THE PREPARATION OF HYDROGEN POLYSULFIDE IN THE GAS PHASE

by

H. William Bruce

John L. Mattana

Submitted in Partial Fulfillment of the Requirements

for the Degree of Bachelor of Science

from

Massachusetts Institute of Technology

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Signature of students

Signature redacted

Signature redacted

Signature of supervisors

Signature redacted

Signature redacted

Signature of Head of Department

____

Dept. of Chemical Engineering
Massachusetts Institute of Technology
Cambridge 39, Massachusetts
May 18, 1951

Professor Joseph S. Newell
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

The thesis entitled "The Preparation of Hydrogen Polysulfide in the Gas Phase" is hereby submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

Respectfully submitted,

Signature redacted
H. William Bruce

Signature redacted
John L. Mattana

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I SUMMARY

Hydrogen polysulfide, a yellow oily liquid at room temperature, consists of a variable mixture of the compounds H_2S_4, H_2S_5, H_2S_6, and higher polysulfides, probably including H_2S_8. The object of this investigation was to determine whether hydrogen polysulfide could be produced by a gas phase reaction involving sulfur and hydrogen sulfide gas and to find the empirical formula of the product H_2S_x, if it is formed.

The experimental apparatus consisted of a stainless steel reactor constructed so as to conform with the upper limits of temperature and pressure to be used. The reactor, heated by being place in a furnace, was attached to a high pressure system interconnected by copper tubing. Experimental technique consisted of two parts. The first set of runs was an attempt to form the polysulfide, while the second set was an attempt to decompose the polysulfide.

In the first method, hydrogen sulfide gas, under pressure, was passed into the air-water free, stainless steel reactor, containing a weighed amount of solid sulfur. The procedure was a batch operation. The two chemicals were allowed to remain in contact with each other for periods of time ranging from thirty to forty minutes, under pressures from 210 to 245 psig and at temperatures from 23° to 380°C. The reactor, containing about fifteen cubic inches in volume, remained connected to the high pressure system during heating in a furnace until it was removed from the furnace and quenched in water in order to condense any product. The product, if it had formed, would have been analyzed by using a technique which utilizes the fact that the polysulfide decomposes completely into hydrogen sulfide and sulfur when brought into contact with powdered quartz.

In order to investigate the decomposition of hydrogen polysulfide, a weighed amount was allowed to remain in contact with sulfur and

and hydrogen sulfide using a procedure similar to the one used in attempting formation. For safety purposes, as much work as possible was done from behind a sheet of boiler plate steel, on which the high pressure system was mounted.

The results of the experimental work were:

(a) In attempting the formation of polysulfide, under no condition investigated did hydrogen sulfide and sulfur react so as to produce a detectable amount of polysulfide. By using the limited amount of thermodynamic data on the given system, preliminary calculations had indicated, assuming a product of H_2S_2 alone, that a yield of a fraction of one percent conversion could be obtained at high temperatures. Since there were no data on the higher polysulfides however, there was no evidence that these polysulfides would not form in greater amounts.

(b) In attempting the decomposition of polysulfide, it completely decomposed at a pressure of 135 psig and a temperature of 500°C. and also decomposed at a pressure of 290 psig and a temperature of 330°C. Under less severe conditions the polysulfide appeared to decompose but slightly, or to remain apparently stable. Dispersion of solid sulfur indicated the degree of decomposition.

Since the polysulfide could not be formed under the conditions investigated, it was concluded, considering only these results, that either the free energy for the formation of the polysulfide was not favorable so that the equilibrium yield was too low, or that the rate of reaction was too small. Results based on the decomposition experiments alone, indicated that the liquid could not be stabilized at the high temperatures and pressures and that therefore, the formation and condensation of the polysulfide under the same conditions was impossible. It could not be concluded that the polysulfide could have formed under conditions where it was apparently stable because the rate of decomposition might have been too slow to show that it was thermodynamically unstable. Based on the knowledge that the equilibrium constant for the formation of H_2S_2 increases with temperature, the same general trend might be concluded for the higher polysulfides. It is on this basis and on the basis that increased pressure would help condense any polysulfides, that it is recommended that experimentation be continued employing higher temperatures and pressures in attempting formation. It is possible that although, as shown here, the polysulfides were unstable at the conditions investigated, they could be formed and condensed under even more severe conditions.

It is recommended that:

(1) The influence of catalysts on the formation be studied.

(2) Since no corrosion problem was encountered in the investigation, although anticipated due to the corrosive mixture of the chemicals and the high temperatures employed, that the author's material of construction, type 316 stainless steel, be used in any construction of a new reactor.

(3) Since some deformation in parts of the reactor took place in attempting to obtain a complete seal during this investigation, the parts of any new reactor designed for more severe conditions should be designed considering this fact in addition to the fact that steel loses much of its strength at high temperatures and thus leading to the necessity of thicker walls, flanges, heads, and bolts.

II INTRODUCTION

Hydrogen polysulfide is a yellow viscous oil which consists of a mixture of the compounds, H_2S_4, H_2S_5, through H_2S_8 (and even higher polysulfides) in various amounts, mostly below H_2S_6, most of which have been prepared as pure compounds in laboratory reactions in solution. Hydrogen polysulfide has usually been prepared by reacting an alkali polysulfide with hydrochloric acid. Recently, some attempts have been made to prepare it in various organic solvents and also electrolytically. The product must usually be separated into its constitutents by fractional distillation. As far as is known, no one had attempted to produce the hydrogen polysulfide in a gas phase reaction. Since hydrogen polysulfide is reactive towards unsaturated compounds and is thus a potentially useful chemical, the possibility of preparing it by the reaction

$$H_2S + XS = H_2S_{X+1} \qquad (1)$$

was investigated.

