CONF-891013--5

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DE90 001958

Conversion of Enriched Isotopes of Sulfur from SF_6 to a Suitable Compound for Feed to the Electromagnetic Calutron Separators

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To be presented at the Sixth Symposium on Separation Science and Technology for Energy Applications, Knoxville, Tennessee, October 22-27, 1989.

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Conversion of Enriched Isotopes of Sulfur from SF_6 to a Suitable Compound for Feed to the Electromagnetic Calutron Separators

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ABSTRACT

Enriched isotopes of sulfur are becoming attractive for use as tracers in a variety of environmental and scientific experiments. Many stages of separation are needed, especially for ^{33}S and ^{36}S, which exist in low natural abundances. Small amounts of highly enriched sulfur isotopes can be provided by means of electromagnetic separation in the calutrons. However, the cost is prohibitively high for enrichment of large amounts needed by many experiments. Thus, a two-stage process is planned to obtain large amounts using gas centrifuges for preenrichment, followed by final enrichment in the calutrons.

Sulfur hexafluoride is the most efficient form for processing sulfur in the centrifuges; however, SF_6 is unacceptable as feed to the calutrons because it has excellent insulating properties for the high voltage apparatus used to ionize the feed. An efficient process is needed to convert the preenriched sulfur isotopes from SF_6 to a suitable form for calutron feed.

Development of a process is difficult because of the relatively high stability of SF_6. Reiner and Simmons[1] have successfully converted SF_6 to SO_2 in pilot studies using a propane/oxygen flame reactor. However, H_2S is a more desirable intermediate for producing metal sulfides or sulfur halides. Thus, experiments have been made using direct hydrogenation at temperatures of >900°C. Conversion to cadmium sulfide has been accomplished by scrubbing the H_2S product gas with 5% $CdCl_2$ and product yields of >90% have been achieved. A developmental program to convert SF_6 to CdS, or another more efficient form is being carried out. Optimum conditions for the conversion are being determined and the products are being evaluated in calutron test runs.

INTRODUCTION

Enriched stable isotopes of sulfur are important in many areas of research, including environmental and biomedical. At the present, there is a real interest in using sulfur isotopes for DNA sequencing in the human genome project. The sequencing method is not a topic for discussion for this paper, but it is important to note that it will require all four of the sulfur isotopes enriched to ~99%, a level of enrichment that has not previously been achieved for the minor isotopes: ^{33}S, ^{34}S, ^{36}S. To achieve the required enrichments, a number of separation processes were considered which included: molecular laser isotope separation, atomic vapor laser isotope separation, plasma separation process, thermal diffusion, gas centrifuge, and the electromagnetic isotope separation (calutron). The separation method that is presently being pursued utilizes the calutron in tandem with the gas centrifuge. Gas centrifugation is used for initial preenrichment of the minor isotopes of sulfur. The final enrichment will be carried out in the calutron using the preenriched sulfur.

The gas centrifuge process is amenable to enriching the minor isotopes of sulfur in that the feed abundance is modified to enhance either the heaviest or lightest isotopes. This process is further characterized by large throughput with relatively low separation factors. A schematic representation of the gas centrifugation process for sulfur enrichment is shown in Figure 1. Sulfur feed enters the system at the center; enrichment is accomplished by centrifugation and thermal diffusion due to the countercurrent motion of the molecules. The product and depleted tails are withdrawn by scoops located at the top and bottom of the centrifuge.

The electromagnetic separation, in contrast to other methods, is that all isotopes of multiisotopic elements are enriched simultaneously. Also, the process has large separation factors with a relatively low throughput. The principal components of the separator are an ion source, an electrostatic accelerating system, a series of isotopic collectors, a magnetic field and a vacuum system. The ion source and collector are internal to the analyzing magnet, as shown in Figure 2. Feed material, in either elemental or compound form, is introduced into the arc discharge directly as a gas or vapor from heating the feed. The particles are ionized, extracted from the source at a final energy of ~40 keV, deflected through 180°, and the individual isotopic beam refocused at the collector.

The process efficiency, defined as the ratio of the total quantity of all isotopes reaching the collectors to the quantity of feed vaporized, ranges from 5% to 25%. A portion of the unresolved feed can be recovered and recycled. For expensive feeds, such as the preenriched sulfur, the compound selected must be based on the process and recycle efficiency as well as the beam throughput, resolution, and isotopic purity.

