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University of Alberta

A New Route to Sulfur Recovery via Acid Contacting Process

by

Mohan A. Chitale ©

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree
of Master of Science

Department of Chemical Engineering

Edmonton, Alberta

Spring 1996

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22nd Dec. 1995

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis titled *A New Route to Sulfur Recovery via Sulfuric Acid Absorption Process* submitted by *Mohan A. Chitale* in partial fulfillment of the requirements for the degree of Master of Science.

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Abstract

The field of lean sour gas processing is still developing and an economical, high efficiency sweetening process is still sought. A new process called the "Acid Contacting Process", for sulfur recovery using sulfuric acid (H_2SO_4) as the reagent is evaluated in the present work.

Concentrated H_2SO_4 is well known as an excellent dehydrating agent. Attempts to use it in the Claus reaction system for water vapor removal showed its reactivity with hydrogen sulfide (H_2S). The following two reactions were found to explain the observed phenomena.

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$..............................(7)

$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$......................................(8)

The performance of this process is indicated by H_2S removal efficiency and the SO_2 formation in the effluent gases. Thermodynamic simulations showed that 100% H_2S conversion and zero SO_2 formation are feasible. Hence, an experimental evaluation of the laboratory-scale performance of this process was done. The objectives were: establishing the experimental equipment, obtaining reproducible and reliable data, parametric study of the process, and defining reaction stoichiometry and kinetic regimes.

The experimental results showed laboratory evidence of virtually zero SO_2 formation and 100% H_2S conversion. The effect of process variables shows that these results can be achieved in the temperature range of 120°C -150°C, high pressures, acid concentrations about 90 wt%, and high acid and gas velocities in a cocurrent downflow packed column for the experimental conditions studied. The regime of operation of reaction (7) was inferred to be the kinetic regime for low acid concentrations and fast reaction regime for higher acid concentrations (above 90 wt%).

Acknowledgements

I am extremely grateful to Dr. I.G. Dalla Lana and Dr. K.T. Chuang for their technical and personal guidance and advice during this work. They gave generously of their time and expertise during my times of need.

My special thanks are due to the whole sulfur recovery clan, particularly Dr. Qinglin Zhang and Dr. Huseni Rangwala for their constant support, encouragement, help and guidance throughout this work. Also, I would like to express my gratitude to Dr. Huseni Rangwala and Dr. Ramesh Sadhankar for sharing their knowledge with me and pointing out several finer points of academic penmanship.

The workshop staff and the technologists were very cooperative and helpful throughout. My thanks are due to them.

Also my stay during this program was made very lively and interesting by the cherished companionship of several friends and colleagues. I appreciate this companionship.

Financial support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Above all, I express my sincerest gratitude to my beloved parents for their unconditional love, care and support throughout my life regardless of whatever endeavor I was involved in and in particular during my stay here on the other side of the globe.

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Nomenclature

A= Four way valve in Figure 4.1
A_i= Interfacial area at the gas-liquid interface
A, B, C, D= Specific heat coefficients of equation (2) and species involved in reaction (7)
a_i = Activity
a, b, c, d, ν_i = Stoichiometric coefficients
(a)= Aqueous phase
C_i= Interfacial hydrogen sulfide concentration in the liquid phase in Figures 5.25(a) and (b), mole/cc
C_p= Specific heat as defined by the equation (2), kcal/mole°C
CO= Carbon monoxide
CO_2= Carbon dioxide gas
COS= Carbonyl sulfide
$CGCA_x$= The GC area of gas x in the chart for equation (16)
CMP_x= Calibrated gas mole percent of gas x in equation (16)
cc = Cubic centimeter
ccm= Cubic centimeter per minute
CS_2= Carbon disulfide
E_h = Electrode potential, volts
G= Gas flow rate
G= Gibbs free energy, kcal/mole
(g)= Gas phase
GCA_x= GC area of gas component x for equation (16)
G/L= Volumetric gas flow rate/Liquid flow rate (sccm/ccm)
$\Delta G°$= Standard Gibbs free energy change, kcal/mole
$\Delta G°_r$= Standard Gibbs free energy change in a reaction, kcal/mole
gmole = gram mole
H= Enthalpy, kcal/mole
H_{tr}= Enthalpy of phase transformation, kcal/mole
$H^0(T)$= Standard state enthalpy at T in K, kcal/mole
ΔH= Enthalpy change, kcal/mole
ΔH_{120C}= Heat of formation at 120°C
$H_f(298)$= Heat of formation at 298 K, kcal/mole
ΔH_r= Enthalpy change in a reaction, kcal/mole
H_2= Hydrogen gas
H_2O= Water in liquid state
$H_2O(g)$= Water in gas state
H_3O^+= Protonated water
HSO_4^-= Hydrogen sulfate ions
HSO_3^-= Hydrogen sulfite ions
HS^-= sulfide ions

$H_2SO_4*2H_2O$= The HSC program representation of the formulae with stoichiometric numbers
H_2S= Hydrogen sulfide gas
$H_2S(a)$= Hydrogen sulfide dissolved in water
$[H_2S\ ]$= Hydrogen sulfide concentration in aqueous phase
H_2SO_4= Sulfuric acid of any concentration
$H_2SO_4(a)$= Sulfuric acid of very high dilution
$H_2SO_4(g)$= Gas phase sulfuric acid
$H_2SO_4.H_2O$= Monohydrate of sulfuric acid
He= Helium gas
K= Equilibrium constant
k_c= Forward rate constant of the Wackenroder reaction (8)
L=Liquid flow rate, ccm
(l) = Liquid phase
M= Molar
m= Normality of sulfuric acid in equation (21)
MP_x= Mole percent of gas x in equation (16)
N_2= Nitrogen gas
N_{H2SO4}= Normality of H_2SO_4 in equations (20) and (21)
N_{NaOH}= Normality of NaOH in equations (20) and (21)
NaOH= Sodium hydroxide
O= Oxygen atom
o= Weight of acid present in sample taken for equation (22)
O_2= Oxygen gas
$OH^-(a)$= Aqueous hydroxyl ions
OH(-a)= The HSC program representation of the aqueous ions
P= Pressure, psig
P_1= Pressure in equation (15) and inlet pressure in Figure 4.1, psig
P_2= Pressure in equation (15) and outlet pressure in Figure 4.1, psig
P_i = Interfacial partial pressure of hydrogen sulfide in Figures 5.25(a) and (b), psig
P.P.= Partial pressure of water over sulfuric acid, bar
ppm= Parts per million
psig= Pounds per square inch, gauge
R= Universal gas constant = 1.987 cal/gmole°C
$R.F._x$= Response factor for gas x in equation (16)
r_{H2S}= Rate of reaction in equation (1)
S= Entropy, kcal/mole
ΔS= Entropy change, kcal/mole
$S^0(T)$= Standard state entropy at T in K, kcal/mole
ΔS_r= Entropy change in a reaction, kcal/mole
S= Elemental sulfur in either liquid or solid state
S'= Excited state sulfur
$S^\bullet$= Sulfur in reference to the Neyman (1952) reference
S^{-2}, S^{+4}, S^{+6} = Ionic states of sulfur
S-8= Rings of sulfur atoms containing eight sulfur atoms

S_n= Sulfur aggregates of n sulfur atoms in liquid state
α-S, β-S, γ-S= Various forms of polymorphous sulfur
sccm= Standard cubic centimeter per minute
SO_4^{-2}= Sulfate ions
SO_2= Sulfur dioxide gas
$SO_2(a)$= Sulfur dioxide dissolved in water
$[SO_2]$= Sulfur dioxide concentration in aqueous phase, mole/cc
SO_3= Sulfur trioxide gas
T= Temperature, Kelvin
t= Time
T_1= Temperature in equation (15) and preheater temperature in Figure 4.1, °C
T_2= Temperature in equation (15) and reactor temperature in Figure 4.1, °C
T_{Tank}= Acid tank temperature in Figure 4.1, °C
T_{Oil}= Oil tank temperature in Figure 4.1, °C
T_{in}= Reactor inlet acid temperature in Figure 4.1, °C
T_{out}= Reactor outlet temperature in Figure 4.1, °C
T_{tr}= Phase transformation temperature, K
TLV= Threshold Limit Value
V= Volume, cc
v_1, v_2= Volumetric flow rates, ccm
V_{NaOH}= Volume of NaOH in equations (20) and (21), cc
V_{H2SO4}= Volume of H_2SO_4 in equations (20) and (21),cc
V.P.= Vapor pressure of water, bar
wt% = Weight percent
X, Y= Volumes of feedstock acid and distilled water required in equations (18) and (19), liter
X_i= Mole fraction of component i
x= Weight of acid sample taken in equation (23) and gas component in equation (16)
α= Extent of reaction (7) or reaction (10)
β= Extent of reaction (8)
γ= Activity coefficient

Chapter 1

Introduction

Removal of hydrogen sulfide (H_2S) and other acid gases is an indispensable operation in the industries where they are present as unwanted compounds in the feedstock or are produced as a waste. Typically, the natural gas processing industry, petroleum refineries and hydrometallurgical industry face acid gas removal problems. Gases such as hydrogen sulfide, sulfur dioxide (SO_2) and carbon dioxide (CO_2) are called acid gases because they form corrosive acidic solutions in aqueous systems. These gases, especially hydrogen sulfide, are not only highly toxic and environmentally damaging, but are also harmful for industrial operations in terms of catalyst poisoning and corrosion. Therefore, the processes used for the removal of acid gases from the sour gas streams are called "sweetening" processes. Table 1.1 lists various processes that require acid gas removal.

Most of the acid gases originate in the processing of fossil hydrocarbons, especially natural gas and coal. Sulfur (S), which is the principal element in these gases, occurs almost entirely in the combined form in its divalent state although the exact nature of the sulfur compounds varies according to the fuel. For example in natural gas, sulfur exists mostly in the form of hydrogen sulfide. But in oil and coal it is largely present in organic compounds such as mercaptans, sulfides, disulfides and heterocyclic compounds such as thiophens. With an ever increasing demand for energy, also the utilization of fossil fuels with increasing sulfur content is on the rise; hence, the innovations and modifications to the sweetening processes continue. The required acid gas removal efficiencies are legislated according to the size of the plant and the location.

Table 1.1 **Major industrial processes that need gas processing** (Astarita et al., 1983)

Process	Acid Gas Involved	Accepted Limits
Hydrogen Manufacture	CO_2	< 0.1% CO_2
Petroleum Desulfurization	CO_2+H_2S+COS	10 ppm H_2S
Coal Liquefaction		
Chemicals		
Ammonia Manufacture	CO_2	<16 ppm CO_2 and CO
(H_2/N_2 Mixture)	CO_2+H_2S+COS	0.01 ppm H_2S
Natural Gas Purification		
Pipeline gas	H_2S, CO_2, COS, RSH etc.	< 4 ppm H_2S, < 1%CO_2
LNG feedstock		1-2 ppm H_2S, < 50 ppm CO_2
Syn Gas for Chemicals (H_2/CO)		< 500 ppm CO_2, 0.01 ppm H_2S
Coal Gasification		
High Btu gas	CO_2+H_2S+COS	500 ppm CO_2, 0.01 ppm H_2S
Intermediate Btu gas		
Low Btu gas		100 ppm H_2S
Oil Desulfurization	H_2S	100 ppm H_2S
Refinery Fuel Gas Treating	H_2S, CO_2, COS	100 ppm H_2S
Ethylene Manufacture (Steam Cracker gas treating)	H_2S, CO_2	~1 ppm H_2S, 1 ppm CO_2
Flue Gas Desulfurization Utilities (electric), Refineries, etc.	SO_2	90% removal

To the public, sulfur tends to be associated with pollution and generally the much discussed term 'acid rain'. But the vital role that sulfur plays in the well-being of mankind largely remains in the dark. Its direct importance in agriculture as a plant nutrient and as a soil conditioning agent is well recognized. Sulfur is an important feedstock for a variety of industries, e.g. fertilizers, sulfuric acid and rubber industries. It is crucial to the fertilizer industry in general and the phosphate industry in particular. Most of the sulfur used is burnt to sulfur dioxide first and then converted to sulfuric acid. Sulfuric acid (H_2SO_4) is one of the most vital heavy industrial chemicals due to its widespread use. The world consumption of sulfur is much more than its production through ores via the Frasch process. Currently sixty percent (Sander et al., 1984) of the world demand for sulfur is met by the sulfur recovered through hydrocarbon and gas processing. Hence sulfur recovery rather than just its removal is an important aim of all the sweetening processes used commercially.

In general amine absorption processes are used for the removal of hydrogen sulfide and other sulfur containing acid gases from various sour gases. These acid gases are then stripped from the reagent solutions. These acid gases and sour gases containing relatively large percentages of acid gases are processed in the modified Claus process plants to remove and recover sulfur. The selection of a given sulfur recovery process is determined by economics. For gases containing a relatively low percentage (up to 10 volume percent) of acid gases, especially hydrogen sulfide, the amine processes or the modified Claus process prove to be costly or technically not feasible. This has been one of the reasons why many gas wells in Alberta are presently capped . Also the off gases coming from various sources contain relatively smaller proportions of hydrogen sulfide. The off gases coming from the Claus plant invariably contain some hydrogen sulfide which is conventionally burnt.

A one-step process which proves economical and removes and recovers sulfur to acceptable limits is definitely desired for such cases. The sulfur recovery research group, headed by Dr. I.G. Dalla Lana and Dr. K.T. Chuang, at the Department of Chemical

Engineering, University of Alberta, has been studying the dehydration of acid gases with strong dehydrating agents such as concentrated sulfuric acid to improve the Claus plant efficiency. They observed the formation of sulfur due to the reaction between hydrogen sulfide and sulfuric acid, besides getting excellent water (H_2O) removal. The observed reaction was deemed significant for sulfur recovery as well as water removal, due to the low cost of sulfuric acid and its possible reconcentration and reuse. Hence, we have carried out a detailed preliminary analysis of this sulfur recovery process. The possible applications as brought out earlier have been the principal incentives for the studies carried out in this thesis.

We have investigated the reaction chemistry and preliminary kinetic behavior of the reactions involved. The general thrust in the gas sweetening industry is to meet the local environmental regulations rather than eliminating the acid gases completely. Hence the aim of this research work is to find the optimum reaction conditions for minimizing the acid gas emission, as well. Since the process based on the above observations is not in commercial use and has not been cited or mentioned in recent literature regarding gas purification, an application for a US patent has been filed. An extensive literature survey in support of this application is covered in the next chapter.

Further research to find the reaction rate equations and the related intrinsic constants, the mass transfer phenomena and the finally the scale up of the process are absolutely vital for the development of this process. Capped Gas well stats in alberta, pipeline specs, bibliography, Why basant tewari didin't observe our reaction. 10%
variation in mt data, lists of table fig. datasheet claim. include

Chapter 2

Literature Review

Recovery of sulfur from its native ores is achieved via different routes. Formerly, the major process used for sulfur mining was the Frasch process. In this process, originally developed by H. Frasch between 1894 and 1903, hot water is injected directly into the sulfur deposits and the molten sulfur is brought to the surface. Currently, sixty percent of the world sulfur supply comes from hydrocarbon and gas processing (Sander et al., 1984). Hence, this chapter focuses on a brief review of those processes that are developed and/or used for hydrocarbon and sour gas sweetening and sulfur recovery through gas processing. The principal focus is on the literature regarding sulfur recovery through reaction of H_2S with H_2SO_4. Because many chemical reactions will be indicated herein, a complete listing of these reactions is presented in Appendix A.

