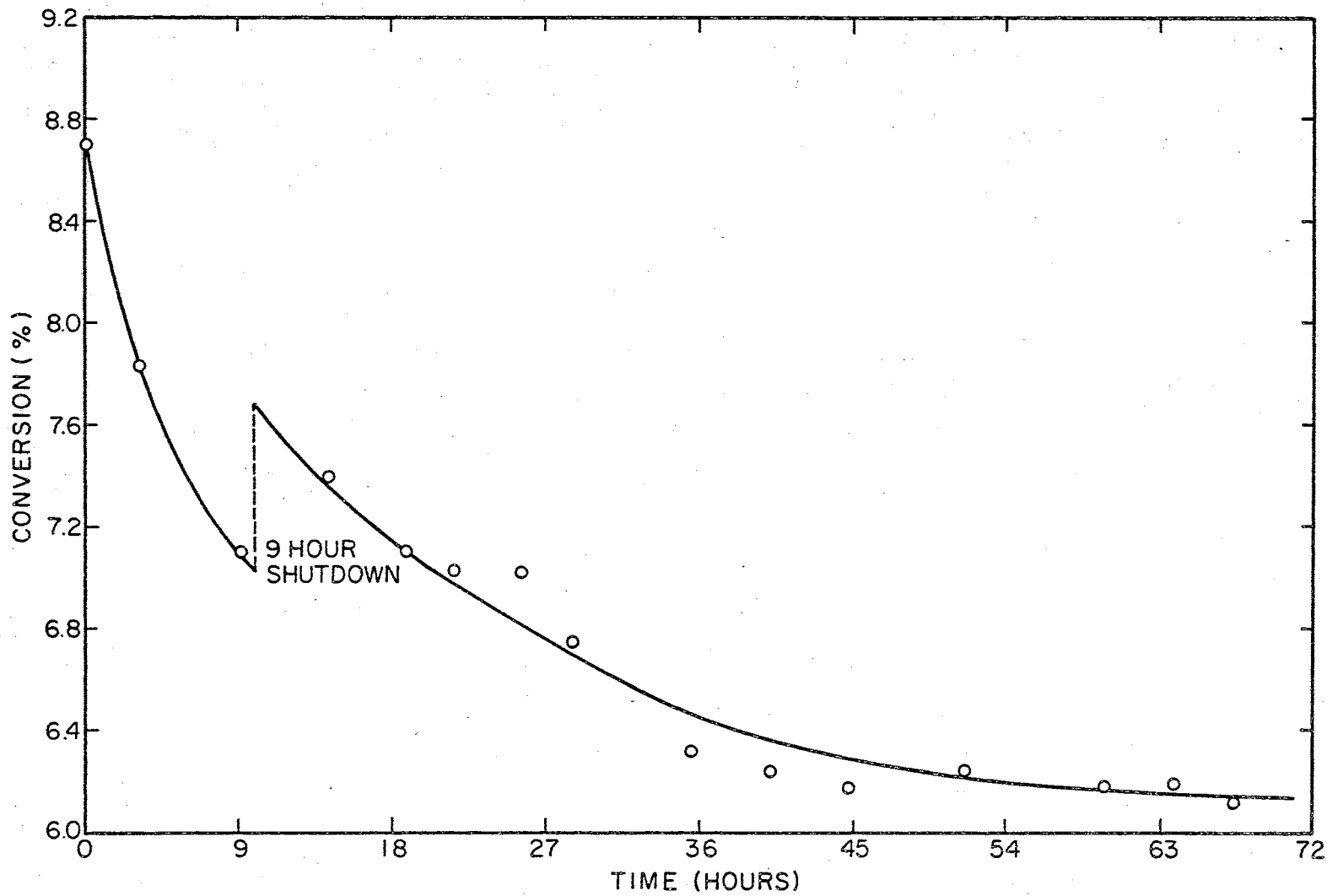
Figure 6. First Order Confirmation Plot 152 Gram Bed