The enriched SF_6 product from the gas centrifuge is not suitable as feed for the calutron. It must be converted to a more condensible or reactive species so that the unresolved component of the calutron feed can be trapped within the vacuum chamber (Fig. 2), recovered, and recycled. Prohibitive losses of the valuable preenriched sulfur will result unless substantial recycle of unresolved calutron feed is attained. Gettered pumping is a desirable recovery technique for unresolved feed where feasible. It minimizes the amount of material that must be leached from the vacuum chamber walls.

The approach in our conversion studies is to reduce the SF_6 with hydrogen according to the following equation.

$$SF_6 + 4H_2 \rightarrow H_2S + 6HF \ .$$

This reaction is particularly attractive because the H_2S can be quantitatively converted to CdS and separated readily from the other reaction product HF. The CdS itself is a candidate feed material for the calutron; however, it is easily converted back to the desirable intermediate of H_2S by acidification, or to free sulfur by reaction with acidic ferric chloride.[2] H_2S is a desirable intermediate to form almost any metal sulfide or sulfur chlorides. Sulfur is particularly attractive for the synthesis of carbonyl sulfide. Although the literature[4-7] contains several ways of converting SF_6 to other forms of sulfur, none are as attractive as direct reduction of SF_6 with H_2.

The work reported here is our progress to date on optimizing the conditions for reacting H_2 with SF_6. The common hydrogenation catalysts (Ni, Pd, and Pt) were also investigated in regard to lowering the reaction temperature.

EXPERIMENTAL

The tests on the reaction of SF_6 with H_2 were carried out in horizontal Vycor tubes which were heated by a nichrome wound furnace (Fig. 3). Tests were always conducted with large a excess of H_2 (5-10 fold excess). Temperatures were controlled by a chromel-alumel thermocouple. All chemicals employed were reagent grade or better. Flow rates of SF_6 were determined by weight difference measurements of the feed cylinder. Most of the HF formed in the reaction (Eq. 1) is removed by the H_2O bubbler trap (Fig. 3) whereas the H_2S is converted to CdS in the subsequent traps which contain $CdCl_2$ (5 wt %) solution. The conversion yield for the reaction is determined from the weight of sulfur recovered as CdS and the weight of SF_6 feed to the system. In preliminary tests where water vapor was introduced in the feed, a prehumidifier (not shown) was inserted in the SF_6 entry line and a $BaCl_2$ (5 wt %)

trap was employed instead of the water trap in Fig. 3 to detect any SO_2 or SO_3 that was formed via precipitation of barium sulfite or sulfate.

Initial tests of the uncatalyzed reaction were conducted with no packing material in the furnace tube. In subsequent tests, an 18-in. section of the central heated zone of the furnace tube (2-3/4-in. diam x 34-in. length) was packed with hollow cylinders of a ceramic material ($MgO \cdot SiO_2$) to obtain better mixing and heating of the reactant gases. The dimensions of the hollow cylinders were 5/16-in. OD, 3/16-in. ID, and 1/2-in. long. Also, to determine the relative effectiveness of Ni, Pt, Pd as catalytic materials, the hollow cylinders were coated with the appropriate metal. This coating of ~0.7 liter batches of the cylinders was accomplished by the following procedure.

1. Boil the ceramic cylinders in a 5 wt % solution of the metal nitrates for 30 min.
2. Decant the metal salt solution and dry the hollow cylinders at 120°C.
3. The dried cylinders are then transferred to a tube furnace and heated under argon to 600°C to decompose the nitrates to oxides.
4. The furnace atmosphere is then changed from Ar to H_2 and heated to 850°C and held for two hours for reduction of the oxides to metal.

Tests on the feasibility of CdS and ZnS as calutron feed materials were conducted using the high temperature ion source previously discussed by Normand, Love, Bell, and Prater.[3] The sulfides are carefully dried and protected from moisture before introduction as ion source feed.

RESULTS AND DISCUSSION

Conversion of SF_6

SF_6 is thermodynamically unstable relative to reactions with hydrogen or water (Table 1). These reactions are kinetically impeded by the fluorine shielding of the sulfur, particularly in the lower temperature regions. Reaction of H_2 or H_2/H_2O mixtures with SF_6 to produce H_2S would be an acceptable conversion method provided satisfactory reaction rates are attained.