2.1 General gas processing methods

Several processes are used commercially for the removal of acid gases. Typical acid gas constituents are H_2S, SO_2 and CO_2. Also, if present, organic sulfur compounds such as COS, CS_2, and mercaptans etc. are required to be removed from gas streams due to their malevolent character (especially catalyst poisoning and toxic properties). This is achieved either directly in one step by treatment of the original sour gas to produce sulfur or in two discrete steps, first separating the acid gases from the original sour gas followed by processing of the acid gas to convert the acid gas to sulfur, usually by the modified Claus process. In the later case a whole range of processes are used to separate the acid gases from the sour gases. Depending upon the reagents used, these processes can be classified as shown in Table 2.1. In the case of physical solvents, the acid gases dissolve in the reagents thus sweetening the feed sour gas and then the dissolved gases are stripped out in the solvent regenerator. In the case of chemical solvents, the acid gases react chemically with the solvents and thus the limitation of physical solubility equilibrium is removed. The advantages of both physical solubility and chemical reactivity through the combination with proper reagents is exploited in the hybrid systems. Adsorption processes are good for gas streams containing relatively low percentages of H_2S and are cyclic in operation due to periodic loading and regeneration of the adsorbents. Processes that directly convert the acid gases into sulfur are listed in the Table 2.2. Many processes based on these techniques and reagents have been developed. A comparison of the operating capability of some of these processes is shown in Figure 2.1.

The most important of the dry bed oxidation processes is the modified Claus process. Originally this process was developed in 1932 and was called the IG Claus process. It divides the feed acid gas in 1:2 ratio and the smaller fraction is fed to the furnace to be burnt to SO_2 by using the stoichiometric amount of air. A modification to this process, now commonly known as the modified Claus process, was suggested by K. Braus in 1936 (Sander et al., 1984). It allows the entire feed acid gas into the furnace with the stoichiometric amount of air. It is used extensively for the purification of gases. Many modifications of this process with improved efficiencies and advantages have been developed. The modified Claus process and its many variations are primarily based on the following reactions.

$$H_2S + 1/2\ O_2 = S + H_2O \quad \text{.....} (1)$$

$$H_2S + 3/2\ O_2 = SO_2 + H_2O \quad \text{.....} (2)$$

$$2\ H_2S + SO_2 = 3/n\ S_n + 2\ H_2O \quad \text{.....} (3)$$

All the three reactions occur in the front-end furnace. However, reaction (3), continued downstream, is catalyzed by alumina in a series of fixed- bed reactors. Reaction (3) is highly exothermic and equilibrium limited .

Table 2.1. Classification of the processes based upon the reagents used for acid gas removal

(Astarita et al., 1983, Kohl and Riesenfeld, 1984 and Sander et al., 1984)

SOLUTE	PHYSICAL SOLVENT	TRADE NAME
H_2S, CO_2	* Propylene Carbonate	Fluor Solvent
H_2S, CO_2	* Propylene Glycol	Selexol
H_2S, CO_2	* Dimethyl Ether N-methyl 2 Pyrrolidone	Purisol
H_2S, CO_2, Organic S	* Methanol	Rectisol
H_2S, CO_2, Organic S	* Oligo-ethylene glycol methyl isopropyl ethers	Sepasolv MPE
H_2S, SO_2, CO_2	* Water	

SOLUTE	CHEMICAL SOLVENT	TRADE NAME
H_2S, CO_2	* MEA(25-35 wt% in water)	
H_2S, CO_2	* DEA(30 wt% in water)	
H_2S	* DGA(60 wt% in water)	Econamine
H_2S, CO_2, COS	* DIPA	ADIP
H_2S	* MDEA	Sulfinol
H_2S, Organic S	* DETA	Amisol
H_2S, CO_2	* Alkaline Salt Solutions	Benfield, Catacarb etc.

	e.g. Promoted K_2CO_3	
H_2S	* Alkali metal salt of an amino acid	Alkazid
H_2S, SO_2, CO_2	* Ammonia Solutions	Diamox

SOLUTE	**HYBRID SYSTEM (Chemical and physical solvents)**	**TRADE NAME**
H_2S, CO_2	* DIPA- Sulfolane- Water (40-40-20 wt%)	Sulfinol D
H_2S, CO_2	* MDEA- Sulfolane-Water (40-40-20 wt%)	Sulfinol M
H_2S, CO_2	* MEA or DEA - Methanol	Amisol
H_2S, CO_2	* DIPAM (diisopropyl amine) or DETA (diethyl amine) - Methanol	Improved Amisol

SOLUTE	**ADSORPTION PROCESSES**
H_2S, SO_2	* Molecular Sieves
H_2S, SO_2	* Activated Alumina
H_2S, SO_2	* Silica Gel

Table 2.2 Processes which directly convert the acid gases into sulfur

(Astarita et al., 1983, Kohl and Riesenfeld, 1984 and Sander et al., 1984)

SOLUTE	DRY BED PROCESS	TRADE NAME
H_2S	* Activated Carbon	
H_2S, Organic S	* Iron Oxide	
H_2S, SO_2	* Bauxite or Alumina	Claus Process

SOLUTE	LIQUID PHASE OXIDATION	
H_2S	* Sodium Carbonate, ADA, Sodium Metavanadate	Stretford
H_2S	* Vanadium Oxidant	Unisulf
H_2S	* Sodium 1,4-naphthoquinone 1-sulphonate	Takahax
H_2S	* Iron Oxide Suspensions	Burkheiser Ferrox Gluud Manchester
H_2S	* Iron Complex Chelate Solutions	Sulfint Cataban

		Konox
H_2S	* Polythionate Solutions	
H_2S	* Thioarsenate Solutions	Thylox Giammarco-Vetrocoke-sulfur
H_2S	* Iron Cyanide Suspensions	Fischer
H_2S	* Organo Metallic Compounds	Lo-Cat
H_2S	* Sulfur Dioxide	Townsend I.F.P.

SOLUTE	**CATALYTIC CONVERSION**
SO_2, CO_2, COS, CS_2, Organic S	* Various Metal Catalysts and Their Suspensions

SOLUTE	**CRYOGENIC DISTILLATION MEMBRANES**
H_2S, CO_2	

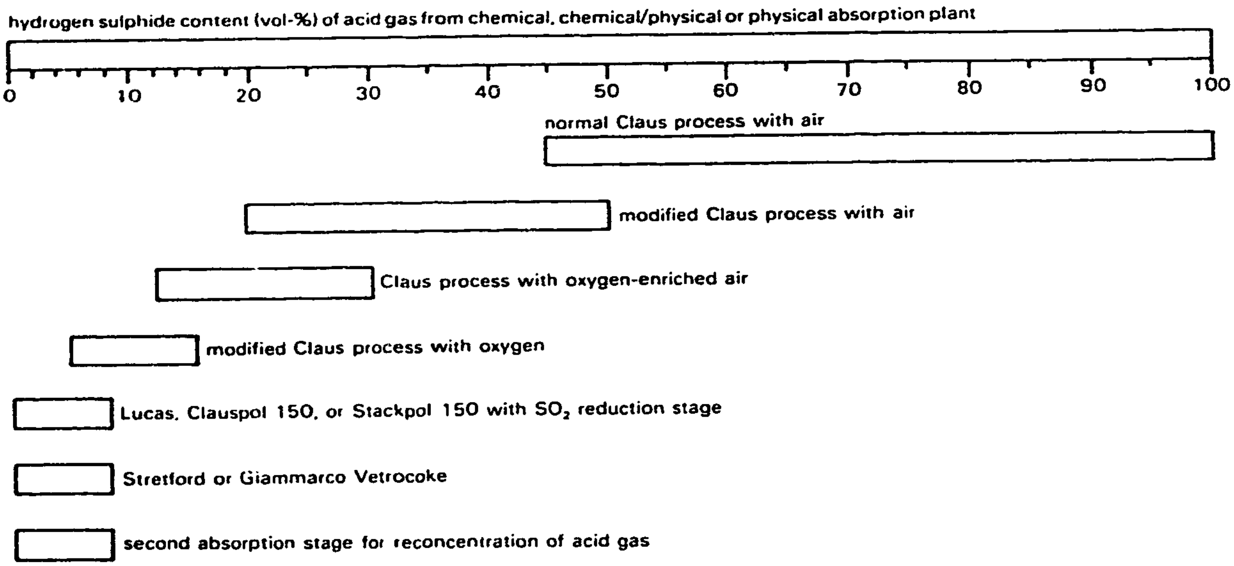


Figure 2.1 **Operating capability of processes for conversion of H_2S into elemental S** (Sander et al., 1984)

According to Le Chatelier's principle, *'The equilibrium will shift in such a manner as to undo the effect of the imposed stress'*; various parameters are optimized in order to achieve maximum equilibrium conversions as follows:

1. Lowering the temperature increases the equilibrium conversion.
2. Pressure increase shifts the equilibrium so as to give higher conversions.
3. Presence of inert gases lowers the partial pressures of the reacting species and therefore lowers the equilibrium conversion.
4. Sulfur vapor removal shifts the equilibrium to right.
5. Similarly, H_2O vapor removal helps to increase the equilibrium conversion.

In industry, therefore, three to four catalytic reactors are used in series with decreasing reactor temperatures. Typical recovery efficiencies are 90-96% for a two stage plant and 95-98% for a three stage plant. Molten sulfur is removed from the exit stream of each reactor at its dew point. Also, H_2S- rich feed gases and oxygen or oxygen- enriched air may be used as feed for the furnace to drive reaction (3) favorably. Thus, more efficient gas purification is achieved. A typical process flow sheet of a modified Claus process using three catalytic reactor stages is shown in Figure 2.2. But even then, this process has some limitations due to equilibrium constraints. To shift the modified Claus reaction equilibrium favorably, H_2O vapor removal from the product stream is desirable as well. But this cannot be easily accomplished due to the extremely corrosive nature of the aqueous product mixture containing sulfurous acid (H_2SO_3) and H_2SO_4 that is formed when H_2S and SO_2 are contacted with liquid water. Also the modified Claus process requires very tight control on the air to H_2S ratio to achieve an exact stoichiometric ratio of 2:1 (H_2S: SO_2) and maximize the conversions. If this ratio is upset slightly, the unconverted acid gas is passed on to the tail-gas unit, creating considerable environmental problems in the form of sour tail gas. The cost incurred in order to meet the environmental regulations by way of a tail gas cleanup plant makes the overall Claus plant very cost intensive.

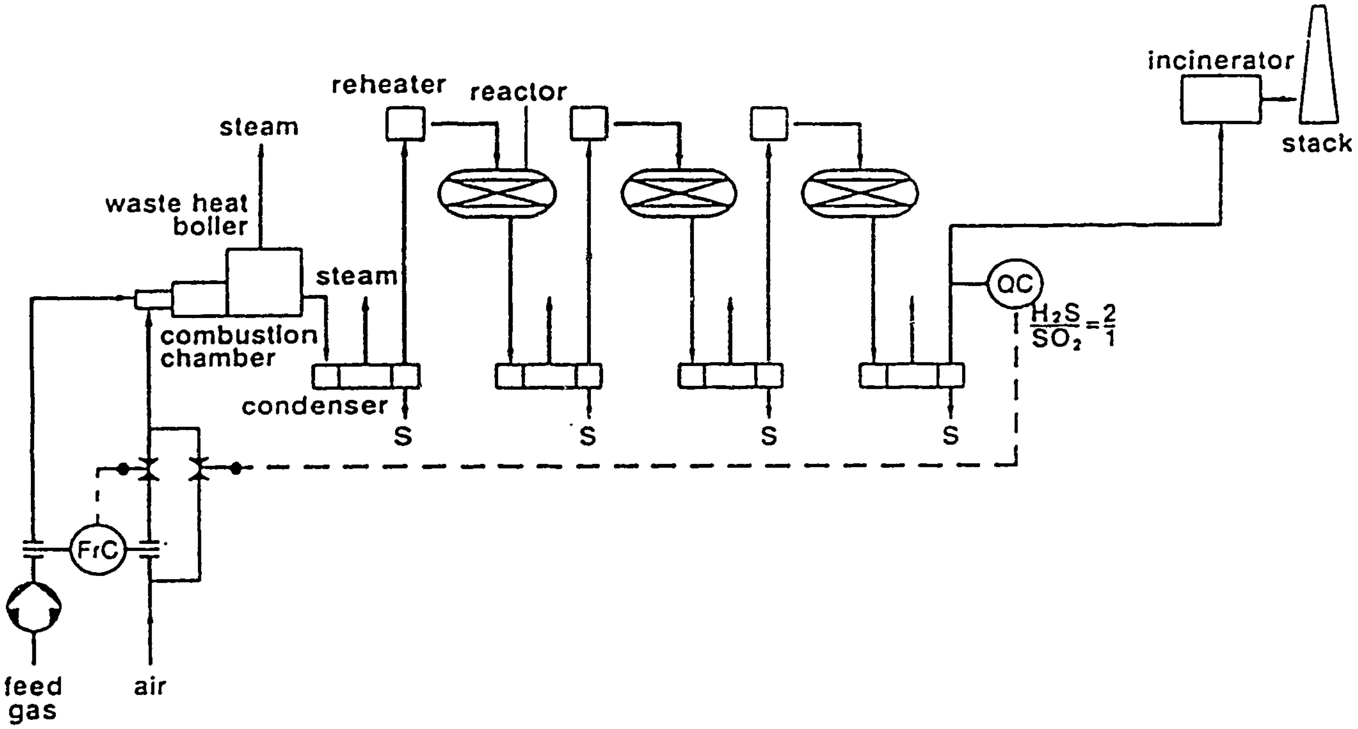


Figure 2.2 **Conventional three stage Claus plant** (Nisselrooy and Lagas, 1993)

For the processing of lean sour gases, a new class of processes called liquid phase oxidation processes are employed in industry, because any of the dry bed processes, particularly the modified Claus process, do not prove effective in the case of the lean gas processing. These processes are based on an oxidation-reduction mechanism and the reagents used act as oxygen carriers. The acid gases reduce the reagents and get oxidized to elemental sulfur. The reduced reagents are then typically regenerated in downstream oxidizing plants. Such processes are listed in Table 2.2. These processes are relevant for comparison with H_2S-H_2SO_4 reactions, since this system can also provide a liquid phase process for lean gas treatment. Liquid phase oxidation processes offer advantages over the dry bed processes due to savings in ground space requirements and labor as well as improved quality of recovered sulfur and easier sulfur recovery. Also, these processes can remove H_2S to very low levels of the order of 10 ppm easily. The emphasis in selection of the reagents is placed on high oxidizing power and stability.

A process called the Townsend process (Kohl, 1985) employs the reaction between H_2S and SO_2 in liquid phase of ethylene glycols. This process has been used successfully to treat high-pressure natural gas streams and is known to meet pipeline specifications of the sweetened gases. Water acts as the catalyst for the reaction in this process. Of the widely accepted liquid oxidation processes, the ones using metallic chelates and organo metallic complexes have gained prominence in recent years, due to excellent stability characteristics of these reagents. The Sulfint process which uses iron-EDTA chelates that stabilize iron in the suspension is one such process. Iron acts as as a catalyst and oxidizes H_2S in this process. Reduced divalent iron is then oxidized in the reagent regenerator. The Stretford process requires low pH for generation of sulfur. The process is costly because of the costly reagents (aqueous anthraquinone disulfonic acid and sodium vanadate) used and their regeneration requires extensive processing. It is plagued by side reactions and bacterial growth that increases the pH. The process has found limited commercial utility to date due to such drawbacks. Perhaps the most important of the liquid phase oxidation processes is the Lo-Cat process. This process was originally developed by ARI Technologies, Inc. (Hardison, 1988). The process basically uses iron chelate complex suspensions, in which iron is stabilized by a proprietary organic chelating agent. Iron acts as the oxidizing agent. Some of the unique characteristics of this process for which it has gained wide acceptance are as follows:

1. Very high activity for H_2S conversion.
2. Great flexibility with respect to the feed composition.
3. Nearly 100 percent H_2S removal efficiency.
4. Dual chelation for stability at any pH.
5. Cheaper reagent.
6. Environmentally acceptable chemical composition.
7. Simple sulfur separation and processing.