Figure 7.   72 Hour Run for Fouling Test

$$k = k_o \exp(-E/RT)(\text{lost work})^{C_1}$$

For flow through a packed bed, Bennett and Myers (3) give an equation for lost work based on the effective diameter of a simulated spherical catalyst particle. Substituting the lost work term in the previous equation for rate constant, the final model becomes:

$$k = k_o \exp(-E/RT)[((C_2/Re + C_3)(3Lu_{bs}^2(1 - e_A)/g_c De_A^3)]^{C_1}$$

When this model was applied to the rate constant data by means of non-linear regression analysis, an absolute average percent error of 4.59 for the 152 gram bed and 5.40 for the 140 gram bed was encountered. The individual deviations from the model along with the values of the constant terms in the model are reported in Tables I and II.

The fact that k_o, C_1, C_2, and C_3 are different should be noted. In regard to this question, a run to determine the effect of fouling of the catalyst bed as a function of time in the hydrogen sulfide environment was made on a fresh 150 gram catalyst bed. After 68 hours, the conversion of the system was only about two thirds of the original levels. Further, if the catalyst bed is subjected to a substantial quantity of hydrogen sulfide and allowed to cool, the catalyst deactivation process is accelerated, and the catalyst is coated with a sulfide film which is detrimental to conversion. The deteriation of the catalyst helps to explain why the 140 gram catalyst bed had a conversion level much lower proportionally than did the 152 gram bed. The conclusion was drawn that, due to numerous false starts caused by tube plugging and leaks, the 140 gram bed was contaminated prior to use. The fact would explain variations in k_o. Further, as is seen in the calculation section, the effective diameters of the two beds were considerably

different. Since the effective diameters are different, the flow pat-
terns through the bed may be reasonably expected to be different. The
flow parameter constants, C_1, C_2, and C_3, should then be different.

In order to confirm the first order nature of the reaction,
Figures 5 and 6 were constructed by plotting the natural logarithm of
one minus the conversion fraction as a function of residence time. The
result was a series of straight lines which did not pass through the
origin as would be expected. The reason for this is the fact that the
definition of residence time used was not extended to include the sur-
face effects of the inside of the reactor. Although the wall effects
are small, the direct intersection with the origin is prevented. Ex-
trapolation revealed a common intersection point on Figures 5 and 6,
although tests on the blank tube did not give a measurable amount of
reaction.

A significant part of this work was the determination of the acti-
vation energy of hydrogen sulfide with a tungsten catalyst. The value
calculated was about 2,500 calories per gram mole. This value compares
with 11,750 reported by Taylor and Pickett (10) for platinum and 25,000
determined by Kingman (5) for a molybdenum filament. The difference in
activation energy between molybdenum and tungsten might seem strange,
but in the catalytic cracking of certain hydrocarbons, a substantial
difference in the activity of the two catalysts towards the same ma-
terial has been noted. Since the activation energy is a measure of the
change in catalyst activity with temperature, tungsten, which has a low
conversion at these temperatures, does not appear to be as satisfactory
a catalyst as molybdenum.

Although the essential objectives of the experiment were

accomplished, certain limitations in the apparatus and procedure deserve comments as to possible improvements:

1. The gas chromatograph with a thermal conductivity cell was unsuited to the range of conversion which was encountered during the course of the operation.

2. The asbestos gasket material leaked and could not be used at temperatures in excess of $1000^{O}F$.

3. The heating elements in the furnace were on one side of the reactor and created a gradient along the diameter of reactor.

4. The sulfur trap in the system proved ineffective during the course of operation. As a consequence, much time was spent removing sulfur plugs and reworking the system.

CHAPTER VI

RECOMMENDATIONS AND CONCLUSIONS

The process of catalytically cracking hydrogen sulfide by means of a cylindrical tungsten catalyst has been demonstrated to yield the desired products of elemental hydrogen and sulfur. The conversion of hydrogen sulfide was not as high as would be desired in an industrial reactor, but with the short bed length in this study the data serves primarily to aid in establishing a simple kinetic model. An activation energy was calculated and found to be lower than that for two previously tested catalysts.