Preliminary tests were conducted on the reaction of SF_6 with H_2/H_2O and with dry H_2 at 900-950°C to determine if reaction could be effected to produce H_2S, sulfur oxides, or their mixtures. These tests were conducted without

Table 1. Free Energy Change (ΔG) for Some Reactions Involved in the Conversion of SF_6 to H_2S or Sulfur Oxides

Reaction[a]	ΔG, Kcal 25°C	ΔG, Kcal 500°C	ΔG, Kcal 1000°C
$SF_6 + 4H_2 \rightarrow H_2S + 6HF$	-135	-185	-237
$SF_6 + 3H_2O \rightarrow SO_2 + 6HF + 1/2\ O_2$	-36	-88	-143
$SF_6 + 3H_2O \rightarrow SO_3 + 6HF$	-52	-102	-155
$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$	-46	-39	-32
$SO_3 + 4H_2 \rightarrow H_2S + 3H_2O$	-83	-82	-80

[a] Reactant and products species in all reactions are the gaseous forms.

any packing in the furnace tube. Although the heating and mixing of reactant gases was poor, the tests showed that reaction was possible at about 900-950°C. In one of the tests where 3.72 g of SF_6 was bubbled through boiling water, mixed with a carrier gas of Ar-5% H_2 and passed through the furnace tube heated to 950°C. About 6% of the SF_6 was converted to sulfide whereas only a trace of the SF_6 converted to sulfite or sulfate. Subsequent tests on the reaction of dry hydrogen showed that gaseous H_2O was not necessary to promote attack of the fluorine-shielded sulfur atom to release SO_2 or SO_3 for subsequent reduction to H_2S by H_2. Hydrogen reduces SF_6 to H_2S directly. Three runs on the reaction of SF_6 with dry H_2 at 950°C in the heated furnace tube indicated the potential for direct reduction of SF_6 to form H_2S in good yield (Table 2). More efficient heating and mixing of the reactant gases could be expected to increase yields and this was demonstrated in subsequent runs using a packed bed zone (18-in. length) within the furnace (Fig. 4). The rate of SF_6 conversion was increased significantly by the packed bed; however, it still was not as rapid as desired and led us to examine certain metal catalysts (Pt, Pd, and Ni) for their ability to accelerate the SF_6 and H_2 reaction. About 1 g/min conversion rate would be satisfactory for the anticipated isotope production program.

Table 2. Effect of SF_6 Flow Rate on H_2S Yield at 950°C in Furnace Tube with No Packing Material to Enhance Heat Transfer and Gas Mixing

SF_6 Flow Rate, mg/min	% Conversion to H_2S
109	77.8
162	56.0
217	44.6

Pt, Pd, and Ni are frequently employed as catalysts for the promotion of hydrogenation and H_2 reduction catalysts; hence these metals were tested for their ability to promote the reaction of SF_6 and H_2. The conversion rates of SF_6 by H_2 in packed beds of catalyst coated particles are compared with uncoated particle beds as a function of temperature in Fig. 5. Near quantitative yields were obtained at 0.8 g/min SF_6 flows with the Pt or Pd catalysts at 700°C and for the Ni catalyst at 750°C. Conversion was still only about 80% at 950°C with no catalytic coating on the packed bed particles. Further tests with the Pt catalyst showed that SF_6 can be converted to H_2S with greater than 98% efficiency using SF_6 flows as high as 1.85 g/min.

Calutron Feed Tests

The criteria for chemical compounds that are used as calutron feed are that they (1) have a controllable vaporization rate when heated, (2) have good chemical stability at high temperature, (3) are readily ionized so that high ion throughputs are attained, and (4) be easily condensed or trapped which permits the unresolved feed material to be recovered and recycled. We have tested CdS, ZnS, and PbS to determine if these compounds were suitable as calutron feeds of the preenriched sulfur isotopes. In the CdS and ZnS tests, pressure instability and erratic ionization behavior indicated decomposition of the feed material which would make recovery and recycle of the unresolved feed components very difficult or unlikely. Lead sulfide feed enabled good control of the vaporization rate, but the current was only 7 mA. An output current of 7 mA is about one-tenth of that needed for an acceptable processing rate.

In future tests, we will be evaluating carbonyl sulfide for the calutron feed. This gaseous charge material was used some years ago for sulfur feeds where the sulfur isotopes were at their natural abundance. In the present application, we must develop a synthesis for the COS feeds of the preenriched isotopes. Equipment required for the operation of the calutrons with a gaseous COS feed is being designed. Calcium pumping or "gettering" will be employed to maximize recovery of unresolved feed material.