Apart from these processes, as seen in Figure 2.1, for lean acid gas processing, the Giammarco Vetrocoke process, and Lucas, Clauspol 150 and Stackpol 150 processes etc. are also employed. The Giammarco Vetrocoke process is widely accepted. However it is primarily used for treatment of coke oven gas. It uses sodium or potassium carbonate solutions containing arsenic compounds. The chemistry of the process is complex and the reagent is costly as well. The process suffers due to build up of thiocyanates and sulfates that require costly processing. The rest of the processes are basically used for the Claus plant tail gas treatment and convert H_2S to SO_2 which is typically recycled to the Claus reactor. Thus they are really not used for lean gas processing.

Recently, a process called 'Berkeley Zero-emission sulfur recovery process" has been developed (Towler and Lynn, 1993). This process is based on the following reactions.

$$H_2S + CO_2 = CO + H_2O + 1/2\ S \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$CO + H_2O = CO_2 + H_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

A process flow sheet of this process is shown in Figure 2.3. As claimed, the zero emissions process based on the above chemistry has significant advantages over the modified Claus process in that it need not produce any tail gas, it allows recovery of the chemical (or fuel)

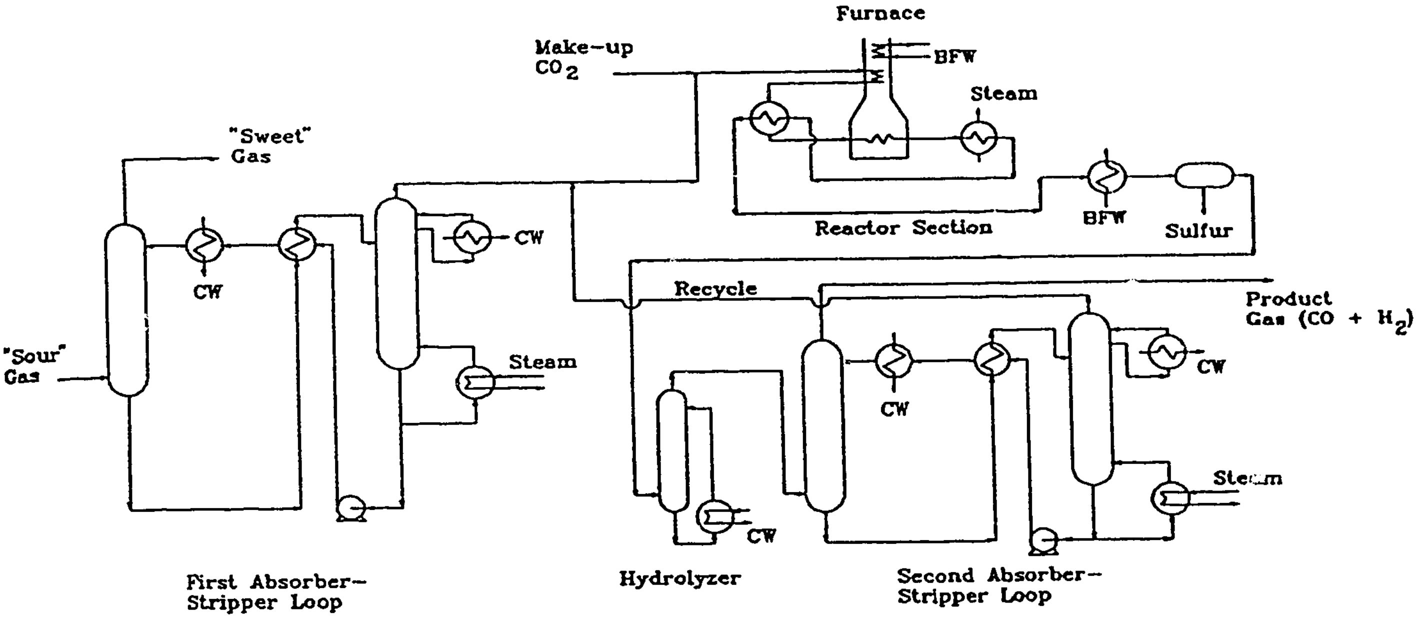


Figure 2.3 **Berkeley Zero emissions sulfur recovery process** (Towler and Lynn, 1993)

value of hydrogen from H_2S, and it requires much less stringent process control. However, the process is still rather complicated and expensive. For gases containing relatively smaller amounts of H_2S, cleanup by either conventional technologies or by new processes becomes a financial burden. Alternative and innovative routes that can provide economical and efficient means to remove sulfur compounds are certainly needed.

2.2 Literature survey on reaction of H_2S with H_2SO_4

The reaction of H_2S with H_2SO_4 has been cited in very old literature. Bussy and Buigne (1864) mentioned that the reaction between H_2S and concentrated H_2SO_4 occurs as

$$3\ H_2S + H_2SO_4 = 4\ S + 4\ H_2O \text{.........................} (6)$$

But Wood et al., (1924) mentioned the reaction between H_2S and concentrated H_2SO_4 as

$$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O \text{...................} (7)$$

Milbauer, (1937) studied the reaction of various elements and compounds with H_2SO_4 at 237°C. He observed the formation of SO_2 as a result of the reaction between H_2S and concentrated H_2SO_4. The rate of SO_2 formation was enhanced in the presence of different catalysts such as selenium oxide. He also found that sulfur reacts with H_2SO_4 to give SO_2 at 237°C. He has explained such an evolution of SO_2 by dissociation of H_2SO_4 into SO_2, H_2O and O.

It was reported by Snurnikov et al., (1967) that H_2S can be decomposed by concentrated H_2SO_4 into elemental sulfur, SO_2 and H_2O. They used a batch of H_2SO_4 and bubbled H_2S-containing gas through it at fixed temperatures and for fixed time at constant flow rate. They studied the effect of temperature on H_2S conversion and SO_2 formation. Possible reactions involved and their thermodynamic feasibility, as shown in Figure 2.4, were discussed. These possible reactions proposed were as follows:

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$....................(7)
$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$...............................(8)
$S + 2\ H_2SO_4 = 2\ H_2O + 3\ SO_2$...........................(9)

The overall reaction for reactions (7) and (9) is

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$...................... (10)

Figure 2.4 shows that reaction (9) is favored at high temperatures whereas reaction (8) is not. They concluded that stoichiometry of reaction (7) is followed below 160° C and above that temperature, reaction stoichiometry (10) is followed. However the complete reaction chemistry involved in the H_2S- H_2SO_4 system was not established. The reaction between H_2S and H_2SO_4 was not recognized as a potential acid contacting process for sulfur recovery.

Stashchuk et al., (1970) tried to explain the formation of sulfur deposits in gypsum- anhydrite beds. In this context they discussed the reaction between H_2S and sulfate ions at various pH values as well as the dependence of the stability of various species involved on the pH of the system (Figure 2.5). They concluded that sulfur is formed as a result of the interaction between H_2S and H_2SO_4 only in highly acidic environment (pH< 4) at 25° C. But they did not provide clarification about this interaction.

Torrence, (1971) in his patent, has used the reactions between H_2S and H_2SO_4 adsorbed in charcoal beds to regenerate the charcoal bed. Previously H_2SO_4 used to be reduced by charcoal. The possible reactions are mentioned as follows:

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$......................(7)
$3\ H_2S + H_2SO_4 = 4\ S + 4\ H_2O$...........................(6)

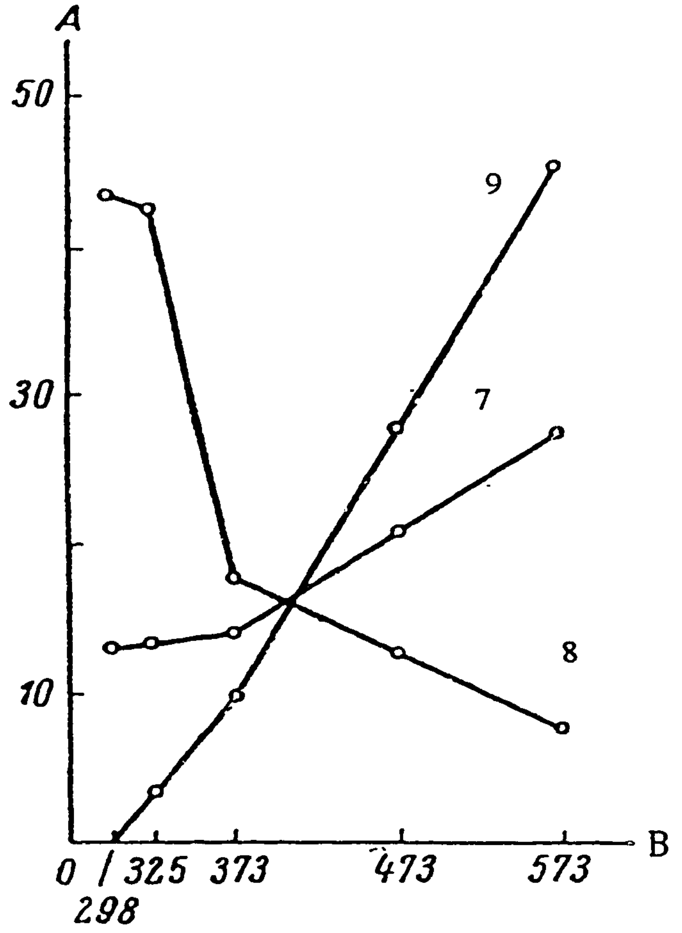


Figure 2.4 Variations of free energies of the reactions with temperature. A: Free energy (kcal/mole), B: Temperature (K) (Snurnikov et al., 1967)

$H_2S + H_2SO_4 = S + SO_2 + 2H_2O$ ....(7)

$S + 2H_2SO_4 = 3SO_2 + 2H_2O$ ....(9)

$2H_2S + SO_2 = 3S + 2H_2O$ ....(8)

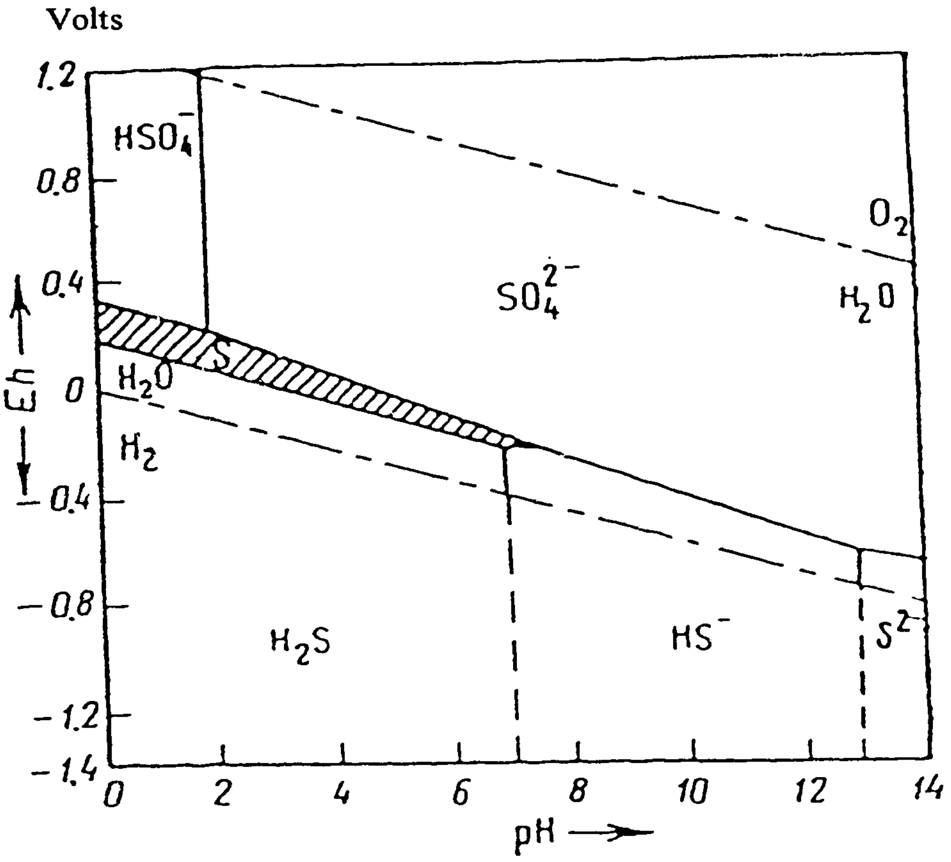


Figure 2.5 **Stability fields of various forms of sulfur with $\Sigma S = 10^{-1}$ mole/litre at 25°C** (Stashchuk et al., 1970)

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$ ....(10)

He mentions that in order to promote production of sulfur via reaction (6), the temperature has to be below 177°C. He achieved sulfur recovery of up to 98.6 % in the form of elemental sulfur. However, he has not mentioned any details of these reactions. These reactions were observed to occur over charcoal which acted as an adsorbent for H_2S and SO_2 and catalyst for the reactions and thus the mechanism of these reactions would be different from that in only gas-liquid systems containing H_2S and H_2SO_4. Similarly, Torrence et al., (1975) have again used the above reactions for SO_2 removal from waste gases using charcoal bed as an adsorbent for SO_2 and catalyst for the oxidation of SO_2 to SO_3. Thus the flue gases were purified and SO_2 was recovered by the above scheme of reactions. They mention that reaction (6) is predominant at temperatures below 250°F (120°C). Between 250°F and 570°F reaction (7) is dominating and above this temperature range reaction (10) becomes major. The main purpose of Torrence's invention is to remove SO_2 rather than recover sulfur. He has not considered the effect of acid concentration on selective sulfur recovery. Instead he has focused on the effect of temperature on the above three reactions.

2.3 Literature survey on reaction of H_2S with SO_2 over aqueous H_2SO_4

As brought out in the literature, the reaction between H_2S and SO_2 over aqueous H_2SO_4 is relevant to the reaction system containing H_2S and H_2SO_4. Hence information on this reaction was collected as well.

It is well known that dry H_2S and SO_2 do not react and the reaction is slow in nonaqueous media (Andreev et al., 1970). But the reaction proceeds rapidly over any wet surface, even at room temperature. This reaction between H_2S and H_2SO_4 in or over aqueous media is called the Wackenroder reaction, as it was first discovered by Wackenroder in 1846 (Volinskia, 1971). As seen previously, this reaction has been used commercially for natural gas desulfurization in the Townsend process (Kohl, 1985). This reaction differs from the modified Claus reaction in that it uses water as the medium of reaction unlike catalysts used by reaction (3). Also the temperature required for this reaction to proceed at a fast rate is much less than that required by the modified Claus reaction. Also in the modified Claus reaction, vapor phase sulfur species are involved whereas in the Wackenroder reaction the sulfur formed is generally in the liquid phase. Since the discovery of the Wackenroder reaction, many attempts have been made to explain its mechanism. It reportedly proceeds through complex reactions involving both reacting species and follows the overall stoichiometry:

$$2H_2S + SO_2 = 3\ S + 2\ H_2O \ldots\ldots\ldots\ldots (8)$$

There is a possibility of side reaction involvement in the Wackenroder reaction. Formation of thiosulfate was observed by Neyman, (1952) when a mixture of SO_2 and H_2S was passed into an alkaline solution containing sodium sulfite, according to the following scheme proposed:

$$2\ H_2S^{*} + SO_2 = 2\ S^{*} + S + 2\ H_2O \ldots\ldots\ldots\ldots (8a)$$

$$3\ Na_2SO_3 + 2\ S^{*} + S = 2\ Na_2S^{*}SO_3 + Na_2S_2O_3 \ldots (11)$$

It was experimentally shown that 2/3rd of the S formed was due to H_2S and 1/3rd due to SO_2 .

Volinskia, (1971) considered the Wackenroder reaction as a combination of two different processes.