Up to the present time, K.K.Kelley (2) appears to have prepared the most accurate data on the thermodynamic chemistry of sulfur. Data on the system consisting of the substances, S_2, S_6, S_8, H_2S and H_2S_2, are fairly complete; however, there are no accurate data on the higher polysulfides. By utilizing the thermodynamic data, the equilibrium yield of H_2S_2, assuming it is the only product, according to the reaction

$$H_2S + 1/8\ S_8 = H_2S_2 \qquad (2)$$

can thus be predicted at various conditions. Although the equilibrium conversion to H_2S_2 was calculated to be only a fraction of a percent even at a temperature of 1000°C, the gas phase reaction, as proposed, was attempted because there was no evidence that the mixture of polysulfides would not form.

It was the purpose of this investigation to attempt the proposed reaction by allowing H_2S to remain in contact with sulfur in an airmoisture free, batch reactor. It was planned that the reaction be carried out under pressures varying from one to fifty atmospheres and over a temperature range of 20° to 500°C. for various periods of time. It was planned to analyze the product, should it form, at each set of conditions, by a simple decomposition technique, thus observing whether different polysulfides would form under different conditions.

The results of such a proposed investigation would be valuable for several reasons. They should give some indication as to whether it is thermodynamically possible to produce the polysulfide under the conditions proposed. The experience gained in the investigation should also increase the knowledge on the subject of corrosion in such a reaction. The reactants and products attack many substances and thus a satisfactory material of construction micht be proposed. The results might also indicate whether the industrial production of polysulfide, if possible by this method, would be feasible considering the high pressures and temperatures which might be involved. By observing the time of reaction, some indication as to whether the process should be a batch or flow operation could be advanced.

III PROCEDURE

Briefly, the apparatus consists of a short length of stainless steel pipe with a piece of similar stainless steel welded on to the bottom. A flange is screwed on the opposite end of the pipe and to this flange, the head is bolted on my means of six, quarter inch bolts. Leading into the reactor, through the head, are the thermocouple well and the tube for the reaction gases.

In attempting the formation of hydrogen polysulfide by reacting hydrogen sulfide with sulfur, a weighed amount of dry sulfur, in a small crucible, was placed in the reactor cylinder. The flange was screwed on the cylinder, so that with the gasket in place, the head could be tightened sufficiently to compress the gasket, by means of the bolts. The reactor was attached to the high pressure system (see schematic diagram) by the inlet pipe in the head, and with the H_2S and N_2 valves closed, the vacuum valve was opened and the air withdrawn from the system by the pump. The vacuum valve was then closed and nitrogen was let into the system and then withdrawn by vacuum to make sure that the air in the reactor had been completely removed. The dry, air-free reactor, placed in this condition so as to prevent sulfur oxidation and limit corrosion, was filled with hydrogen sulfide and placed in the furnace and heated. From this point until the reactor was disconnected from the system, the work was done from behind a steel panel for safety purposes. Static pressure was measured with the bourdon gauge in the system and the temperature was measured with a thermocouple inside the reactor. The hydrogen sulfide tank valve was closed and readings of pressure and temperature were taken at short time intervals. After the steady state conditions were reached, i.e., constant temperature and pressure in the reactor, and supposed equilibrium for the reaction, the valve leading to the reactor was closed and the bomb disconnected from the system. The bomb was then carefully quenched in cool water in order to condense any products of reaction. The bomb was then exhausted of the hydrogen sulfide gas, opened, and the contents were examined.

In attempting the decomposition of hydrogen polysulfide, the same procedure was used with the exception that the starting materials were sulfur, hydrogen sulfide gas, and the polysulfide.

IV RESULTS

The formation of hydrogen polysulfide with sulfur at its vapor pressure:

Reactants: H_2S and S.

Table I
Data on Attempted Formation

Run	Wt. of S	Total Pressure	Final Temp.	Reaction Time	Result
1	------gm	--- psig	20 °C.	40 min.	yellow S
2	------	---	100	40	yellow S
3	1.000	245	333	30	black
4	1.348	210	381	40	black

The decomposition of hydrogen polysulfide: Reactants: H_2S, S, and H_2S_X.

Table II
Data on Decomposition Reaction

Run	Wt of S.	Wt.of H_2S_X	Total Pressure	Final Temp.	Time	Result
5	1.00gm	2.26 gm	135 psig	501 °C.	60 min.	decomposed
6	1.00	3.00	290	329	30	decomposed
7	2.00	6.00	260	322	75	partly "
8	----	3.00	100	110	30	slightly "
9	----	3.00	282	124	60	slightly "

The black solid which was left after runs 3 and 4 was dry and hard. No evidence of liquid was present. The material burned with a blue flame, characteristic of sulfur. The sulfur was placed in aluminum foil for these runs, and it was discolored. After every run, the sulfur was found condensed on the walls of the reactor and was always dark brown or gray. No explanation is offered for this color, except that sulfur could have formed a compound with some of the impurities found in the aluminum foil or in the stainless steel walls.

The degree of decomposition of the polysulfide could be observed by noticing the amount of sulfur dispersed in the liquid polysulfide. In the case of complete decompostition, only the solid sulfur remained.

No serious corrosion of the reactor resulted from any run. The inside surface of the reactor became darker with each run as it became more difficult to clean away the condensed film of sulfur. No peeling or other evidence of corrosion of the stainless steel was noticed.

V DISCUSSION OF RESULTS

The results based only on the attempts to form the polysulfide indicate several situations:

(1) that the equilibrium constants for the reactions to form the various polysulfides were so small that practically no polysulfide could form under the experimental conditions. This means thermodynamically that the free energies of the reactions were undoubtedly large and positive.

(2) that a small amount of polysulfide vapor formed and that it could not be condensed and therefore measured. This means that the partial pressure of the polysulfide was so low that it did not separate as a liquid phase.

(3) that polysulfide formation was possible, i.e., that the constants were reasonably large but that the rate of reaction was slow so that the reaction did not reach equilibrium and that therefore no product was measured.

The results based only on the attempts to decompose the polysulfide indicate:

(1) that since at the temperature of 501°C. and pressures of 135 psig (as in run 5 for example), the polysulfide completely decomposed, the formation and condensation of polysulfide under these same conditions is impossible.