Based on the results of the data correlations, several recommendations come to light. First, due to the low activation energy and low conversions of tungsten and the cost per pound considerations, molybdenum appears to be more suited for catalytic work. The judgement is made in the absence of any fouling data on molybdenum or possibilities of regenerating either catalyst. The reactor should be designed to contain only stainless steel gaskets so the higher temperatures of interest may also be studied. The sulfur trap should be redesigned to have a heated top containing the entrance and exit lines. This would facilitate the operation of such an apparatus a great deal. Since up to this time no work has been done on a natural gas stream containing hydrogen sulfide to determine the effects on a metal catalyst, the pure hydrogen sulfide source should be discarded in favor of an industrial

gas stream. Operations of this nature are necessary to determine the
feasibility of bulk stream processing to remove hydrogen sulfide. A
more sophisticated diffusion limited kinetic model should be employed
in analyzing temperatures. Since the catalyst in this experiment was
shown to foul under the effects of hydrogen sulfide and time, work must
be done in the area of regeneration of the catalyst to determine if ex-
pensive metal catalysts can be revived for further usage.

NOMENCLATURE

A_x -- cross sectional area of catalyst bed

C_{Ao} -- initial concentration of A

C_1, C_2, and C_3 -- flow parameters

D -- effective diameter of a catalyst particle

e_A -- void fraction of catalyst bed

E -- activation energy

g_c -- gravitational constant

k -- rate constant

k_o -- frequency factor

L -- length of catalyst bed

n -- order of reaction

R -- gas constant

Re -- Reynolds number = $Du_{bs}/((1 - e_A))$

t -- residence time

T -- temperature

u_{bs} -- bulk velocity through an empty tube

v_o -- volumetric flow rate through the reactor

v_x' -- volumetric flow rate of x at ambient conditions

V -- reactor volume

X_A -- fraction conversion of A

z_A -- fractional change in volume on reaction

41

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       Journal of Physical Chemistry, 31, 1212-19 (1927).

APPENDIX A

CALIBRATION OF PROCESS ELEMENTS

APPENDIX A

CALIBRATION OF PROCESS ELEMENTS

TABLE IV

PRESSURE GAUGE CALIBRATION

(p.s.i.g.)

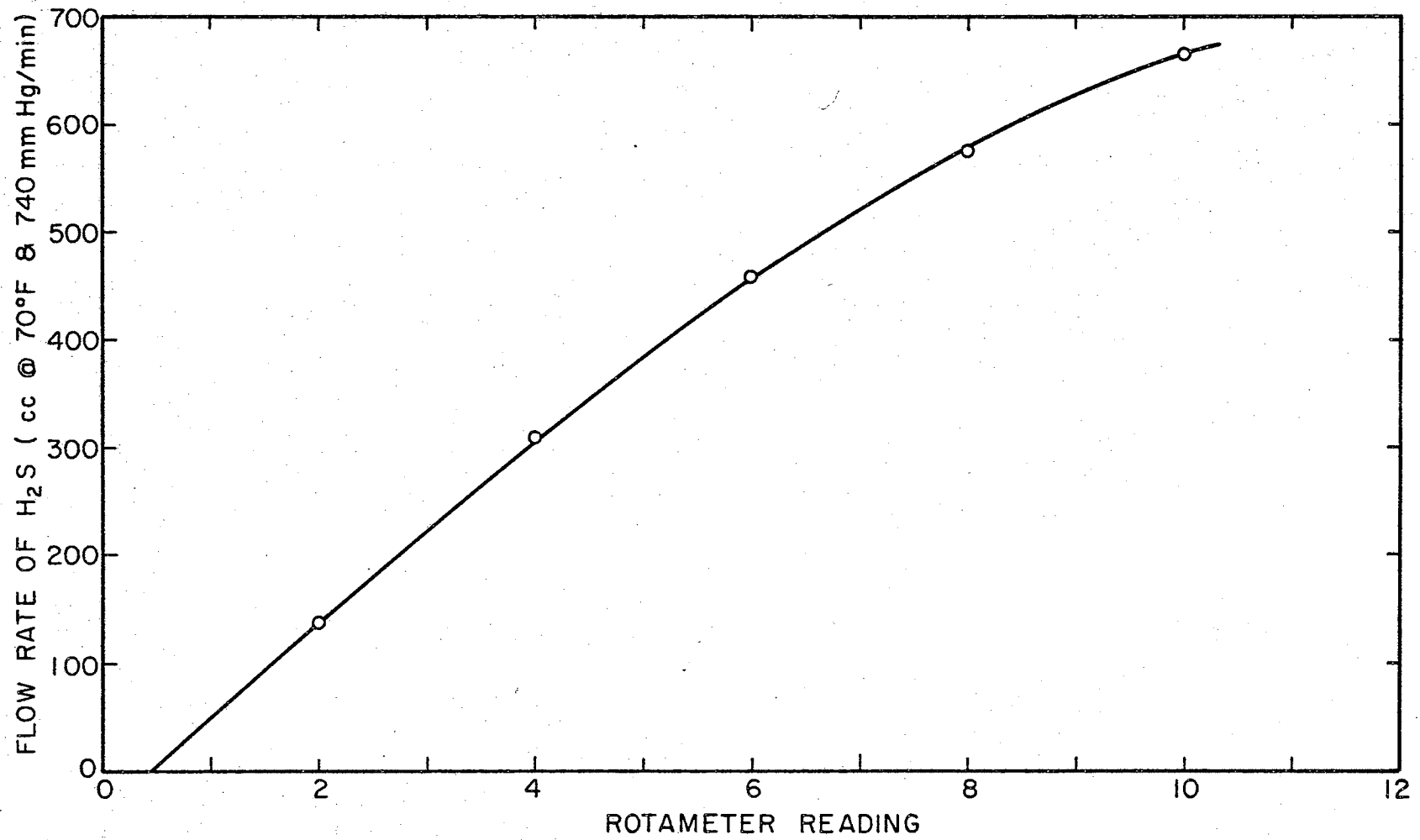| Actual Pressure	Pressure Gauge Reading
10	9.8
20	19.7
30	30.0
40	40.0
50	49.8
60	60.0