1. Reaction between H_2S and SO_2 and
2. Formation of polythionic acids.

He postulated the following mechanism for the reaction between H_2S and SO_2 in aqueous medium.

$$H_2S + SO_2 = H_2S_2O_2 \ldots\ldots\ldots\ldots (12)$$

$$H_2S_2O_2 = H_2SO_2 + S \ldots\ldots\ldots\ldots (13)$$

$$H_2SO_2 + H_2S = H_2S_2O + H_2O \ldots\ldots\ldots\ldots (14)$$

$$H_2S_2O = S_2(2S) + H_2O \quad \text{.......................................(15)}$$

The overall reaction is the same as reaction (8). He has commented about the side reactions responsible for polythionic acid formation in the Wackenroder solution. According to him, a reaction such as (16) gives rise to polythionic acids.

$$H_2S + SO_2 + 1/2\ O_2 = H_2S_2O_3 \quad \text{...............................(16)}$$

In 1971 Opferkuch et al., patented the use of the reaction between H_2S and SO_2 over aqueous H_2SO_4 for gas sweetening. They, however, did not study the kinetics of the reaction in the acid media. This study has been done by Tiwari (1976). He used very mild conditions of temperature below 40° C and acid concentrations below 3 M (i.e. 26 wt %). Some relevant information is represented in Figures 2.6 to 2.8. The rate expression developed by him is as follows: (All equations in this thesis are summarized in Appendix B)

$$\frac{d[H_2S]}{dt} = -k_c A_i [H_2S][SO_2] \qquad = r_{H2S} \qquad (1)$$

A similar rate expression can be derived from the reaction mechanism proposed by Volinskia. The value of k_c depends upon the pH and temperature. Above 1M H_2SO_4 (i.e. 9 wt%), k_c was shown to be independent of pH. The reaction occurs on the interface and the area of this interface is vital in the rate expression. Also, the reaction was shown to be very fast even at mild conditions. As seen in Figure 2.6, the value of k_c depends on the H_2SO_4 concentration. This suggests that the reaction proceeds through an intermediate complex whose stability and hence, the overall rate constant is pH dependent. Thus the reaction of equation (8) is not an elementary reaction and does not describe the mechanism of reaction between H_2S and SO_2.

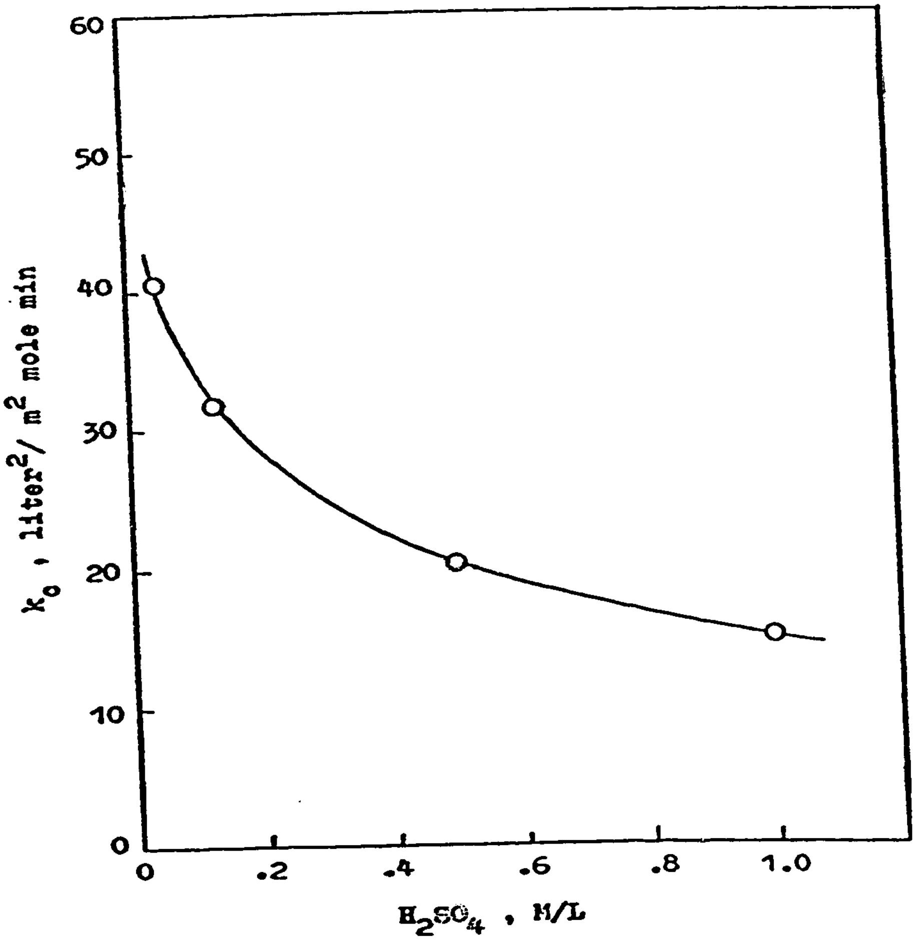


Figure 2.6 Effect of H_2SO_4 concentration on the rate of reaction at 24.5°C and 50 rpm (Tiwari, 1976)

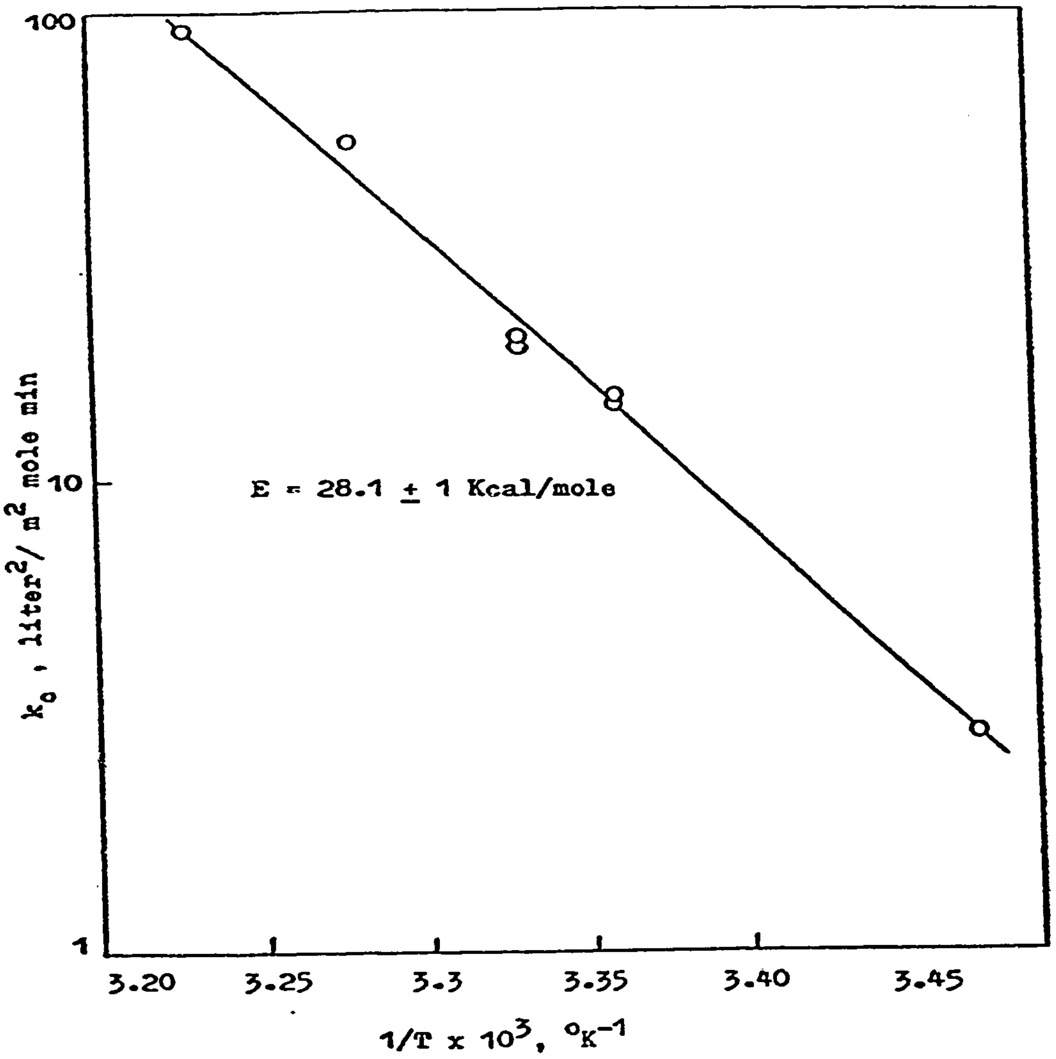


Figure 2.7 Arrhenius plot for the reaction between H_2S and SO_2 in the presence of 1M H_2SO_4 (Tiwari, 1976)

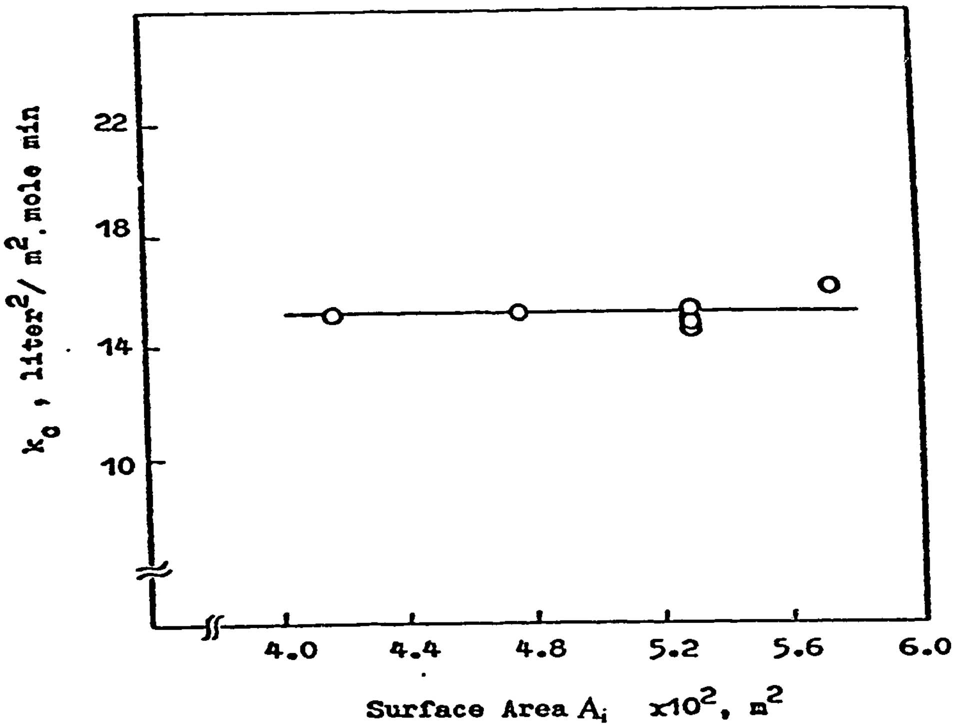


Figure 2.8 Effect of interfacial area on the rate of reaction for 1M H_2SO_4 and 24.5°C (Tiwari, 1976)

At high acid concentrations, k_c seems to be independent of pH. This indicates that the intermediate complexes become unstable and thus, above 1M H_2SO_4, k_c value approximates the value of the rate constant for the forward reaction of equation (8). The high value of activation energy for reaction (8), as seen in Figure 2.7, shows that the reaction is highly temperature sensitive.

2.4 Properties of sulfur containing chemicals of interest

Some important properties of the chemical compounds encountered in the H_2S-H_2SO_4 system are needed in the subsequent chapters. Hence, it is helpful to discuss and elucidate the nature and some of the relevant properties of these chemicals.

2.4.1 Hydrogen sulfide

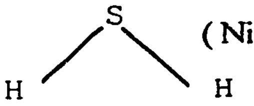
Hydrogen sulfide (H_2S) is a colorless, flammable, toxic gas having a foul smell described as that of rotten eggs. Some of the important physical properties of this gas are listed in Table 2.3. As seen from this Table, H_2S is heavier than nitrogen and air; hence, H_2S gas has a tendency to settle. This causes H_2S to separate in calibrated H_2S - N_2 mixture cylinders; hence the use of pure H_2S gas is preferred in the laboratory even if it is required in mixtures.

It is a very toxic gas. Exposure to 600 ppm H_2S for even 30 minutes can be fatal. Its Threshold Limit Value (TLV) is 10 ppm. Even though the foul smell of H_2S is easily detectable by olfactory sense at low concentrations, it becomes unreliable as a warning of its presence, because continuous respiration leads to quick olfactory fatigue. Hence, a H_2S gas detector must be used in the laboratory for H_2S leak monitoring (Braker and Mossman, 1980).

Table 2.3 **Physical properties of hydrogen sulfide** (Sander et al., 1984)

Molar mass	34.076 g/gmole
Vapor pressure at 21.1 °C	1840 kPa
Molar specific heat at 1 atm and 25 °C (constant pressure)	34.218 J/mole K
Thermal conductivity at 1 atm and 15.6 °C	0.014004 W/m K
Solubility in water at 1 atm and 25 °C	2.257 cc/1cc water
Relative density at 1 atm and 25 °C (air =1)	1.188

H_2S is a reducing reagent in acid and alkaline solutions. It dissolves in water substantially to give HS^- ions. Oxidation normally yields sulfur but in the presence of strong oxidants, H_2S can give S (IV) or S(VI) compounds. H_2S is a bent molecule with a S-H bond distance of 1.328A° and H-S-H bond angle of 92.2°.



(Nickless, 1968)

2.4.2 Sulfuric acid

Perhaps the most important of all heavy industrial chemicals is sulfuric acid (H_2SO_4). Although its consumption has lost the status of the national economic health indicator, H_2SO_4 consumption still follows the general economic trends. Currently the price of pure H_2SO_4 is approximately US $ 80 per ton. Sulfuric acid is a colorless, water white and more viscous than water liquid. Anhydrous H_2SO_4 (100 wt%) is the monohydrate of SO_3. Its molecular weight is 98.08 g/gmole, the melting point is 10.4°C and the boiling point is 279.6°C. Its density is 1.8356 g/cc. It can be mixed in any ratio with H_2O. Aqueous H_2SO_4 solutions are defined by their H_2SO_4 content in weight percent (wt%). Sulfuric acid also dissolves any quantity of SO_3 forming oleum which means fuming H_2SO_4. The concentration of oleum is expressed in weight percent of dissolved SO_3 in 100 wt% H_2SO_4.

Physical properties of H_2SO_4 and oleum are dependent on the H_2SO_4 and SO_3 concentration, temperature and pressure. Table 2.4 shows the specific gravities of H_2SO_4 solutions as a function temperature and concentration. H_2SO_4 density peaks at 98 wt%. On account of this clear relationship between density and concentration at defined temperatures in the lower concentration range, density measurement provides a very quick method of determining concentrations up to about 95 wt%. Hydrometers used for this purpose directly measure the acid specific gravity. These data were used in the preparation of acid of varying concentrations, as will be elaborated subsequently.