(2) that although the polysulfide appeared stable (in runs 8 and 9 for example), the rate of decomposition might be very slow and the polysulfide might have decomposed completely if enough time were allowed, thus again leading to the conclusion that formation under these conditions might be impossible.

Feher and Heuer (1) give the equilibrium constants as a function of temperature for the reaction: $H_2S + \frac{1}{2}S_2 = H_2S_2$ (2')

Kelley gives the free energy of the reaction: $\frac{1}{2}S_2 = 1/8\ S_8$ (2) (3)

Thus, by manipulation of these equations together with the formula for the vapor pressure of sulfur as a function of temperature, we may calculate the percent conversion, defined as :

$$\% \text{ conversion} = \frac{P_{H_2S_2}}{P_{H_2S} + P_{H_2S_2}} \times 100$$

for the reaction $H_2S + 1/8\ S_8 = H_2S_2$, as a function of temperature. The result is shown in Fig. 1 page 12. This calculated value of percentage conversion assumes the product H_2S_2 alone. Since there is no such data on systems of the higher polysulfides, percentage conversions must be guessed by approximation methods. No attempt was made to predict the conversions of these higher polysulfides. Since no yield of polysulfide of any kind was obtained, no correlation with these preliminary calculations can be made.

In attempting to analyze the system of compounds present the fact that hydrogen polysulfide, H_2S_X, consists of variable amounts of the compounds, H_2S_4, H_2S_5, etc., must be remembered. Thus in attempting to stabilize H_2S_X one is attempting to stabilize, under one set of conditions, all of the polysulfides at once. The maximum one can hope to do is to reduce the decomposition of the polysulfide as much as possible under a definite temperature and pressure. It is known that hydrogen polysulfide is thermodynamically unstable at room temperature although the rate of decomposition is slow. The placing of the polysulfide in a system of hydrogen sulfide gas and sulfur vapor at room temperature would no doubt cause the decomposition to be even slower.

The experimental results based on the two methods of attack gave no indication as to whether there are conditions where a given polysulfide might be stable. The results do indicate, however, that a polysulfide of given composition cannot be condensed in a gas phase reaction at the conditions specified for the run. It is possible that the reaction to form the polysulfide is possible under conditions less severe than those of the run, but that the rate of reaction is too slow. Since, however, the equilibrium constant for the reaction (2) increases with temperature, it could be possible that although hydrogen polysulfide is thermodynamically unstable at room temperatures, its rate of decomposition is slow, and that at moderate temperatures and pressures, its decomposition is rapid and at high temperatures and pressures, it could form with ease.

It is recommended, on this basis, that hydrogen polysulfide formation be tried at higher temperatures and pressures than investigated here. Since it is possible that although the equilibrium conditions could be favorable at these conditions, but that the rate would be slow, the effect of catalysts on the reaction involved should be investigated.

The attempt of more severe conditions for the reaction would lead to several difficulties. (1) Although the authors' choice of type 316 stainless steel for reactor construction proved satisfactory for the conditions investigated, the increase in corrosion with temperature might possibly cause difficulties. An alternate material for use at these conditions could be chromium, which could be plated on the reactor walls. (2) Much difficulty with leaks of hydrogen sulfide gas, which is very toxic, was encountered during the experiments. The gasket material used here, aluminum foil, replaced with each run, was not completely satisfactory is this respect. The possibility of using some other inert material should be investigated. Of course, if the seal was effected without a gasket, as in some high pressure equipment, this problem could be avoided.

MAY 18, 1951 H.W.B.
J.L.M.