CONCLUSIONS AND FUTURE WORK

Laboratory-scale tests show that SF_6 can be converted to H_2S in high yield (>98%) by direct reduction with an excess of hydrogen at acceptable rates (1.9 g/min SF_6). The reactant gases were passed through a packed, horizontal bed of Pt coated ceramic particles at 700°C. The reaction is much slower without the presence of catalytic coatings on the ceramic particles. Pd and Ni were also good catalysts for the reduction. Longer term tests of catalytic performance are planned for the immediate future. To date, tests have been for periods of 24 hr or less. The H_2S is converted to CdS by reaction with a $CdCl_2$ solution. The sulfur bound to Cd can be converted back to H_2S or to elemental sulfur for subsequent synthesis when desired.

Now that we have demonstrated the feasibility of the reduction of SF_6 by H_2, we expect to turn our attention to equipment development and further process optimization. Alternative materials for the furnace tube and the ceramic particles used as catalyst support such as alumina and zirconia will be examined. We have experienced modest attack of the Vycor furnace tube and the ceramic support material by the HF evolved in the reactions. Also, we need an improved design of the liquid scrubbers to improve liquid reagent usage, to prevent blockage of gas flow by solids, and to improve collection and washing of the CdS precipitate.

Calutron tests using metal sulfide feeds (CdS and PbS) have not been successful. Ion beam currents could not be established that were sufficiently high for acceptable processing rates of sulfur isotopes. Plans are in progress to test carbonyl sulfide (COS) as calutron feed. The use of COS would require that a synthesis pathway be developed to transform the CdS product obtained from the SF_6 conversion to COS. We expect to begin such synthesis work in the near future.