Table 2.4 **Specific gravity of H_2SO_4 as a function of its concentration and temperature** (Perry et al., 1984)

%	0°C.	10°C.	15°C.	20°C.	25°C.	30°C.	40°C.	50°C.	60°C.	80°C.	100°C.
80	1.7482	1.7376	1.7323	1.7272	1.7221	1.7170	1.7069	1.6971	1.6873	1.6680	1.6493
81	1.7597	1.7489	1.7435	1.7383	1.7331	1.7279	1.7177	1.7077	1.6978	1.6782	1.6594
82	1.7709	1.7599	1.7544	1.7491	1.7437	1.7385	1.7281	1.7180	1.7080	1.6882	1.6692
83	1.7815	1.7704	1.7649	1.7594	1.7540	1.7487	1.7382	1.7279	1.7179	1.6979	1.6787
84	1.7916	1.7804	1.7748	1.7693	1.7639	1.7585	1.7479	1.7375	1.7274	1.7072	1.6878
85	1.8009	1.7897	1.7841	1.7786	1.7732	1.7678	1.7571	1.7466	1.7364	1.7161	1.6966
86	1.8095	1.7983	1.7927	1.7872	1.7818	1.7763	1.7657	1.7552	1.7449	1.7245	1.7050
87	1.8173	1.8061	1.8006	1.7951	1.7897	1.7842	1.7736	1.7632	1.7529	1.7324	1.7129
88	1.8243	1.8132	1.8077	1.8022	1.7968	1.7914	1.7809	1.7705	1.7602	1.7397	1.7202
89	1.8306	1.8195	1.8141	1.8087	1.8033	1.7979	1.7874	1.7770	1.7669	1.7464	1.7269
90	1.8361	1.8252	1.8198	1.8144	1.8091	1.8038	1.7933	1.7829	1.7729	1.7525	1.7331
91	1.8410	1.8302	1.8248	1.8195	1.8142	1.8090	1.7986	1.7883	1.7783	1.7581	1.7388
92	1.8453	1.8346	1.8293	1.8240	1.8188	1.8136	1.8033	1.7932	1.7832	1.7633	1.7439
93	1.8490	1.8384	1.8331	1.8279	1.8227	1.8176	1.8074	1.7974	1.7876	1.7681	1.7485
94	1.8520	1.8415	1.8363	1.8312	1.8260	1.8210	1.8109	1.8011	1.7914		
95	1.8544	1.8439	1.8388	1.8337	1.8286	1.8236	1.8137	1.8040	1.7944		
96	1.8560	1.8457	1.8406	1.8355	1.8305	1.8255	1.8157	1.8060	1.7965		
97	1.8569	1.8466	1.8414	1.8364	1.8314	1.8264	1.8166	1.8071	1.7977		
98	1.8567	1.8463	1.8411	1.8361	1.8310	1.8261	1.8163	1.8068	1.7976		
99	1.8551	1.8445	1.8393	1.8342	1.8292	1.8242	1.8145	1.8050	1.7958		
100	1.8517	1.8409	1.8357	1.8305	1.8255	1.8205	1.8107	1.8013	1.7922		

The electrical conductivity of H_2SO_4 is shown in Figure 2.9. It can be explained as follows: Pure H_2SO_4 dissociates slightly and hence has a minimum conductivity. When diluting the acid, dissociation occurs according to the following mechanism.

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^- \text{ ....(17)}$$

This allows the conductivity to rise. Between 92 and 84.5 wt% H_2SO_4 , the monohydrate, $H_2SO_4.H_2O$ predominates in equilibrium with the ionic species and hence the conductivity decreases slightly. At lower acid concentrations the degree of dissociation increases and hence the conductivity increases. At high water contents, the second stage of dissociation becomes significant and the conductivity increases further.

$$HSO_4^- + H_2O = H_3O^+ + SO_4^{2-} \text{ ....(18)}$$

However, on account of the diminishing overall acid concentration, the conductivity peaks at about 30 wt% acid and then falls sharply as the acid is diluted further. This is the reason why secondary cells use this particular concentration of H_2SO_4.

Figure 2.10 shows the phase diagram of aqueous H_2SO_4 solutions. This Figure clearly shows that H_2SO_4 forms an azeotrope at a concentration of 98.3 wt% and it has a maximum boiling point of 339°C. This point represents the ultimate limit in the concentration that can be reached by thermal methods of concentrating H_2SO_4 aqueous solutions.

The vapor pressures of H_2O, SO_3 and H_2SO_4 over H_2SO_4 solutions and oleum as a function of acid concentration and oleum concentration at 60°C are shown in Figure 2.11. As can be seen, the vapor pressure of water and H_2SO_4 over aqueous H_2SO_4 is quite low. This suggests the hygroscopic behavior of concentrated H_2SO_4. The dehydrating effect of concentrated H_2SO_4 is due to the formation of hydrates.

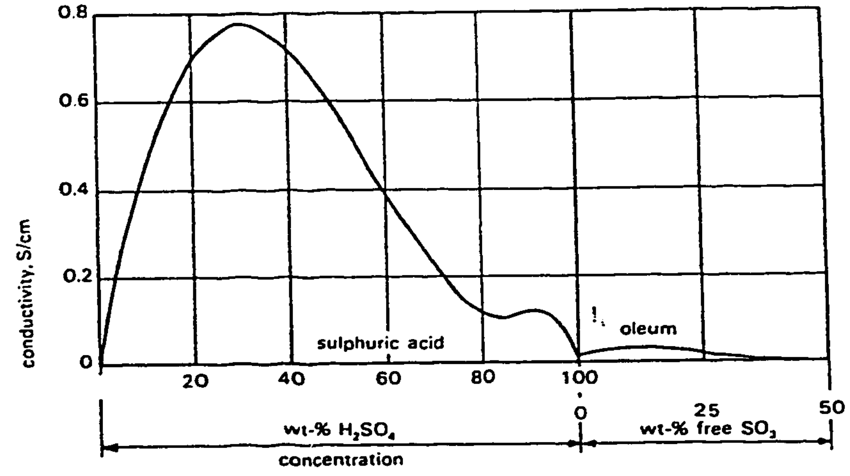


Figure 2.9 Electrical conductivity of sulfuric acid and oleum at 20°C (Sander et al., 1984)

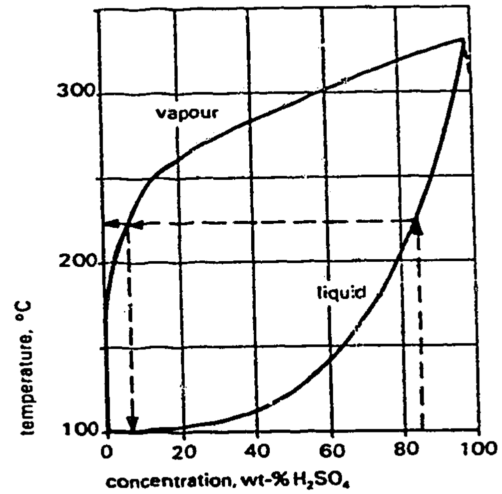


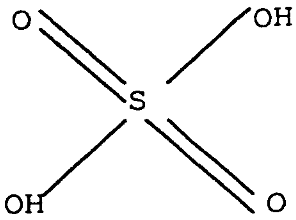
Figure 2.10 Boiling curves for sulfuric acid at 1013 mbar (Sander et al., 1984)

The specific heat of H_2SO_4 decreases with increase in acid concentration as shown in Figure 2.12. Figure 2.13 shows the enthalpy diagram for H_2SO_4 and oleum. This Figure is based on the assumption that the enthalpy of pure water at 0°C is 0 kJ/kg and it allows us to determine the amount of heat liberated or absorbed when H_2SO_4 or oleum are diluted from one concentration to another by adding water. Figure 2.14 is important for finding the heat liberated while diluting sulfuric acid from 98.3 wt% to any other concentration. As seen, considerable heat evolves during the dilution of H_2SO_4 with H_2O due to the strong hydrogen bond interaction resulting in the formation of H_2SO_4 monohydrate. The mixing can cause overheating and violent splashing if proper care is not taken. To dilute H_2SO_4, acid is added to the pool of water slowly with constant stirring to allow the heat of hydration to be dissipated evenly. Also, due to the density difference between H_2O and H_2SO_4 , the mixing occurs completely and minimum water is evaporated due to the evolved heat of hydration.

The pH of 1M (~10 wt%) H_2SO_4 is nearly zero. Sulfuric acid of 100 wt% strength is considered to be one of the strongest acids. Its acidity is nearly 10 times that of 1M H_2SO_4. Hence the pH of such acids is very low. For strong acids, the pH scale becomes impractical for use; and so, another term called acidity function (Gillespie, 1991) is used to quantify the acidity of such acids. Dilute H_2SO_4 is a dibasic acid. At concentrations above 90 wt%, however, it exerts a strong oxidizing effect. Since its dissociation is limited, it acts more like an oxidizing agent than as an acid.

Hot concentrated H_2SO_4 reacts with sulfur and reduces itself to SO_2. Sulfuric acid is extremely stable but decomposes at very high temperatures, well above its boiling temperature, into SO_3 and H_2O.

The following is the molecular structure for H_2SO_4:



(Nickless, 1968)

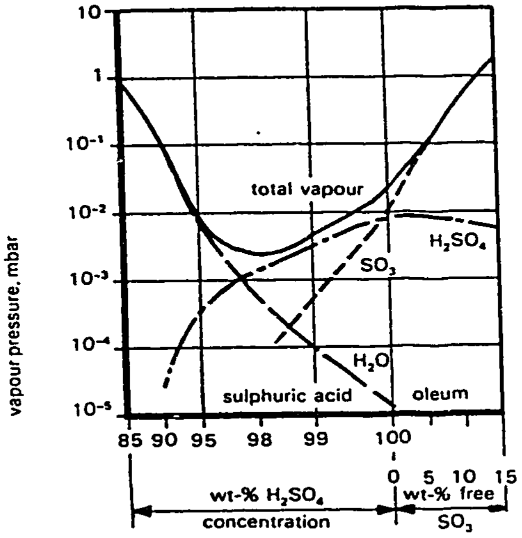


Figure 2.11 **Equilibrium vapor pressure over sulfuric acid and oleum at 60°C**

(Sander et al., 1984)

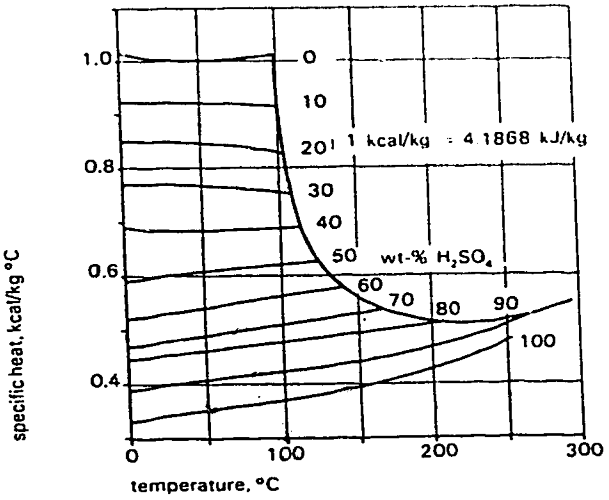


Figure 2.12 **Specific heat of sulfuric acid** (Sander et al., 1984)

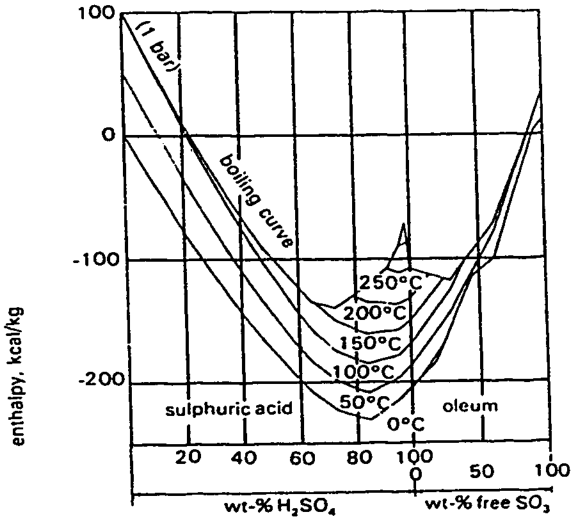


Figure 2.13 **Enthalpy diagram for sulfuric acid and oleum** (Sander et al., 1984)

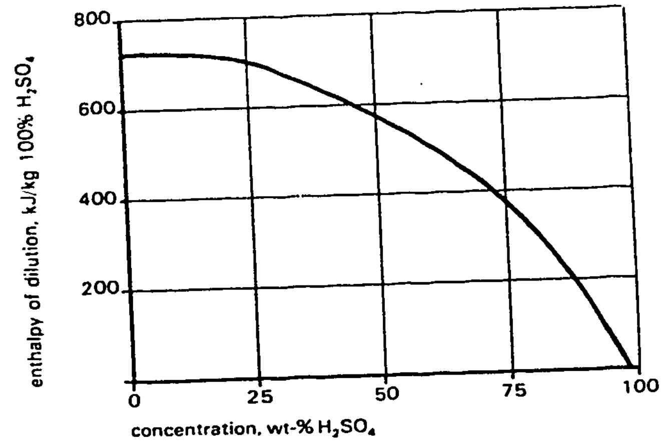


Figure 2.14 **Heat of dilution or dehydration of sulfuric acid at 20 °C**

(Sander et al., 1984)

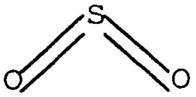
2.4.3 Sulfur dioxide

Sulfur dioxide (SO_2) is a colorless, non-flammable, toxic gas with a characteristic pungent smell and acid taste. The important physical properties of SO_2 are listed in Table 2.5. Sulfur dioxide gas is toxic in nature and exposure to concentration of 500 ppm SO_2 for a few minutes is very dangerous (Braker and Mossman, 1980).

Table 2.5. Physical properties of sulfur dioxide (Braker and Mossman, 1980)

Molar mass	64.063 g/gmole
Vapor pressure at 21.1°C	339 kPa
Molar specific heat at 1 atm and 25°C (constant pressure)	39.884 J/mole K
Thermal conductivity at 1 atm and 15 °C	0.0088 W/m K
Solubility in water at 1 atm and 20 °C	11.28 kg SO_2 / 100 kg water

Sulfur dioxide dissolves in water forming H_2SO_4 and sulfurous acid (H_2SO_3) which are very corrosive. It acts as an oxidizing agent in the presence of reducing agents. Sulfur dioxide is a bent triatomic molecule with S-O bond length of 1.432 A° and O-S-O bond angle of 119. 53°.



(Nickless, 1968)

It dissolves substantially in water to give $HSO3^{-}$ ions. Its solubility in H_2SO_4 is of industrial importance and is shown in Figure 2.15. It shows that SO_2 solubility decreases with rising H_2SO_4 concentration and reaches a minima at around 85 wt% H_2SO_4. Then it starts to rise again.

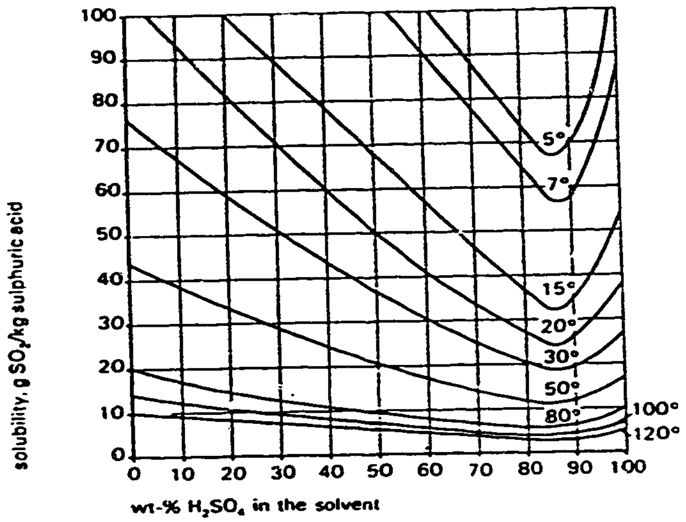


Figure 2.15 **Solubility of sulfur dioxide in sulfuric acid at p(SO2) = 1013 mbar**

(Sander et al., 1984)

2.4.4 Sulfur

Elemental sulfur (S) is a yellow solid at normal temperatures. The important physical properties of sulfur are shown in Table 2.6. It is polymorphous. It is normally in the crystalline rhombic (α) form. At about 95°C a transition to the monoclinic(β) form occurs. This form is stable up to the normal melting point (119.3°C) of sulfur. When this sulfur is heated, it transforms into a fluid, light yellow melt called λ- S. The melting point of the melt, if kept still for some time above 119.3°C, drops to 114.5°C. When sulfur is cooled suddenly from the liquid state, an amorphous form called μ- S which is insoluble in carbon disulfide is formed. Sulfur, if formed in aqueous solutions is formed in colloidal form which is amorphous. Sulfur is normally in the form of S-8 rings that remain stable until the boiling point of sulfur is reached.

Table 2.6 **Physical properties of sulfur** (Sander et al., 1984)

Molar mass	32 g per gmole
Melting point (monoclinic sulfur)	119.3°C
Boiling point	444.6°C
Density of solid monoclinic sulfur at 20°C	1.96 g/cc
Density of liquid sulfur at 125°C	1.7988 g/cc
Sp. heat of liquid S between 118.9°C to 444.6°C	$C_p = (5.4 + 0.005*T)*4.1868$ J/mole K

If the melt temperature is raised, the viscosity of sulfur shows a peculiar behavior as seen in Table 2.7. As seen the viscosity is minimum at 157°C and then steeply rises to a maximum at about 187°C. This can be explained by the breaking and subsequent polymerization of S-8 units.