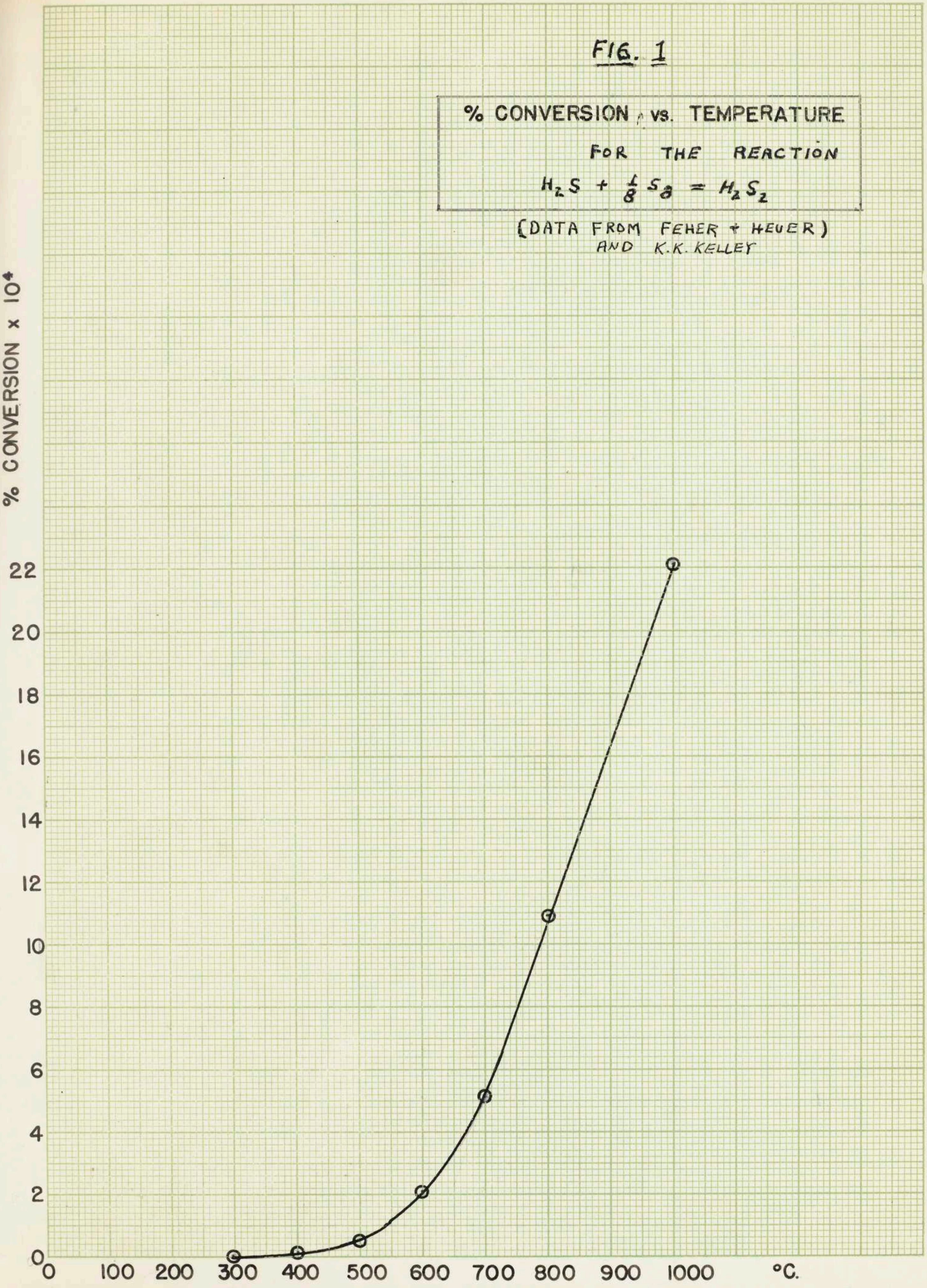
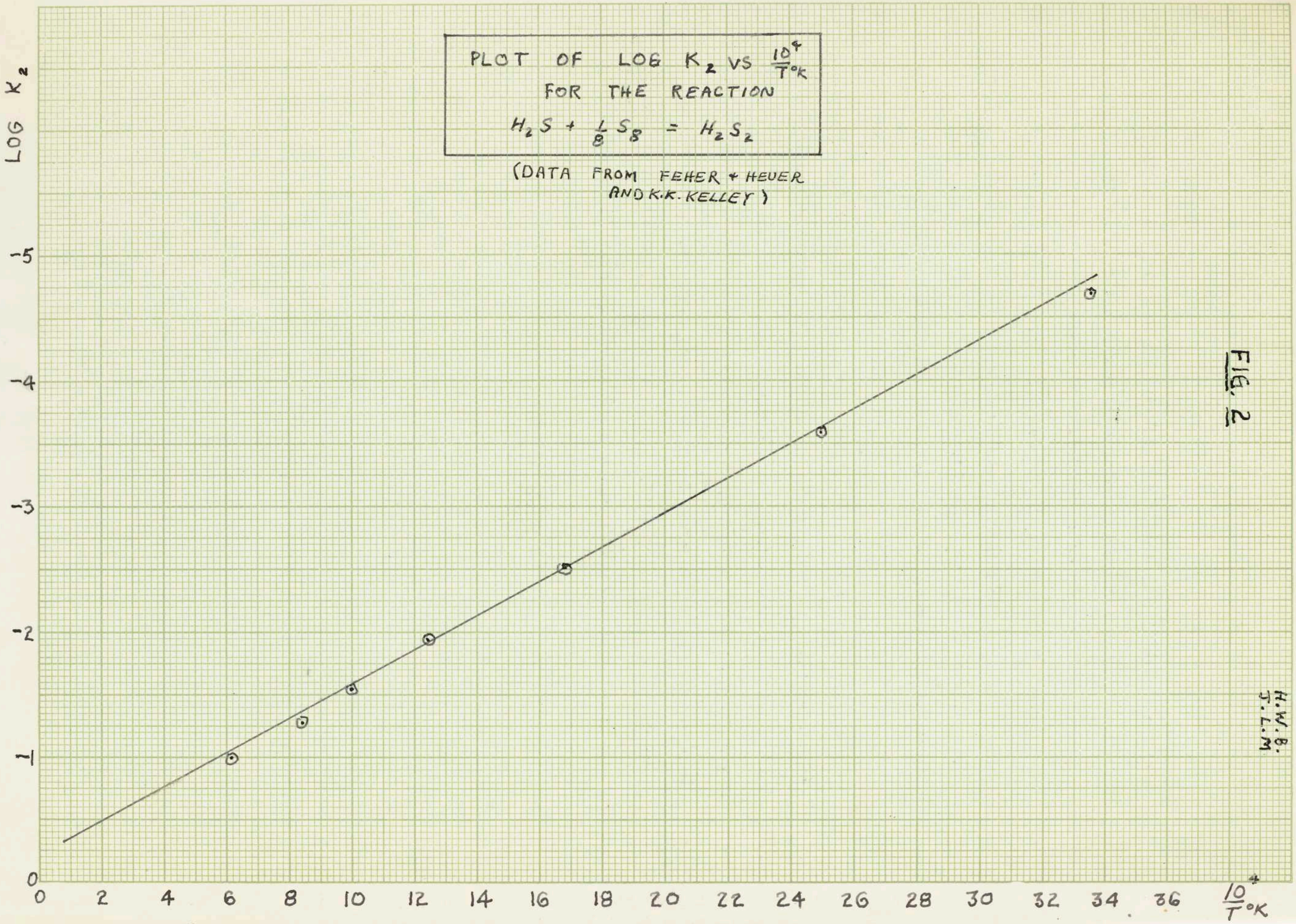


FIG. 1

% CONVERSION vs. TEMPERATURE FOR THE REACTION $H_2S + \frac{1}{8} S_8 = H_2S_2$

(DATA FROM FEHER + HEUER) AND K.K. KELLEY



PLOT OF LOG K_2 VS $\frac{10^4}{T°K}$
FOR THE REACTION
$H_2S + \frac{1}{8}S_8 = H_2S_2$

(DATA FROM FEHER + HEUER
AND K.K. KELLEY)

FIG. 2

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VI RECOMMENDATIONS

It is recommended:

(1) that the reaction proposed be investigated further, especially under conditions of higher temperature and pressure.

(2) that the influence of catalysts be studied.