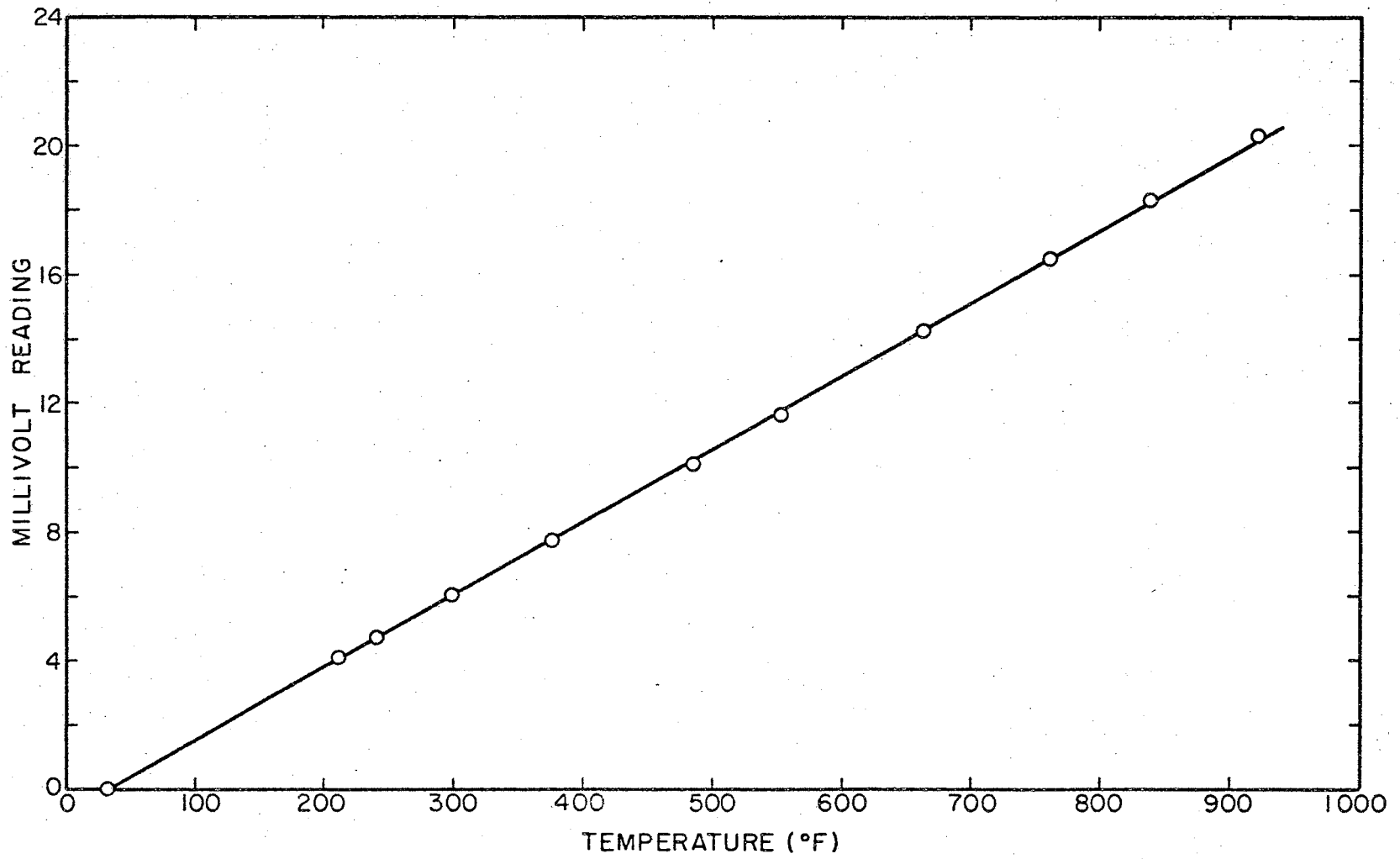Figure 8. Rotameter Calibration Curve

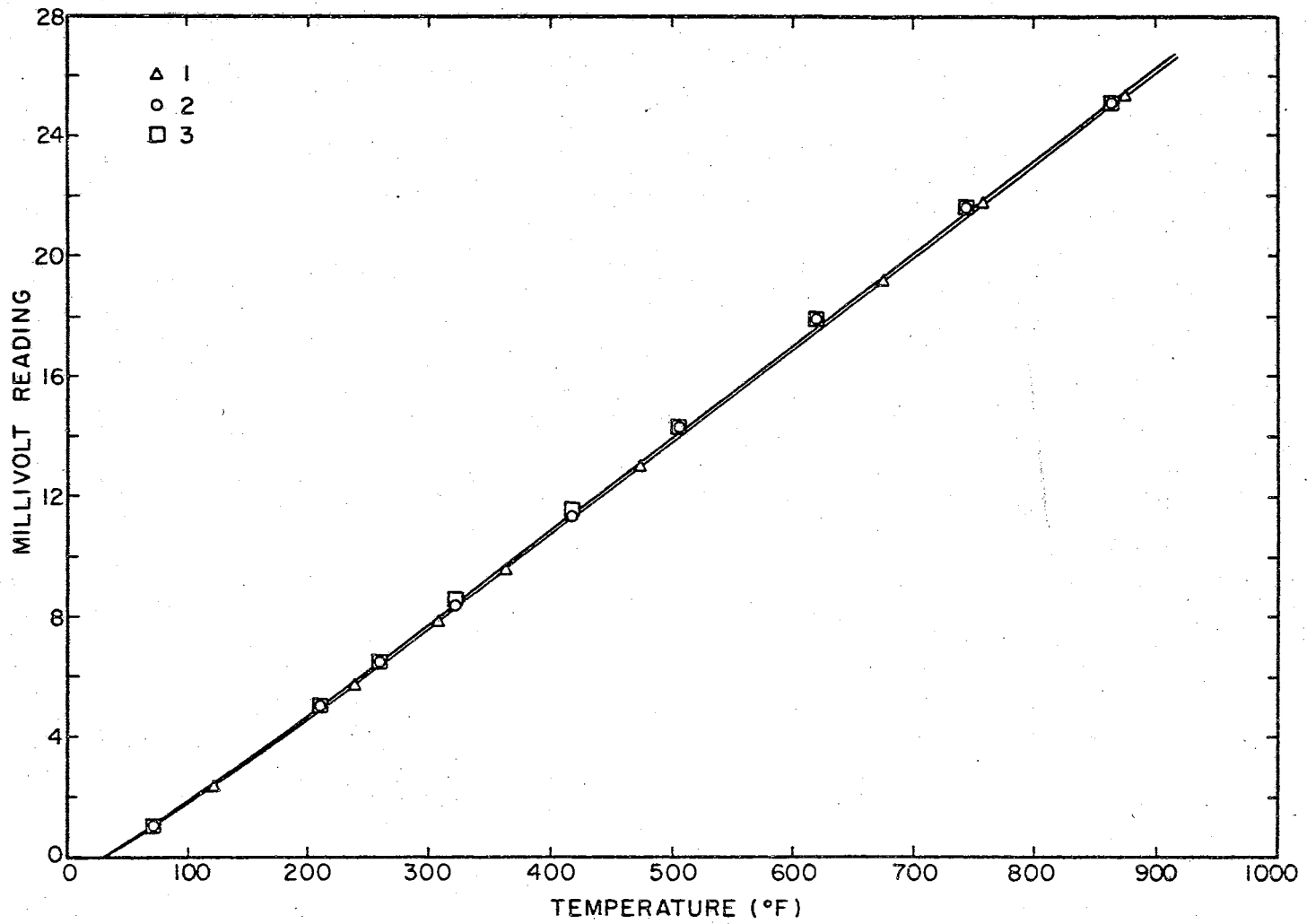Figure 9. Standard Thermocouple

Figure 10. Thermocouples 1, 2, and 3

APPENDIX B

SAMPLE CALCULATIONS

APPENDIX B

SAMPLE CALCULATIONS

First, the catalyst cylinders were individually measured so the sur-
face area could be calculated. All rough surfaces were assumed to have
twice the unit surface area as the smooth surfaces. The specific area
was calculated in area per unit weight.

Next, the conversion data was refined into a usable form:

$$v'_{H_2} = 24.5 \text{ cc/5min} = 4.9 \text{ cc/min}$$

From the rotameter reading of 2 cm. Figure 7 enables one to calculate