Table 2.7 Dynamic viscosity of liquid sulfur, Pa S (Sander et al., 1984)

120°C	0.017
140°C	0.008
158°C	0.0064
160°C	5.952
180°C	86.304
187.8°C	93.0
200°C	78.864
300°C	3.72

2.5 Summary of the H_2S-H_2SO_4 literature

From the literature review of the H_2S-H_2SO_4 system, it is clear that not much is known about the details of the reaction between H_2S and H_2SO_4. The reactions involved have not been proven conclusively . Experimental information is lacking about this chemical interaction. Also, the kinetics of the reaction between H_2S and H_2SO_4 has not been studied. Some of the data available are useful only for comparisons, as will be seen in subsequent chapters. It is very important to understand the reaction chemistry of this sulfur recovery process for achieving the ultimate goal of complete H_2S conversion without the formation of SO_2 in tail gases. Because of the possibility of obtaining elemental sulfur from H_2S without any emission, further studies on the reaction between H_2S and H_2SO_4 have been undertaken. To obtain information on the equilibrium behavior of this system, we carried out detailed a thermodynamic analysis as brought out in the next chapter.

Chapter 3

Thermodynamic Analysis

Knowledge about the equilibrium in any chemically reactive system is vital for the characterization and development of the related process. Thermodynamic calculations provide us with the following information about chemical reactions:

1. The feasibility of the reaction and the maximum possible extent of the reaction, and
2. The amount of heat liberated or absorbed in the reaction.

As can be observed from previous chapters, the performance of the H_2S-H_2SO_4 reaction system was gauged by H_2S conversion and SO_2 concentration in the exhaust gases. Thermodynamic analysis is necessary for evaluating the performance of this process as it may indicate whether zero SO_2 production with complete H_2S removal is feasible. To optimize the reactor conditions to obtain zero H_2S and SO_2 emission, knowledge of the effect of various process variables on the equilibrium behavior (cause-effect analysis) is essential. Also, the precise reactions occurring in the H_2S - H_2SO_4 system have not been conclusively established in the literature. The feasibility of the possible reactions can be determined by thermochemical analysis. Hence the purpose of this chapter is to predict the equilibrium behavior of the H_2S - H_2SO_4 system in order to characterize it because detailed experimental equilibrium studies of the H_2S - H_2SO_4 system are not available.

Any system naturally moves towards its equilibrium state by maximizing its entropy, i.e. chaos, and minimizing its energy content. For a system under constant pressure, the work energy available is quantified by the Gibbs free energy, G. Thus, the ΔG of a spontaneous reaction is always negative. It is related to the entropy change, ΔS, of the system through the relation $\Delta G = \Delta H - T\Delta S$. In the present work, the minimum Gibbs free energy has been predicted by using the PC version 1.1 of HSC Chemistry for Windows simulation program. Traditionally, thermodynamic calculations have been based on published experimental data. The HSC offers a consistent set of thermodynamic data and powerful calculation method of studying the effects of different variables on the chemical system at equilibrium. This program makes the calculations very easy and fast and is reported to be fairly accurate and extensive for many inorganic chemicals. It can provide the user with various thermochemical properties for a number of reacting systems.

3.1 About the HSC program

The HSC chemistry program was developed by Roine et al. at Outokumpu Research, (1993). It uses the Gibbs Free Energy Minimization Program for equilibrium calculations. The term HSC means H (enthalpy), S (entropy) and C (specific heat). The HSC software contains an extensive thermochemical database (for about 5600 chemical compounds) called the 'main' database. Another database called the 'own' database can be edited by the user, and data for up to additional 1000 chemical species can be stored. The HSC uses the own database first and then the main database. This program and the main database are very reliable with inorganic chemicals (Roine, 1993).

3.1.1 Notations and abbreviations in the HSC

Some of the notations and abbreviations used by the HSC relevant to the present work are as follows:

Chemical species are denoted by the usual chemical formulae. Phases and numbers are not shown by any superscript or subscript but are shown as, e.g. $H_2S(g)$ for gaseous H_2S. In fact no superscripts or subscripts are allowed. Similarly (s) and (l) mean solid and liquid phases respectively; while (a) means aqueous phase. All aqueous phase species must be accompanied by water in the equilibrium composition option. Thermodynamic data for solid and liquid phases are saved under the same formula name. But with a suffix (l) the program automatically searches the record for liquid phase. Gas compounds have their own records and names. Chemical formulae with stoichiometric numbers at the beginning start with *, e.g. H_2SO_4*$2H_2O$, or *2MgO. Aqueous ions are shown as e.g. H^+ = H(+a), OH^- = OH(-a) etc. Similarly gaseous ions are shown as e.g. H(+g) for gaseous proton. Final parentheses are always reserved for special declarations such as phase etc., whereas inner parentheses are not allowed at all.

3.1.2 Standards, units and assumptions in the HSC

Some of the values used or calculated by this program are based on the following assumptions, units and standards. To calculate various properties, the HSC uses the following formulae:

Specific heat: $C_p = A + B\bullet 10^{-3}\bullet T + C\bullet 10^{5}\bullet T^{-2} + D\bullet 10^{-6}\bullet T^{2}$ (2)

Enthalpy : $H^0(T) = H_f(298) + \int_{298}^{T} C_p(T)dT + \sum H_{tr}$ (3)

Entropy : $S^0(T) = S^0(298) + \int_{298}^{T} (\frac{C_p}{T})dT + \sum \frac{H_{tr}}{T_{tr}}$ (4)

Gibbs energy: $G^o = H^o - T\bullet S^o$ (5), where

A, B, C, D are experimental coefficients whose units are defined by equation (2)

T= Temperature, K

H_f (298) = Enthalpy of formation at 298 K, kcal/mole

H_{tr} = Enthalpy of phase transitions such as melting, kcal/mole

$S^0(298)$ = Standard entropy at 298 K, kcal/K

T_{tr} = Phase transformation temperature, K

The enthalpy and entropy scales of elements are fixed by setting $H^o = 0$ at 25°C and 1atm, and $S^o = 0$ at 0 K and 1 atm. (according to the third law of thermodynamics).

The standard state of an aqueous species is the theoretical 1mole/kg solution, which has been extrapolated from infinite dilution. Enthalpy and entropy scales for aqueous ions have been fixed by assuming the enthalpy and entropy values for hydrogen ion (H^+) to be zero in a hypothetical ideal solution (1mole/kg) at 25°C and 1 atm, i.e. $\Delta H^o(H^+) = 0$ at 25°C and 1 atm and $\Delta S^o(H^+) = 0$ at 25°C and 1 atm. This makes it very important to use the suffix (a) with aqueous ions.

Some modifications to the data for aqueous ions as changed by the HSC program are as follows:

1. Since thermodynamic properties of aqueous ions are traditionally given only at 25°C, this program extrapolates the heat capacity values of these ions to higher temperatures using the Criss-Cobble method. Interested readers are directed to the reference of Criss and Cobble, (1964). In the case where the coefficients of the heat capacity function A, B, C and/or D are fed to the program, then this method is not used by the HSC. The Criss -Cobble method has been found to give consistent heat capacity values up to 300°C when compared with experimental data.
2. The entropy scale of aqueous ions is changed to the normal absolute entropy scale by subtracting 5 cal/mole•K from the hydrogen ion scale at 25°C, as described above, since this is the experimental value for the hydrogen ion entropy in the absolute scale.
3. The entropy values of aqueous ions contain the mixing entropy for a one molal solution (1mole/kg), therefore, this entropy $R \bullet \ln X_i = 1.987 \bullet \ln(1/55.51) = 7.981$ cal/mole•K (6) must be substracted from the entropy values used for the equilibrium calculations. The HSC gives hypothetical pure ion entropies to the GIBBS- program.

3.1.3 Calculation options in the HSC program

This version of HSC contains the following seven calculation options:

1. Reaction equations
2. Heat and material balances
3. Equilibrium compositions
4. Electrochemical cell equilibria
5. Formula weights
6. Phase stability diagrams
7. Eh- pH diagrams

We have used options 1, 3 and 7 viz. Reaction equations, Equilibrium compositions and Eh-pH- diagrams for the calculations in this thesis.

3.1.3.1 Reaction equations

The sample input and output files used for this calculation are shown in Figures 3.1 and 3.2. The program is sensitive towards stoichiometric errors and points them out. The user has to feed the reaction equation, initial and final temperatures, increment steps for temperature, and the various options in the input file. In general, the temperature steps should not be large to avoid errors in the extrapolations done by the program. Figure 3.2 shows that the reaction between H_2S and H_2SO_4 is endothermic at all temperatures shown, and its equilibrium constant, K, is greater than one for the higher temperatures.

For a typical chemical reaction, aA+bB=cC+dD (7), the various properties are calculated as follows:

Enthalpy of the reaction: $\Delta H_r = \Sigma\, v_i H_i(\text{ Products}) - \Sigma v_i H_i(\text{Reactants})$ (8)

$= (c^*H_C + d^*H_D) - (\, a^*H_A + b^*H_B)$

Entropy of the reaction $\Delta S_r = \Sigma\, v_i S_i(\text{ Products}) - \Sigma\, v_i S_i(\text{Reactants})$ (9)

$= (c^*S_C + d^*S_D) - (\, a^*S_A + b^*S_B)$

Gibbs energy of the reaction $\Delta G°_r = \Sigma\, v_i G_i(\text{ Products}) - \Sigma\, v_i G_i(\text{Reactants})$ (10)

$= (c^*G_C + d^*G_D) - (\, a^*G_A + b^*G_B)$

Equilibrium constant

$$K = \frac{[a_C]^c[a_D]^d}{[a_A]^a[a_B]^b} \qquad (11)$$

and $\ln(K) = \Delta G°/(-RT)$ (12)

where,

$[a_A]$, $[a_B]$, $[a_C]$ = Activity or partial pressure of the species A, B, C etc. (in ideal mixture, activity ≈ concentration)

a, b, c, d = Stoichiometric coefficients of the species A, B, C, and D respectively

v_i = General stoichiometric coefficient in the reaction equation for the species i

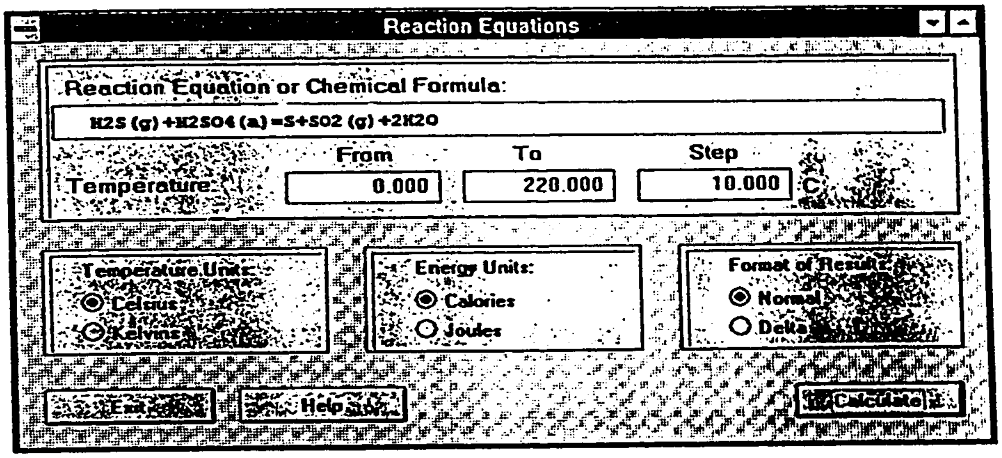
R = Universal gas constant = 1.987 cal/K•mole = 8.314 J/ K•mole

T = Temperature, K

3.1.3.2 Equilibrium calculations

This option is a very useful tool to calculate easily multiphase equilibrium compositions. In other words, the user provides the amounts of reactants for the given chemical reactions and the program calculates the amounts of products at the theoretical equilibrium state. Such calculations are applicable to any reactor irrespective of the contacting pattern.

The species and the phases can be selected by selecting the elements or by directly selecting the species and the phases. Figure 3.3 shows the selection of species from the constituent elements, viz. H, S and O. This option is very practical because it can be used



Reaction Equation or Chemical Formula:

H2S(g)+H2SO4(a)=S+SO2(g)+2H2O

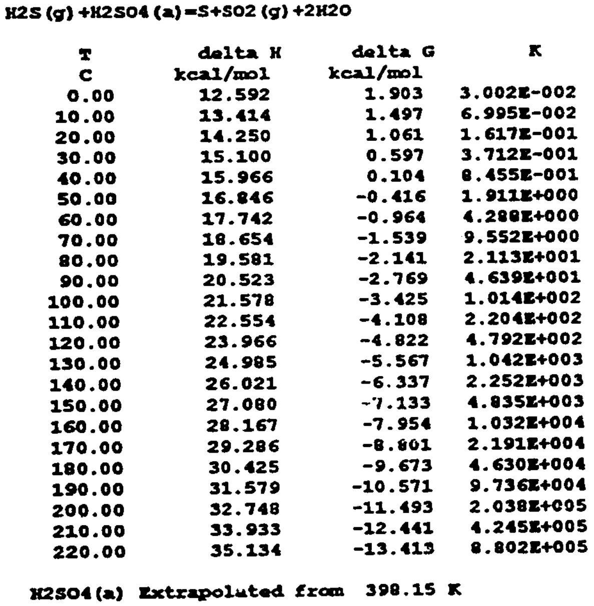
Temperature: From 0.000 To 220.000 Step 10.000 C

Temperature Units: ● Celsius ○ Kelvins

Energy Units: ● Calories ○ Joules

Format of Results: ● Normal ○ Delta

Figure 3.1 Reaction equation input file



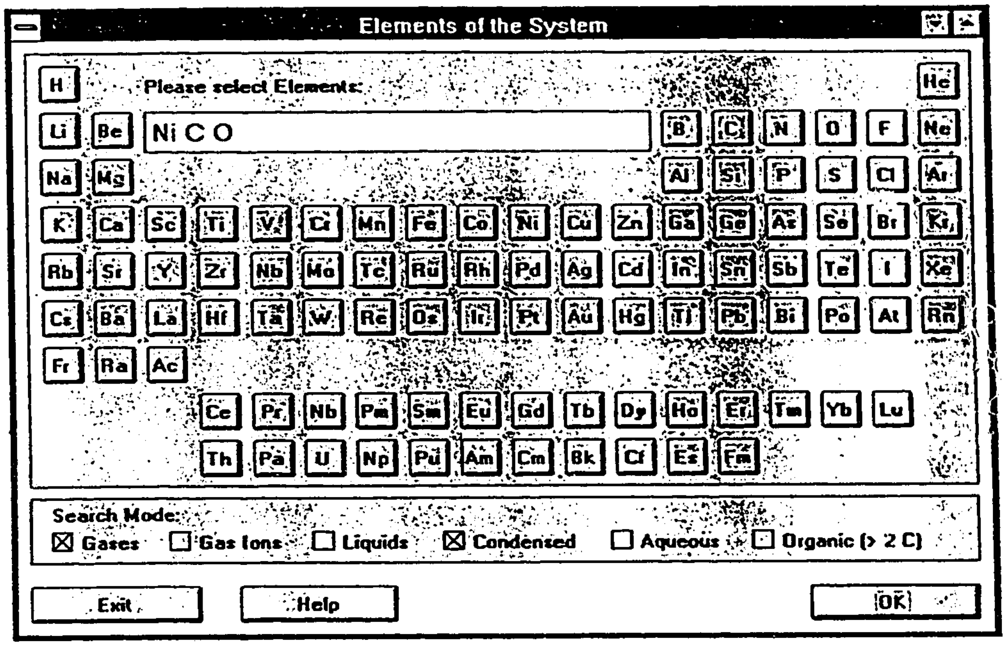
```
H2S(g)+H2SO4(a)=S+SO2(g)+2H2O

    T         delta H      delta G          K
    C        kcal/mol     kcal/mol
   0.00       12.592        1.903     3.002E-002
  10.00       13.414        1.497     6.995E-002
  20.00       14.250        1.061     1.617E-001
  30.00       15.100        0.597     3.712E-001
  40.00       15.966        0.104     8.455E-001
  50.00       16.846       -0.416     1.911E+000
  60.00       17.742       -0.964     4.288E+000
  70.00       18.654       -1.539     9.552E+000
  80.00       19.581       -2.141     2.113E+001
  90.00       20.523       -2.769     4.639E+001
 100.00       21.578       -3.425     1.014E+002
 110.00       22.554       -4.108     2.204E+002
 120.00       23.966       -4.822     4.792E+002
 130.00       24.985       -5.567     1.042E+003
 140.00       26.021       -6.337     2.252E+003
 150.00       27.080       -7.133     4.835E+003
 160.00       28.167       -7.954     1.032E+004
 170.00       29.286       -8.801     2.191E+004
 180.00       30.425       -9.673     4.630E+004
 190.00       31.579      -10.571     9.736E+004
 200.00       32.748      -11.493     2.038E+005
 210.00       33.933      -12.441     4.245E+005
 220.00       35.134      -13.413     8.802E+005

  H2SO4(a) Extrapolated from  398.15 K
```

Figure 3.2 Reaction equation output file even when the user does not know the exact compounds present in the system under consideration. In practice 1 to 5 elements should be selected. The phases possible can be selected from the search mode. The HSC searches all possible species and the user can select specified species up to a maximum of 150. Figure 3.4 shows the species selection window where all species in the HSC database that include H, S and/or O are shown. The unwanted species which definitely will not be present in the system can be deleted. The user should not delete those species, which are guestimates, since the results can be in error if stable species are deleted. However, experimentally, if some stable species is known to be present in negligibly small amounts due to kinetic reasons, it can be eliminated. Figure 3.5 shows the next step. Here remaining needed information can be introduced.