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Schematic of Gas Centrifuge

~~SCOOPS EXTRACT THE PRODUCT AND TAILS STREAMS AT HIGH PRESSURE~~

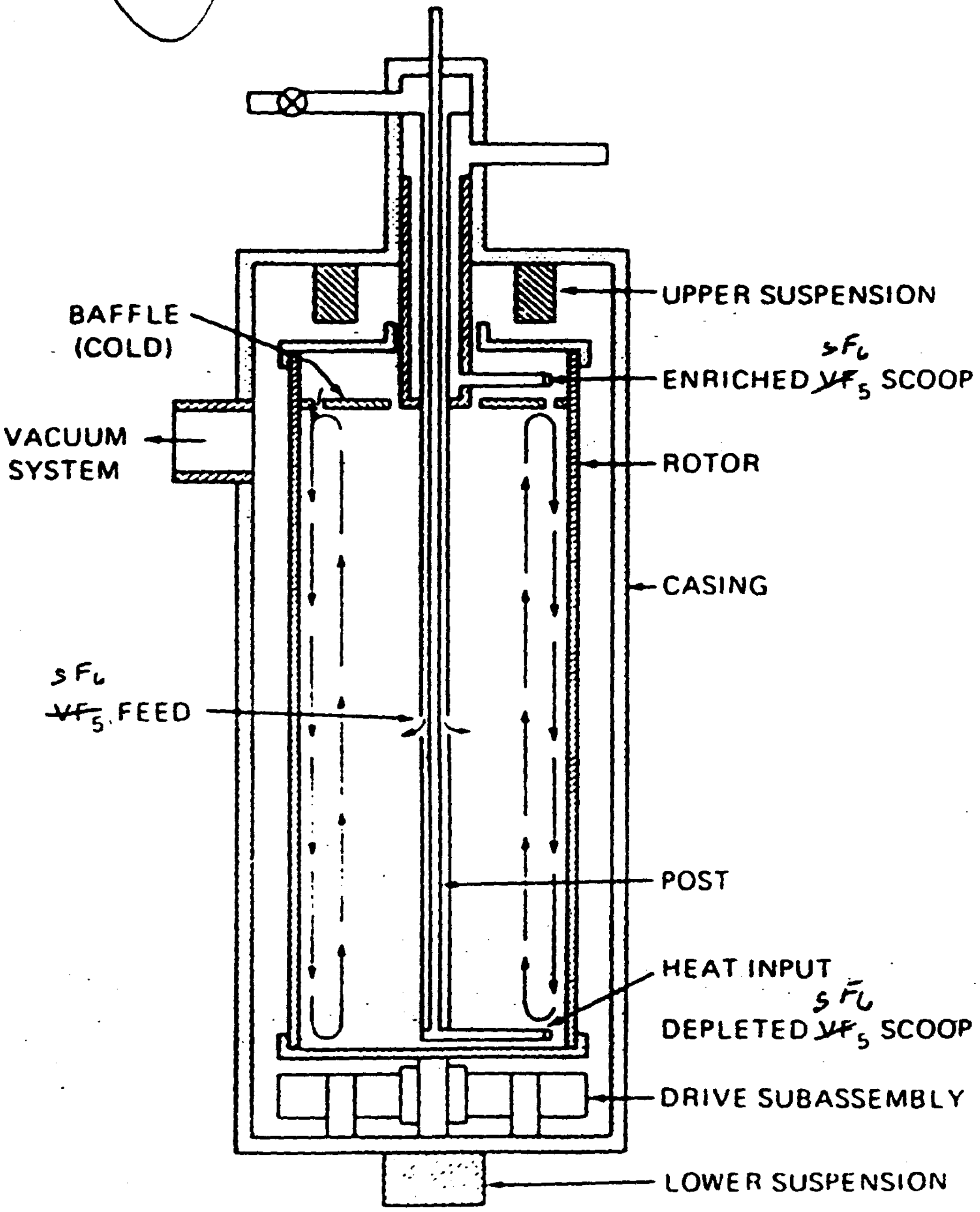

Fig. 8

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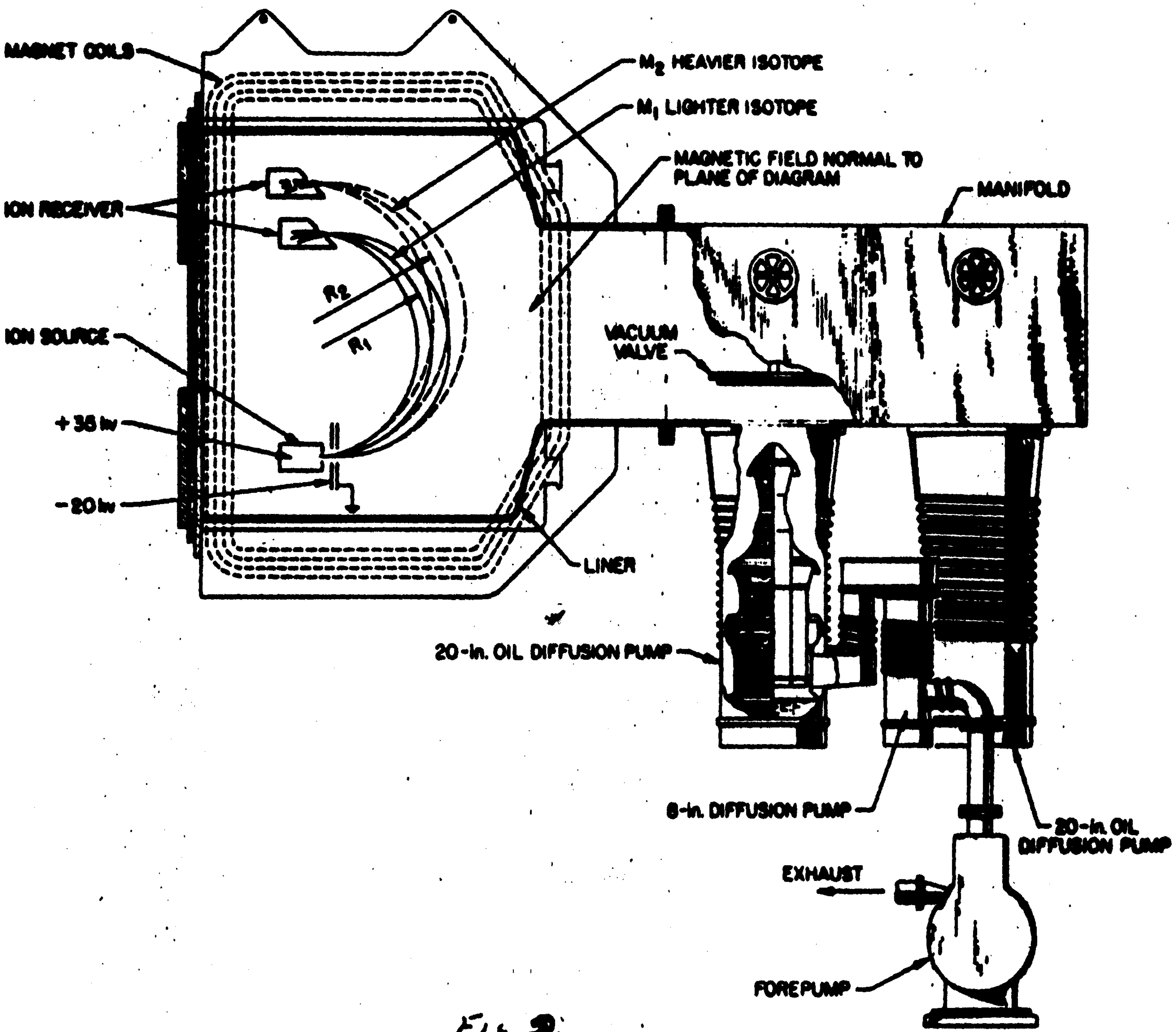
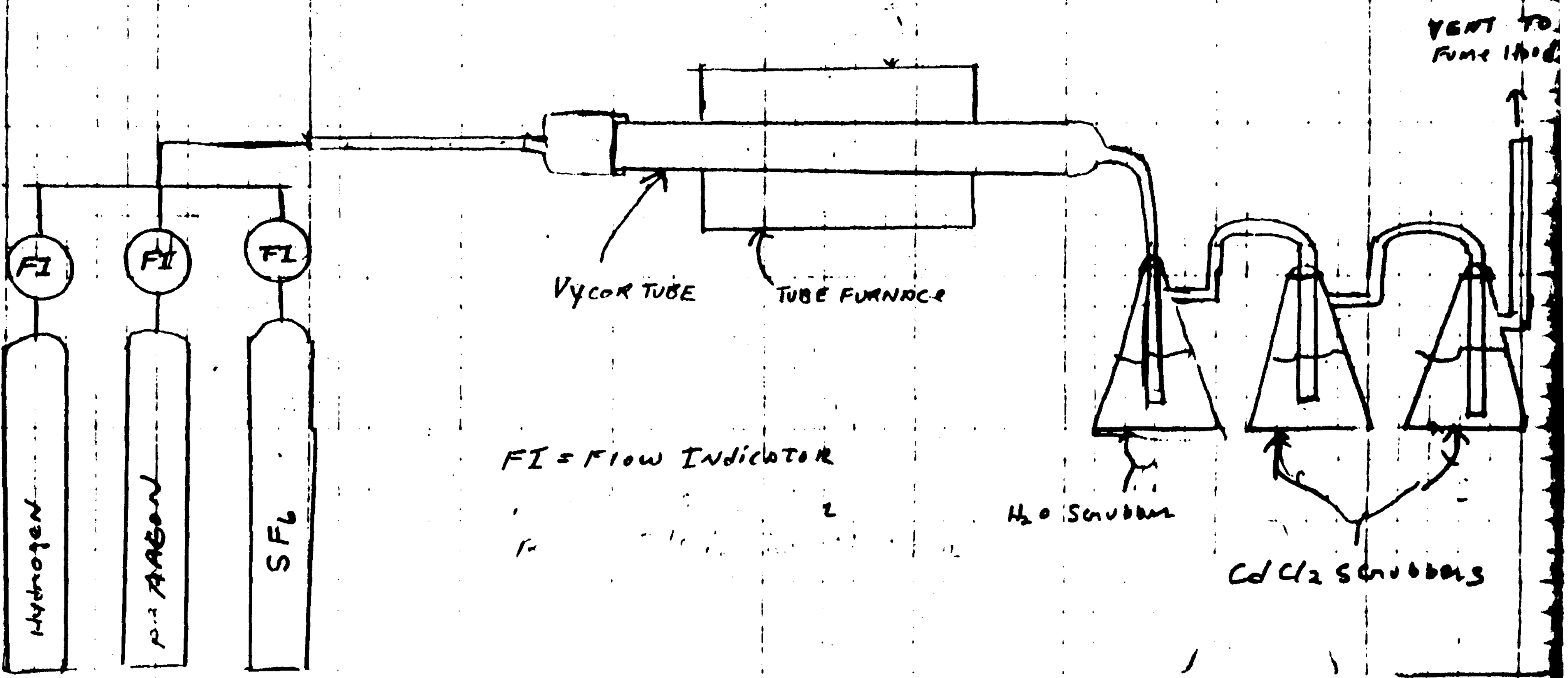