the conversion based on the hydrogen sulfide flow rate:

$$v'_{H_2S} = 138 \text{ cc/min}$$

$$X_A = 4.9/138 = .0300$$

Now, the residence time based on the hydrogen sulfide flow rate through
the reactor is calculated.

$$t = LA_X e_A / (v'_{H_2S} T/T_{STP})$$

$$= (2.54)(1.5)(3.14)(.9525)^2 (.62)/((138)(910/460))$$

$$= .03294 \text{ min.}$$

Substituting in the rate constant equation:

$$k = ((1 + z_A)\log_e(1/(1 - X_A)) - z_A X_A)/t$$

$$= ((1.62)\log_e(1/.97) - (.62)(.0300))/.03294$$

$$= 1.4721 \text{ min.}^{-1}$$

The theory for the dispersion of the sulfur film due to lost work is now utilized:

Specific surface = Surface area of cylinder/Volume of cylinder

$$= 1.712/.11534$$

$$= 14.84 \text{ cm.}^{-1}$$

$$D = 6/\text{Specific surface}$$

$$= .4043$$

The values are substituted in the following equation:

$$k = k_o\exp(-E/RT)[((C_2/Re + C_3)(3Lu_{bs}^2(1 - e_A)/g_c De_A^3)]^{C_1}$$

The constants are determined by nonlinear regression analysis. The results of the data which was processed in 140 gram bed and 152 gram bed batches are given in Tables I and II.

VAPOR PRESSURE OF SULFUR

$T = 450°F = 505°K$

$\log_{10}P = 14.7 - .00622T - 5405/T$

$P = 7.244$ mm. of Hg

$T = 596°K = 615°F$

$\log_{10}P = 14.7 - .00622T - 5405/T$

$P = 83.18$ mm. of Hg

$T = 770°F = 683°K$

$\log_{10}P = 7.433 - 3268/T$

$P = 444.6$ mm. of Hg

$T = 910°F = 760°K$

$\log_{10}P = 7.433 - 3268/T$

$P = 1358.$ mm. of Hg.