(3) that type 316 stainless steel or chromium be considered as reactor material in construction of any new reactor.

(4) that due to the poisonous chemicals involved in the reaction, either a new gasket material be found, or a reactor be designed which does not need a gasket.

(5) that in the design of a new reactor, the parts be larger and therefore stronger. The size of the reactor should not be limited by the size of the available furnace as the authors' was, but if need be, should be electrically wound, but in any case, it should be larger.

(6) that stainless steel bolts not be used in fastening the head because they are relatively weak. A better arrangement would be to have detatchable nuts and bolts for ease of replacement.

VII APPENDIX

DETAILS OF PROCEDURE

The High Pressure System

The high pressure network (see schmatic diagram p.25) was connected by 1/8 " copper high pressure tubing. Although H_2S would have corroded the copper tubing at temperatures above room temperatures, copper tubing was satisfactory because the entire system with the exception of the reactor and the inlet stainless steel pipe of the reactor was at room temperature. High pressure unions and valves were used throughout. The system was constructed so as to be operated from behind a steel boiler-plate panel for safety purposes. A tank containing liquid and gaseous hydrogen sulfide was used as a source of this gas under pressure. Nitrogen served as the supply of inert gas. The pressures were measured with a calibrated bourdon tube and the temperatures by a chromel-alumel thermocouple connected to a millivoltmeter.

The Pretesting of the Reactor

In order to test the reactor for leaks and defects in construction, it was hydraulically tested. It was desired to have a safety factor of about three, but since the metal of the reactor is roughly one-third as strong at the upper temperature limits as at room temperature, the reactor should be hydraulically tested at nine times the pressure to be used in the reaction. The reactor was leakproof until 3000 psig was reached and thus an operating pressure of at least 300psig was permissible. However, it was found that gases would leak much more than the water used in the hydraulic tester. Thus the pretesting of the reactor is only an indication of its strength and not of its leakproof qualities during the reaction.

The Experimentation With Gaskets

It was found that a new, thin aluminum foil gasket had to be placed on the head for each run. Evidently the gasket deformed enough during a run so that gas would leak out if it was used a second time. Several gaskets were considered. Copper would have been a possibility if it could resist sulfur at the high temperatures. Teflon was used for a hydraulic test but it deformed very badly and leaked greatly. An asbestos gasket was tried but it also leaked. Both thin annealed aluminum foil and thick aluminum foil were tried but were unsatisfactory.

Assembling of the Reactor

The flange was screwed on the cylinder as indicated in Procedure, page 6. The thin aluminum foil was then placed in the head, the head placed on the cylinder, and the bolts tightened to the flange by the method of cross tightening to insure uniform distribution of the stress. Even with these precautions, the reactor sometimes leaked badly when filled with gas. The stainless steel pipe was connected to the system and the thermocouple was inserted into the thermocouple well.

THE CONSTRUCTION OF THE REACTOR

Corrosion Considerations

Since mild steel is attacked by the chemicals of this investigation the possibility of its use as a material of construction was eliminated. In general the oxides of most metals will also react with these chemicals, especially the polysulfide. The possibility of using an aluminum coating, applied by metal spray, on a mild steel was also considered but was rejected because aluminum oxidizes easily and might attack the polysulfide, besides the aluminum coating would probably be slightly porous if applied as above. Nickel plating on steel was considered, but rejected because of the difficulties of electroplating. The same considerations apply to chromium. Of the various stainless steels, type 316, of good machining properties and supposedly resistant to sulfur, was sued. The entire reactor, including bolts, was constucted of this material, the screws being chosen of the same steel so that expansion of the head upon heating would be as uniform as possible. The composition of steel 316 is:

C	0.1%	S	0.04%
Mn	2.0	Cr	16/18
Si	1.0	Ni	10/14
P	0.04	—	1.75/2.75

Strength Considerations

All formulas and theory from Perry's Handbook (3). The preliminary calculations were based on a maximum operating pressure of 750psig. The maximum diameter dimentions were fixed by furnace size.

Symbols:

P = pressure (pounds per square inch)
S = hoop stress (pounds per square inch)
E = efficiency of welded joint
R_o = ratio of outside diameter to inside diameter

Considering the reactor of size, O.D. = 1.900", I.D. = 1.600", and 5" long, of the three stresses on the reactor walls, hoop, longitudinal, and compressive, the compressive stress is not controlling, and the longitudinal stress is one-half of the hoop stress. The formula:

$$\frac{P}{S} = \frac{E(R_o-1)}{.6R_o + .4}$$

which is correct as long as R_o does not greatly exceed 1.2 (that is for thin walled cylinders), is applied with P = 750 psig, E = 1 (by assumption), R_o = 1.900/1.608 = 1.19, thus:

$$\frac{750}{S} = \frac{1(1.19-1)}{.6(1.19) + .4} \quad \text{or } S = 4460 \text{ pounds per square inch}$$

which gives the controlling stress set up by the pressure of the gas. alone.

Since the upper limit of temperature is approximately 1000°F, the corresponding creep stress (1% elongation in 10000 hours) is used at this temperature, namely, 25,000 pounds per square inch. Thus we are well within safety limits. However, when the reactor is quenched, the stress on the outside wall will be much greater than the 4460 psi caused by the pressure because of the temperature gradient across the walls. It is possible that the stress could be so great as to crack the reactor. Although this stress can be calculated, the value of ΔT across the wall, must be known. This is less than the overall ΔT between the water and the hot gas due to the ΔT drops across the gas films. Rather than calculate the ΔT across the wall, a scrap piece of type 316 stainless steel pipe, left over from the reactor construction, was heated by a torch until red and then water quenched. The results of this experiment, it was felt, would give a more accurate indication of the possibility of cracking of the wall of the reactor during quenching than would a calculation. Even after repeated flexing the quenched steel showed no signs of cracking. In addition, the piece had been quenched from a temperature probably much higher than the upper operating limits.