The HSC program automatically takes care of the liquid or solid phase for a particular compound and the suffix (l) is required only if the species is to be considered as a liquid below its normal melting point. Phases are specified in column 2. All species belonging to any particular phase must come in one successive sequence. For an unknown system, all gas phase species must come in phase 1, all condensed species in phase 2, all metals should form phase 3 and all aqueous species must be grouped into the fourth phase. In case an aqueous species is present, water must be also be present in that phase. The phases for one species (invariant) must be given their respective phase number. Electrical neutrality of the system must be maintained by showing electrons in the feed since the Gibbs program treats electrons in the same way as the elements. The presence of inerts such as N_2 improves the accuracy of the Gibbs program. The initial equilibrium temperature and incremental steps in that temperature and the initial amounts of the various species and their increments can be specified in this window. The input species temperatures do not affect the equilibrium composition because they are only needed for the heat balance. The various species amounts must be specified accurately. The program accepts only one equilibrium pressure in the present HSC version. The activity coefficients or their correlations can be specified in this window to take into account the nonideal solution behavior. The first approximation of activity coefficient is always unity.



Please select Elements: Ni C O

Search Mode:
☒ Gases ☐ Gas Ions ☐ Liquids ☒ Condensed ☐ Aqueous ☐ Organic (> 2 C)

Figure 3.3 Equilibrium calculations species selection from elements

```
H2O(g)            2   3048   3050
H2S(g)            2   3094   3094
H2SO4(g)          2   3102   3102
SO2(g)            2   6274   6275
H2O               2   3046   3047
H2SO4             2   3101   3101
H2SO4*2H2O        2   3116   3117
S                 2   6172   6176
```

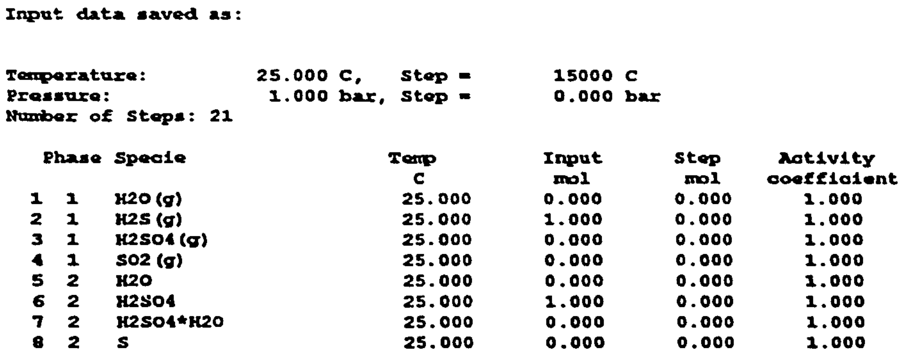
Figure 3.4 Species selection window

This completes the input file to be supplied to the Gibbs Free Energy Minimization program. The Gibbs program is quite robust in that it can be very flexible for various input files without introducing errors. Its accuracy can be increased by increasing the number of iterations as shown in Figure 3.6. The results can be plotted or printed in tabular format. They can be checked by using known equilibrium calculations or mass balances. For aqueous systems the equilibrium verification must be done using the molalities. Any sharp irregularities or random scatter in the plots may indicate errors in the Gibbs program calculations.

3.1.3.3 Eh-pH diagrams

These diagrams are also called Pourbaix diagrams after M.Pourbaix (1966). They show the theoretical stability area of different species in terms of their electrode potentials at different pH. These diagrams are very useful, for instance, to obtain the pH and the potential range in which metals dissolve or form an insoluble phase, or to locate the minimum potential required to precipitate some metals, etc. However these diagrams do not relate to kinetics, thus their applicability to real life situations should be exercised with due caution.

A specimen window to select the elements is shown in Figure 3.7. The main element in this window is that element, the user expects to be central to the system, viz. Cu in this Figure. The maximum number of other elements selected should not exceed 8 in order to reduce difficulty in running the program. The HSC program automatically selects H and O as the additional other two elements. The search mode decides which phases are required to be present in the system. The program shows the result window in Figure 3.8. The species required from those shown can be selected. Those species having a positive ΔG can be eliminated and the program is then rerun. This makes the results more relevant and accurate.

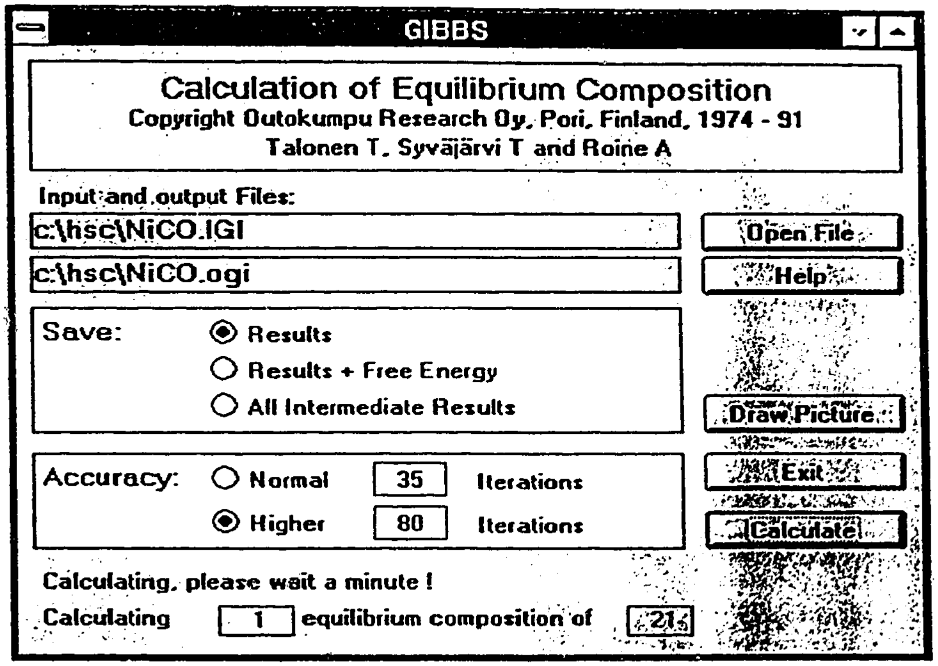


```
Input data saved as:

Temperature:          25.000 C,    Step =       15000 C
Pressure:              1.000 bar,  Step =       0.000 bar
Number of Steps: 21

   Phase Specie                    Temp       Input      Step     Activity
                                    C          mol        mol    coefficient
  1  1   H2O(g)                   25.000     0.000      0.000      1.000
  2  1   H2S(g)                   25.000     1.000      0.000      1.000
  3  1   H2SO4(g)                 25.000     0.000      0.000      1.000
  4  1   SO2(g)                   25.000     0.000      0.000      1.000
  5  2   H2O                      25.000     0.000      0.000      1.000
  6  2   H2SO4                    25.000     1.000      0.000      1.000
  7  2   H2SO4*H2O                25.000     0.000      0.000      1.000
  8  2   S                        25.000     0.000      0.000      1.000
```

Figure 3.5 Input file for equilibrium calculations



Calculation of Equilibrium Composition
Copyright Outokumpu Research Oy, Pori, Finland, 1974 - 91
Talonen T, Syväjärvi T and Roine A

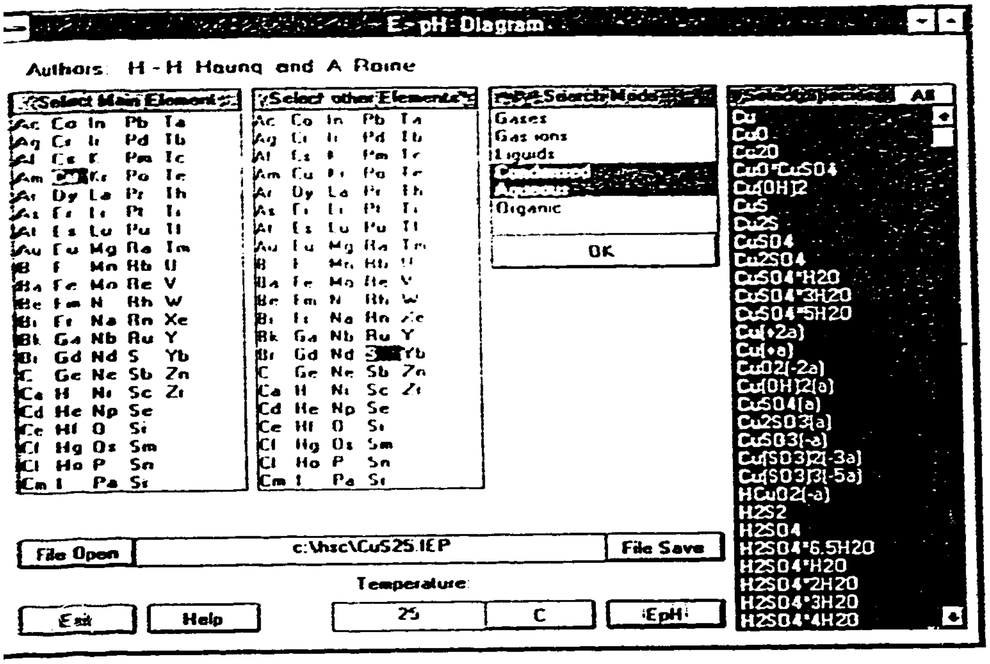
Input and output Files:
c:\hsc\NiCO.IGI
c:\hsc\NiCO.ogi

Save: ● Results
○ Results + Free Energy
○ All Intermediate Results

Accuracy: ○ Normal 35 Iterations
● Higher 80 Iterations

Calculating, please wait a minute !
Calculating 1 equilibrium composition of 21

Figure 3.6 Calculation of equilibrium composition



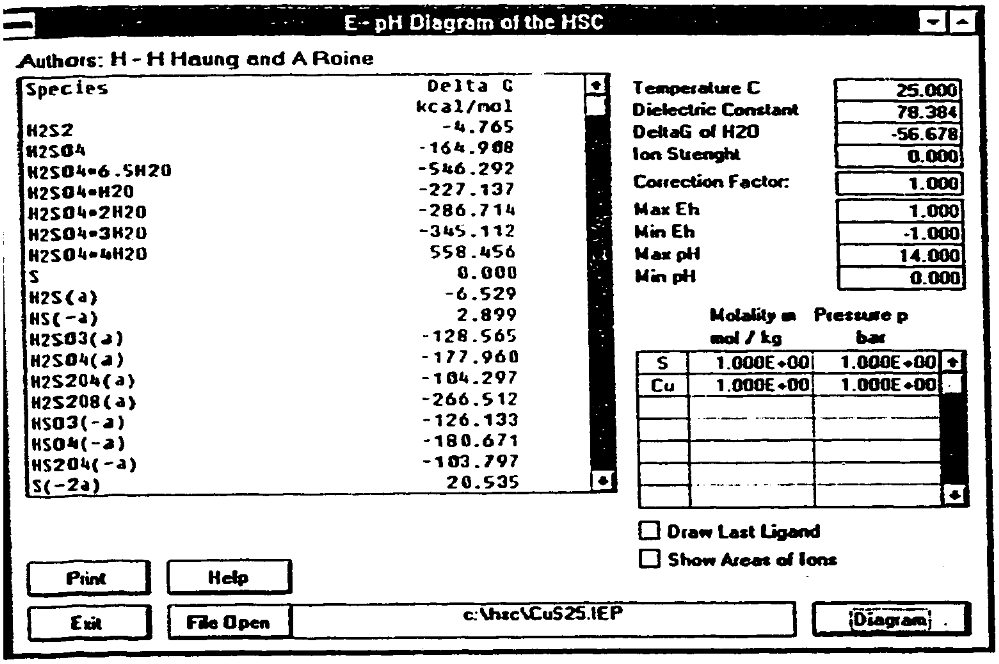
Authors: H - H Haung and A Roine

c:\hsc\CuS25.IEP

Temperature: 25 C

Cu
CuO
Cu2O
CuO*CuSO4
Cu(OH)2
CuS
Cu2S
CuSO4
Cu2SO4
CuSO4*H2O
CuSO4*3H2O
CuSO4*5H2O
Cu(+2a)
Cu(+a)
CuO2(-2a)
Cu(OH)2(a)
CuSO4(a)
Cu2SO3(a)
CuSO3(-a)
Cu(SO3)2(-3a)
Cu(SO3)3(-5a)
HCuO2(-a)
H2S2
H2SO4
H2SO4*6.5H2O
H2SO4*H2O
H2SO4*2H2O
H2SO4*3H2O
H2SO4*4H2O

ure 3.7 Eh-pH species selection



Authors: H - H Haung and A Roine

Species	Delta G kcal/mol
H2S2	-4.765
H2SO4	-164.908
H2SO4•6.5H2O	-546.292
H2SO4•H2O	-227.137
H2SO4•2H2O	-286.714
H2SO4•3H2O	-345.112
H2SO4•4H2O	558.456
S	0.000
H2S(a)	-6.529
HS(-a)	2.899
H2SO3(a)	-128.565
H2SO4(a)	-177.960
H2S2O4(a)	-104.297
H2S2O8(a)	-266.512
HSO3(-a)	-126.133
HSO4(-a)	-180.671
HS2O4(-a)	-103.797
S(-2a)	20.535

Temperature C: 25.000
Dielectric Constant: 78.384
DeltaG of H2O: -56.678
Ion Strenght: 0.000
Correction Factor: 1.000
Max Eh: 1.000
Min Eh: -1.000
Max pH: 14.000
Min pH: 0.000

	Molality m mol / kg	Pressure p bar
S	1.000E+00	1.000E+00
Cu	1.000E+00	1.000E+00

☐ Draw Last Ligand
☐ Show Areas of Ions

c:\hsc\CuS25.IEP

gure 3.8 Eh-pH results file

The HSC program offers a very powerful, useful and cheap tool to locate optimum reaction conditions and yields for experimental investigations without expensive trial-and-error chemistry. This suggests what is feasible or not feasible and provides us with valuable information when making plans for an experimental investigation.