From <u>Sulfur Data Book</u> by Texas Gulf Sulfur Co.

APPENDIX C

RAW DATA

TABLE V

RAW DATA FROM 140 GRAM BED

H₂S FLOW RATE		REACTOR TEMPERATURE (°F)	TIME OF RUN (min)		VOLUME OF EFFLUENT (cc)		AVERAGE CONVERSION (%)
Rotameter Reading(cm)	Flow (cc / min)		Run 1	Run 2	Run 1	Run 2	
2	138	450	5	5	21.0	21.5	3.00
4	309	450	5	6	22.0	28.5	1.50
6	458	450	5	5.5	25.5	27.5	1.10
8	575	450	7	5	36.5	26.5	.95
10	665	450	8	5.5	45.0	29.0	.85
2	138	615	5	5	22.5	21.0	3.30
4	309	615	5	5	26.0	25.5	1.72
6	458	615	5	5.5	29.0	31.0	1.29
8	575	615	5	5.5	32.0	34.0	1.13
10	665	615	5	5	32.5	31.5	1.00
2	138	770	5 5.5	6 5	26.0 27.5	31.0 25.0	3.80
4	309	770	5 5	5 5	30.0 29.0	29.5 30.0	1.98
6	458	770	7 6	5 8	47.0 39.0	33.5 52.5	1.50
8	575	770	6 6	5 5	44.0 42.5	36.5 35.5	1.30
10	665	770	5 5	5.5 5	37.0 36.0	40.6 36.5	1.14
2	138	900	5 5	6 8	28.0 27.5	34.0 44.5	4.20
4	309	900	5 7	5 5	35.0 48.0	34.0 35.0	2.32
6	458	900	5 5.5	7 6	43.0 46.0	60.0 50.5	1.85
8	578	900	5 6	5.5 7	45.0 53.0	49.5 62.0	1.61
10	665	900	5 5	5 5	47.0 45.5	46.5 47.0	1.46

TABLE VI

RAW DATA FROM 152 GRAM BED

H₂S FLOW RATE		REACTOR TEMPERATURE (°F)	TIME OF RUN (min)		VOLUME OF EFFLUENT (cc)		AVERAGE CONVERSION (%)
Rotameter Reading(cm)	Flow (cc/min)		Run 1	Run 2	Run 1	Run 2	
2	138	450	5	5	34.0	33.0	5.05
4	309	450	5	5	38.5	37.0	2.55
6	458	450	5	5	38.0	39.5	1.76
8	575	450	5	5	44.5	43.0	1.58
10	665	450	5	5	44.0	42.0	1.34
2	138	615	5	5	50.0	47.5	7.34
4	309	615	5	5.5	57.0	63.0	3.82
6	458	615	6	5	68.0	56.5	2.55
8	575	615	5	5	58.0	60.0	2.13
10	665	615	5	5	61.0	62.5	1.92
2	138	770	5 5	5 5	61.0 62.5	64.0 62.0	1.36
4	309	770	5 5.5	5 6	70.0 77.5	72.0 84.5	4.72
6	458	770	5 5	5 5	73.0 73.5	74.0 75.0	3.31
8	575	770	5 5	5 5	74.0 73.0	75.0 74.0	2.66
10	665	770	5 5	5.5 5	76.0 78.0	85.0 77.5	2.41
2	138	910	5 5	6 5	64.0 63.0	77.0 64.0	9.61
4	309	910	5 5	5.5 5	70.0 71.0	78.0 71.0	4.75
6	458	910	5 5	5 5	76.5 75.0	78.0 77.0	3.47
8	575	910	5.5 5	5 5	84.0 76.0	76.5 77.0	2.75
10	665	910	5.5 5	5 6	90.5 83.0	82.0 98.5	2.57

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ties include Omega Chi Epsilon and Sigma Tau.