In calculating the strength of the six 1/4" x 28 bolts in the head of the reactor, with increased temperature taken into consideration of course, a safety factor of four was calculated simply by knowing the cross sectional area of the six bolts and the pressure on the head. However, the fact which was completely overlooked in this respect, was that the bolts were prestressed when in the head, to an unknown value. Several bolts were stripped in the course of the investigation while tightening the head. This shows that this calculation was misleading for it gave no indication of the actual stress on each bolt during the experiment. Fortunately the bolts never broke during the experiment, although they were considerably prestressed, evidenced by the severely necked bolts.

The flange was made in the manner indicated and screwed on the cylinder rather than welded so that the head could be more easily removed. The six taped holes for the bolts were located in the flange.

The gas feed pipe was finally welded in the head because the pipe plug connection originally planned leaked. The thermocouple well, holding the chromel-alumel wires and insulators, was also welded in the head and extended halfway into the cylinder. The base of the reactor was welded was shown on page 21.

FIG. A 1

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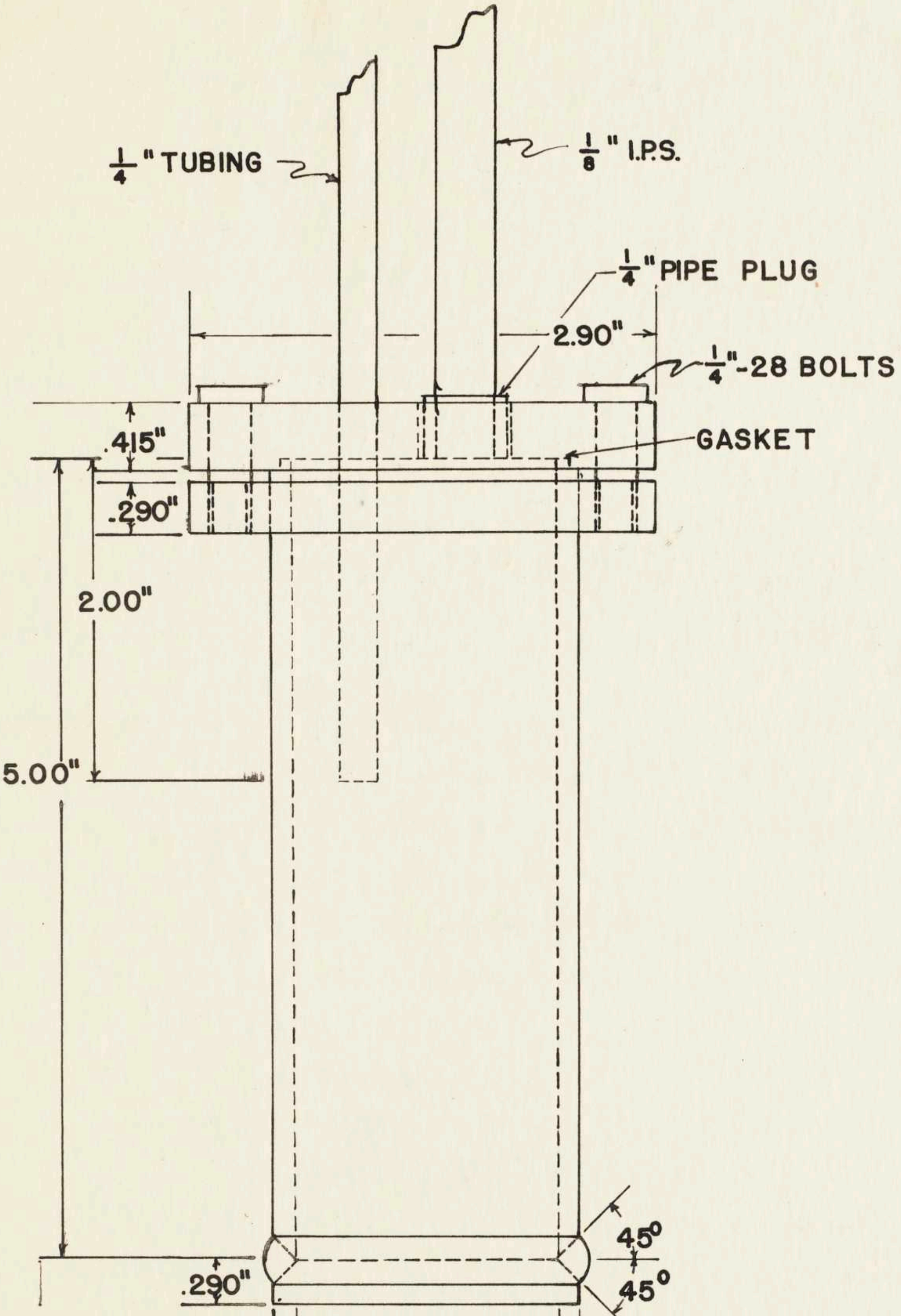

REACTION APPARATUS

CALCULATIONS

The reactions to be considered in the hydrogen-sulfur system are:

$1/2\ S_2 = 1/8\ S_8$ (3)

$H_2 + 1/2\ S_2 = H_2S$ (4)

$H_2S + 1/8\ S_8 = H_2S_2$ (2)

$H_2S + 1/4\ S_8 = H_2S_3$ (5)

$H_2S + 3/8\ S_8 = H_2S_4$ (6)

$H_2S + 1/2\ S_8 = H_2S_5$ (7)

$H_2S + 5/8\ S_8 = H_2S_6$ (8)

and so on for the higher polysulfides.

Feher and Heuer (1) give equilibrium constants at various temperatures for the reaction: $H_2S + \frac{1}{2}\ S_2 = H_2S_2$. (2′) These are given in Table II.

Table II

T, °K	298.1	400.0	600.0	800.0	1000.0	1200.0	1500.0
K	16.8	1.09	.0788	.0223	.0109	.00708	.00462

Kelley (2) reports ΔF° for reaction 3 as a function of temperature: $\Delta F^\circ = -11900 + 1.73\ T \log T + 8.535\ T$, and since $\Delta F^\circ = -RT \ln K$, we know K_2, equal to K_2'/K_3. For example, at 400°K:

$$\Delta F^\circ = -11900 + 1.73 \times 400 \times \log 400 + 8.535 \times 400$$

$$= -1.99 \times 400 \ln K_3$$

Solving: $K_{3,\ 400^\circ} = 4580$.