Fig. 2

Schematic of the

Fig 3 EXPRIMENTAL APPARATUS



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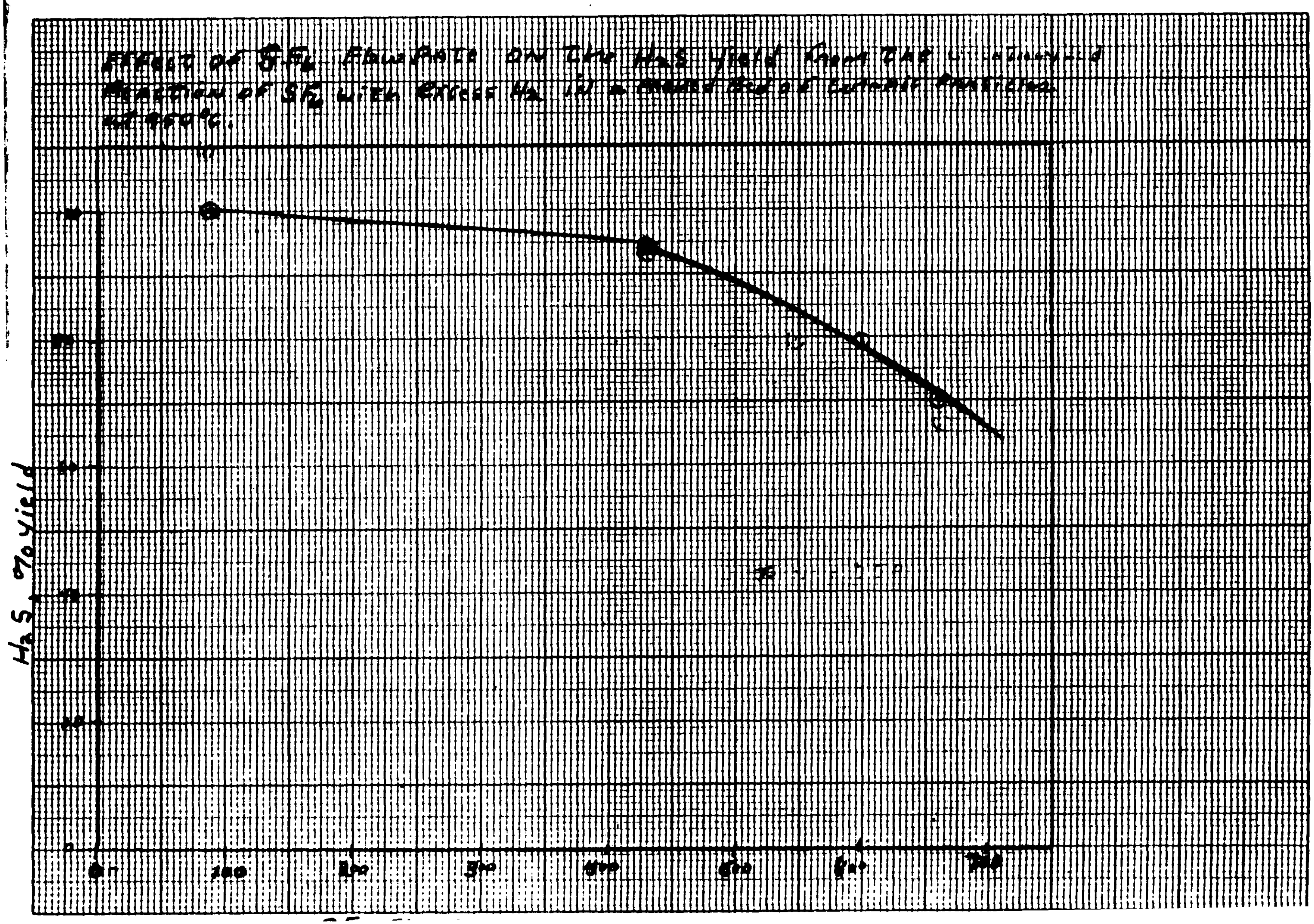

EFFECT OF SF6 FLOWRATE ON THE H_2S YIELD FROM THE [illegible] REACTION OF SF6 WITH EXCESS H_2 IN A [illegible] AT 950°C.

Effect of Temperature on the H_2S Yield from the Catalyzed and Uncatalyzed Reaction of SF_6 with H_2 in a Packed Bed