Also at 400°K., Feher and Heuer (1) give $K_2' = 1.09$

$$\therefore\ K_2 = K_2'/K_3 = 1.09/4580 = 23.9 \times 10^{-5}$$

Thus, K_2 can be calculated at all the temperatures for which there are data. Log K_2 is plotted as a function of temperature on p.13.

Assuming the perfect gas laws, since K is a function of temperature alone, pressure merely serves to help condense the products and has no effect on the percentage conversion if sulfur is at its vapor-pressure.

The percentage conversion may be plotted as a function of temperature based on the following sample calculation:

Using the equations: $1/8\ S_8 = 1/6\ S6$ (9)

$1/2\ S_2 = 1/8\ S_8$ (3)

$P_{S_6} + P_{S_8} + P_{S_2}$ = total sulfur pressure

= vapor pressure of S

since all of these constituents go to make up the total sulfur pressure. The vapor pressure of sulfur may be given by the following equation over the range, 373 to 873°K.:

$$\text{Log } P = \frac{-4940}{T} - 4.08 \times 10^{-3}\, T + 9.81$$

Kelley (2) gives F° for reaction (9) as a function of temperature:

$$F^\circ = \frac{29250}{24} - \frac{4.6}{24}\, T \log T - \frac{27.81}{24}\, T$$

Thus, at 400°K. for example, $K_9 = 2.2$ and $K_3 = 4580$. Using the vapor pressure equation at 400°K., we find:

$$\text{Log } P = \frac{-4940}{400} - 4.08 \times 10^{-3} \times 400 + 9.81 = 4.17$$

$$\therefore P = 67.6 \times 10^{-5} \text{ atmospheres.}$$

Since the percentage yield was based on S_8 in the equation (2) the value of P_{S_8} is needed. The simultaineous solution of the above three equations gives $(P_{S_8})^{1/8} = .295$ atmospheres, and since

$$\frac{P_{H_2S_2}}{P_{H_2S} \times (P_{S_8})^{1/8}} = 23.9 \times 10^{-5}$$ and P_{H_2S} equals one atmosphere,

arbitrarily, $P_{H_2S_2} = 7.08 \times 10^{-5}$ atmospheres.

From such calculations, the percentage conversion, as defined in the following, may be plotted as a function of temperature.

Assuming the perfect gas laws, the percentage conversion of H_2S to H_2S_2 may be defined as :

$$\frac{P_{H_2S_2}}{P_{H_2S} + P_{H_2S_2}} \times 100$$

This is seen to be dependent upon the temperature, and the pressure of sulfur since our reaction (assuming the only product is H_2S_2) is: $H_2S + 1/8\ S_8 = H_2S_2$

and $$K = \frac{(P_{H_2S_2})}{(P_{S_8})^{1/8}(P_{H_2S})}$$

These percentage conversions of H_2S to H_2S_2 may be plotted as a function of temperature with sulfur at its vapor pressure for example. This has been done (see page 12).

Since no thermodynamic data are available on the higher polysulfides, the percentage conversion to H_2S_3, H_2S_4, etc., can be guessed at only by approximation methods alone and will not be attempted here.

FIG. A2

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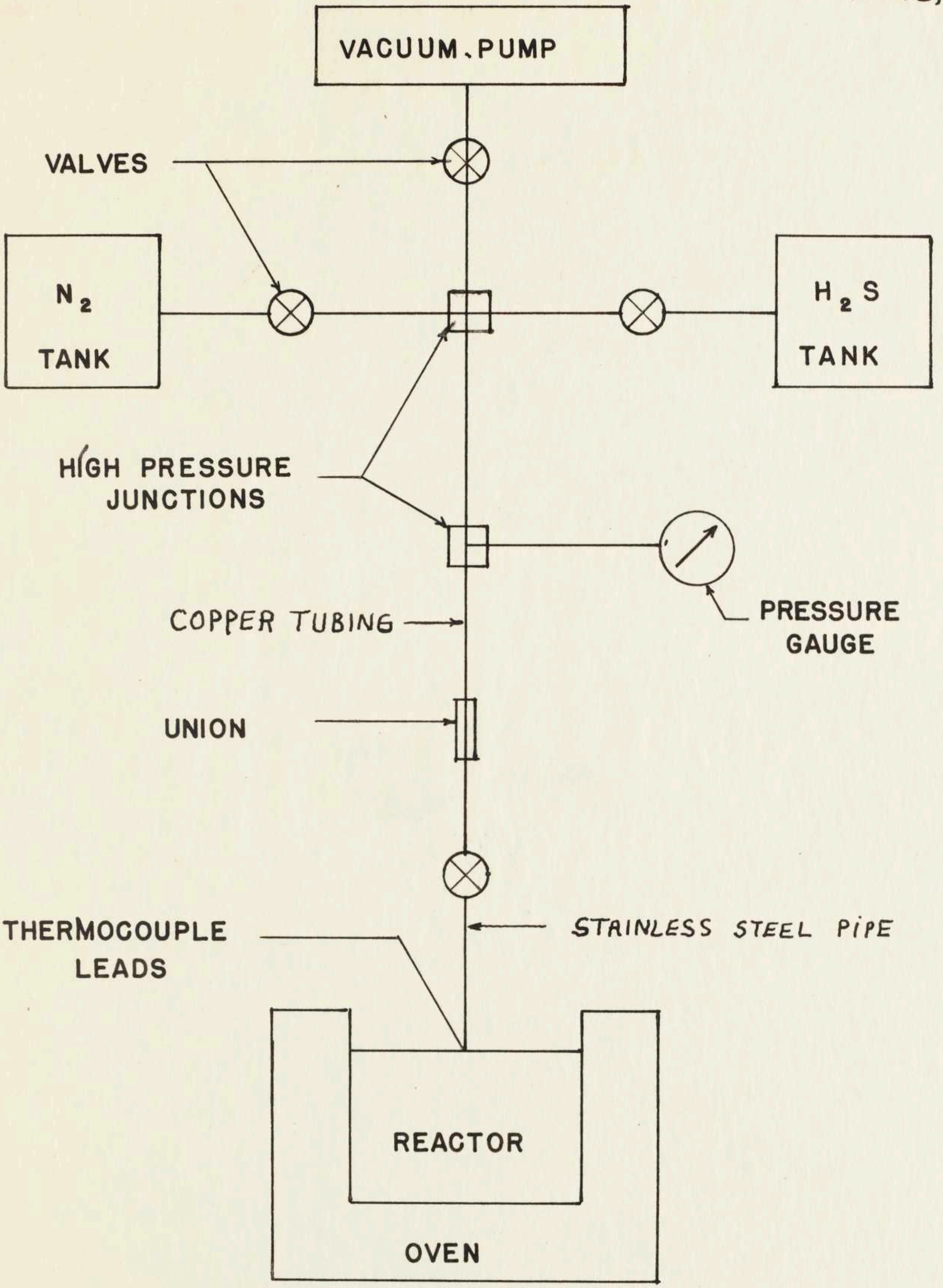

SCHEMATIC DIAGRAM OF SYSTEM

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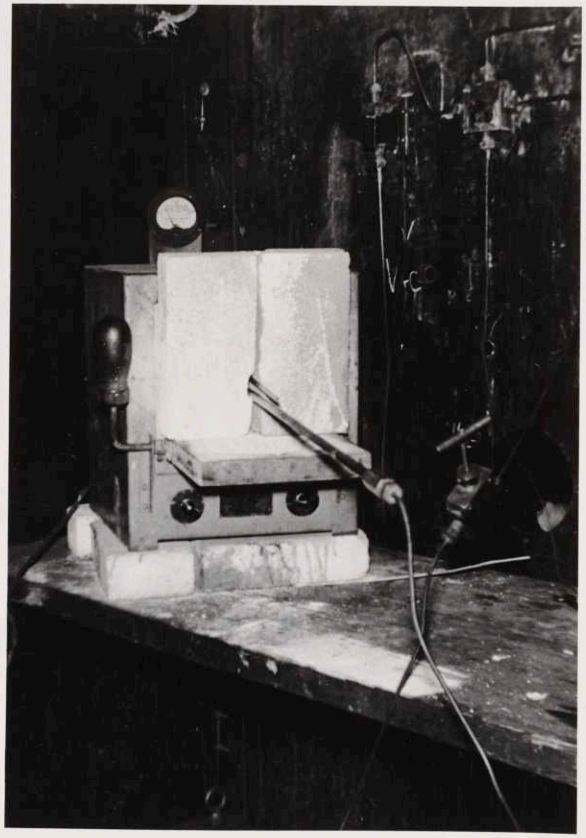
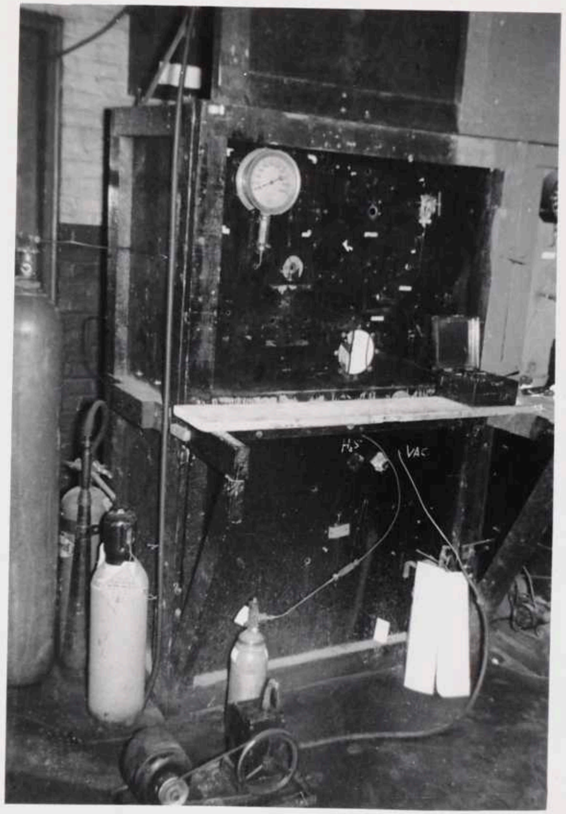
FIG A-3



REACTOR, IN FURNACE,
ATTACHED TO
HIGH PRESSURE SYSTEM

FIG A-4



SAFETY PANEL
WITH EQUIPMENT

METHOD OF ANALYSIS

Although no product was obtained during the experimental work, the following method of analysis is included as an indication of what would have been done. The method of analysis, performed in order to determine the empirical formula of the polysulfide, takes advantage of the fact that H_2S_2 or any of the higher polysulfides, are catalytically decomposed quantitatively and rapidly into H_2S and sulfur when brought into contact with pulverized glass or quartz.

The analysis vessel consists of a small weighing bottle fitted with a cover containing glass wool. The cover fits tightly on the bottle. The bottom of the vessel is covered with a layer of the ground quartz and a small crucible is placed on this layer. The apparatus is weighed. The liquid product is carefully introduced into the crucible and the whole weighed again. Upon slight shaking the small crucible will fall and the ground quartz will immediately decompose the product. The H_2S vapors will rise and leave the apparatus, passing through the glass wool, while the sulfur remains. The glass wool decomposes any product which might be carried upward by the reaction. The apparatus is again weighed, and the empirical formula of the product is determined as in the following example:

weight of sample........................	0.2000 gm.
weight of sample after decomposition....	0.1500
therefore, weight of H_2S lost...........	0.0500
total mols S......	0.00616
total mols H_2.....	0.00147

Therefore: empirical formula is $H_2S_{4.2}$

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