3.2 System parameter effects on the equilibrium performance

After becoming familiar with the HSC program, various options were utilized for studying the H_2S-H_2SO_4 process, as follows:

3.2.1 Reaction equations and Eh-pH diagram

The reaction equation option in the HSC was used to test the feasibility of various chemical reactions in the H_2S-H_2SO_4 system that are cited in the literature.

$3\ H_2S + H_2SO_4 = S + 4\ H_2O$..........................(6)

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$..................(7)

$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$............................(8)

$S + 2\ H_2SO_4 = 3\ SO_2 + 2\ H_2O$........................(9)

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$...................(10)

The results are shown in Table 3.1 and Figure 3.9.

The Eh-pH diagrams were constructed for the H_2S-H_2SO_4 system to test the stability of various species at different pH values. Those species with a negative ΔG were selected for the purpose of the diagram. Eh-pH diagrams at 120, 150 and 300°C are shown in Figures 3.10 to

3.12. The dotted lines indicate the regime of H_2O stability. The results agree well with previous studies (Figure 2.5) regarding the stable species and pH ranges concerned. The other implications of these diagrams will be discussed in the results and discussion chapter.

3.2.2 Equilibrium compositions

We need to select the correct species for the equilibrium compositions to ensure error-free calculations.

3.2.2.1 Selection of species for H_2SO_4 -H_2S system analysis

The species selection was done by selecting elements H, S and O. The phases selected were gas, liquid and aqueous. The HSC gave a list of possible species, out of which the species present in the system must be selected carefully. The species H_2O, S, H_2S, SO_2 and H_2SO_4(a) would be present at equilibrium since all of them are present in the experimental product mixtures. In addition, a number of unknown species may be present. Since the experimental equilibrium for H_2S - H_2SO_4 has not been reported in thc literature, all stable species given by the HSC program should be considered. However, a number of species were eliminated for strong reasons as explained below:

Various sulfur species included in the HSC database are shown in Table 3.2. Since sulfur exists only in elemental form at the temperatures used (120°C -150°C) in the experiments, the remaining sulfur-containing species were eliminated. The program does not possess the excited state of sulfur in its database. The excited state of sulfur can be a different phase of sulfur formed when sulfur is generated as an intermediate and is highly reactive towards other reacting species. Sulfuric acid can be present in several hydrate forms. Among all hydrates of sulfuric acid only the monohydrate form dominates at high acid concentrations and so, the

Table 3.1 Thermochemical data at 120 °C for reaction of H_2S with H_2SO_4

Reaction Equation	ΔH kcal/mol	ΔG kcal/mol	K
$3H_2S(g)+H_2SO_4(a)=4S+4H_2O$	- 27.829	-21.261	$6.604x10^{11}$
$H_2S(g)+3H_2SO_4(a)=4SO_2(g)+4H_2O$	123.694	1.975	$7.981x10^{-2}$
$H_2S(g)+H_2SO_4(a)=S+SO_2(g)+2H_2O$	23.966	- 4.822	$4.792x10^{2}$
$H_2S(g)+H_2SO_4=S+SO_2(g)+2H_2O$	- 6.810	-13.656	$3.905x10^{7}$
$H_2S(g)+3H_2SO_4=4SO_2(g)+4H_2O$	31.367	-24.527	$4.321x10^{13}$
$3H_2S(g)+H_2SO_4=4S+4H_2O$	- 58.605	-30.095	$5.383x10^{16}$
$3H_2S(a)+H_2SO_4(a)=4S+4H_2O$	- 11.696	-31.702	$4.213x10^{17}$
$H_2S(a)+3H_2SO_4(a)=4SO_2(a)+4H_2O$	129.072	- 1.505	6.870
$H_2S(a)+H_2SO_4(a)=S+SO_2(g)+2H_2O$	29.344	- 8.302	$4.125x10^{4}$
$S+2H_2SO_4=3SO_2(g)+2H_2O$	38.177	-10.872	$1.106x10^{6}$
$S+2H_2SO_4(a)= 3SO_2(g)+2H_2O$	99.728	6.796	$1.666x10^{-4}$
$SO_2(g)+2H_2S(g)=3S+2H_2O$	- 51.796	-16.439	$1.378x10^{9}$
$SO_2(a)+2H_2S(a)=3S+2H_2O$	- 33.482	-25.390	$1.305x10^{14}$

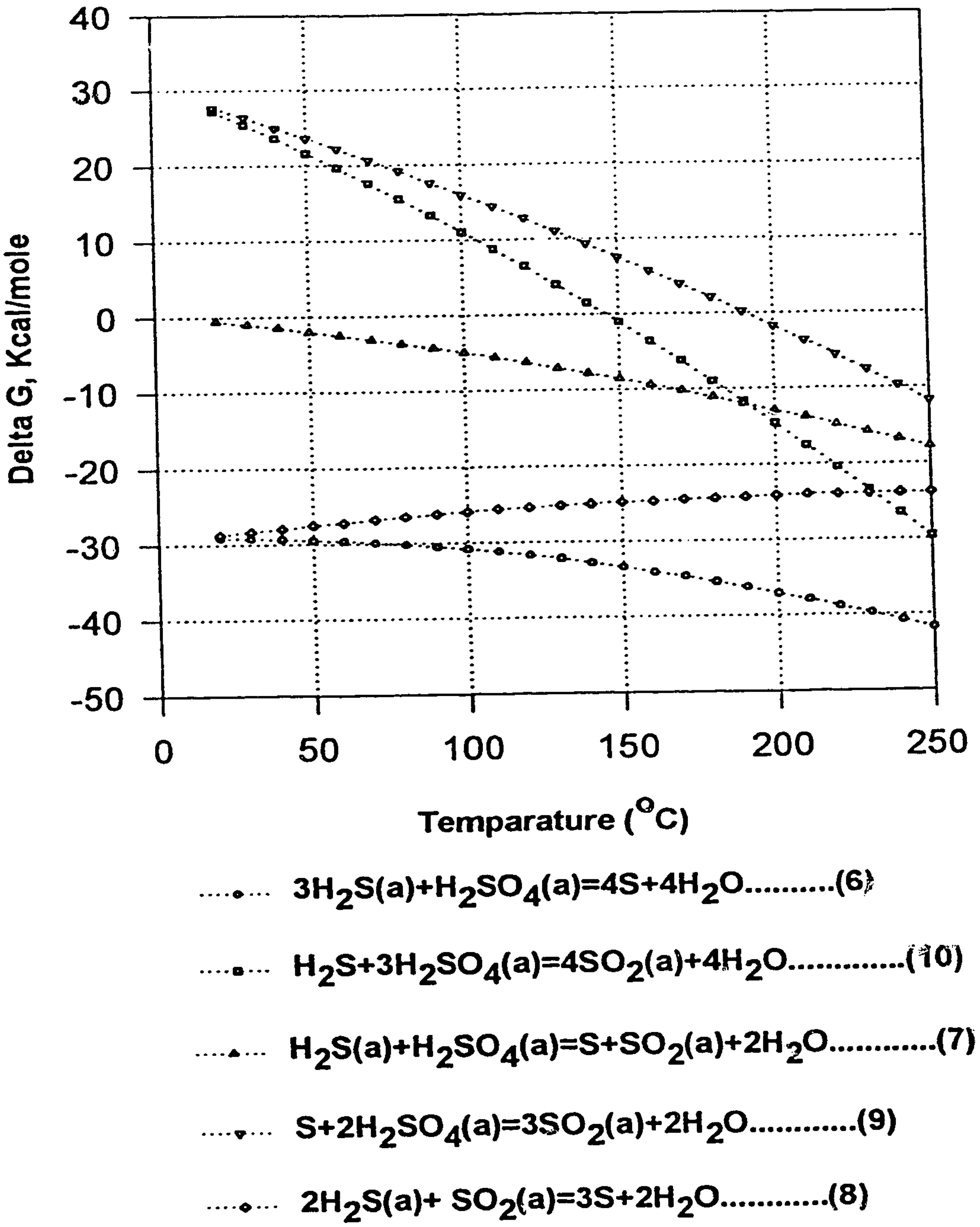


Figure 3.9 Variations of the free energies of reactions with temperature

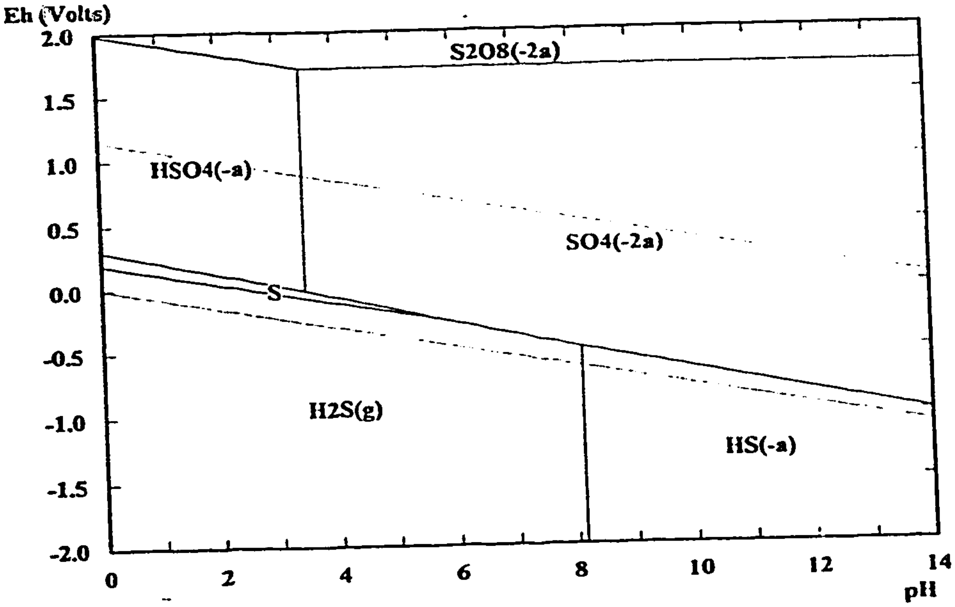


Figure 3.10 Stability fields of various sulfur species at 120°C

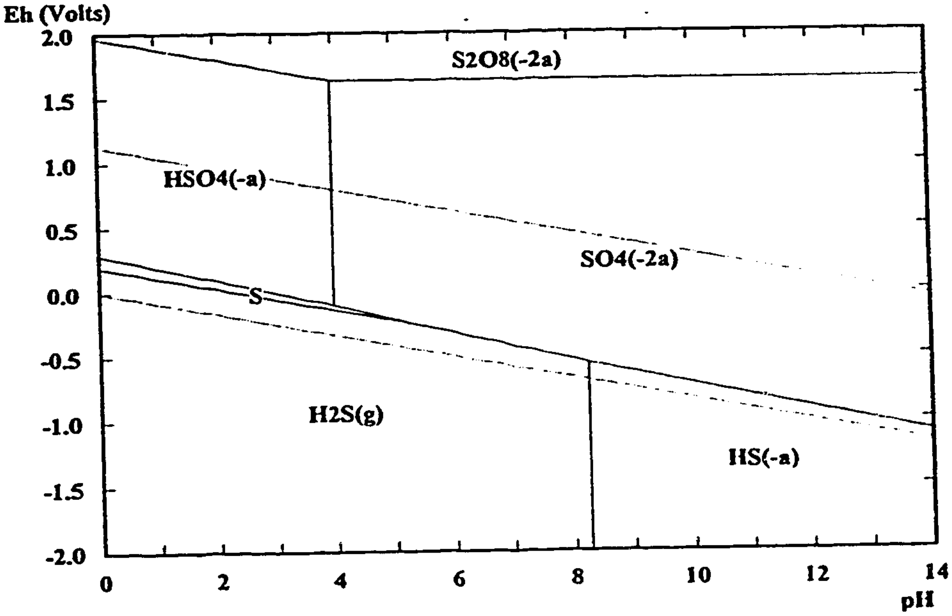


Figure 3.11 Stability fields of various sulfur species at 150°C

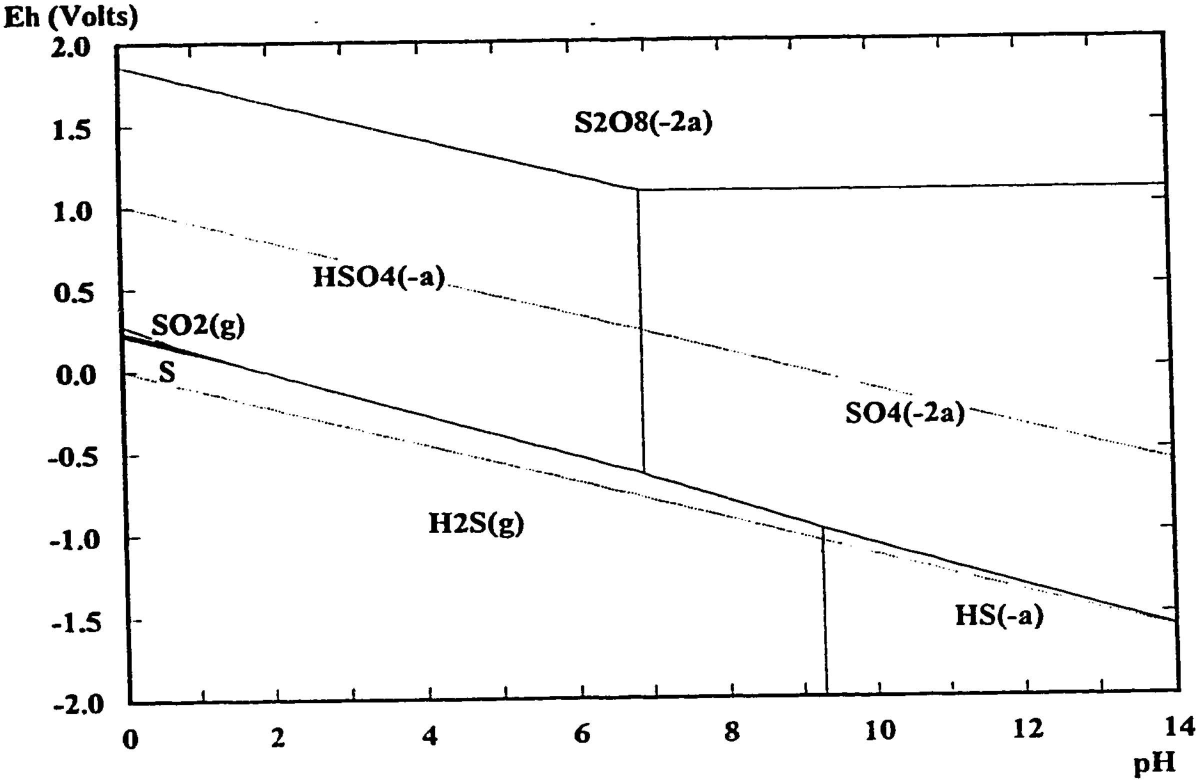


Figure 3.12 Stability fields of various sulfur species at 300°C

other hydrates of H_2SO_4 were neglected. The intermediate complexes and ions cannot exist at equilibrium; hence, all such related intermediate species were excluded from consideration. Also, some of the species which are unlikely to be present and which exist only in very minor quantities were excluded.

Multiple equilibria may occur in the system. First, the dissociation of dissolved H_2S in the acid media may occur according to the equilibrium reaction,

$$H_2S(a) = H^+(a) + HS^-(a) \qquad (19)$$

Table 3.2 All S-containing species in the HSC database

```
    Phase  Specie

 1   1     S(g)
 2   1     S2(g)
 3   1     S3(g)
 4   1     S4(g)
 5   1     S5(g)
 6   1     S6(g)
 7   1     S7(g)
 8   1     S8(g)
 9   1     S(+g)
10   1     S(-g)
11   2     S
12   3     S(-2a)
13   3     S2(-2a)
14   3     S3(-2a)
15   3     S4(-2a)
16   3     S5(-2a)
```

Second, sulfuric acid dissociation in the presence of water must be considered. The literature mentions that at high acid concentrations (above 80 wt%), the acid dissociates according to the equilibrium reaction (17),

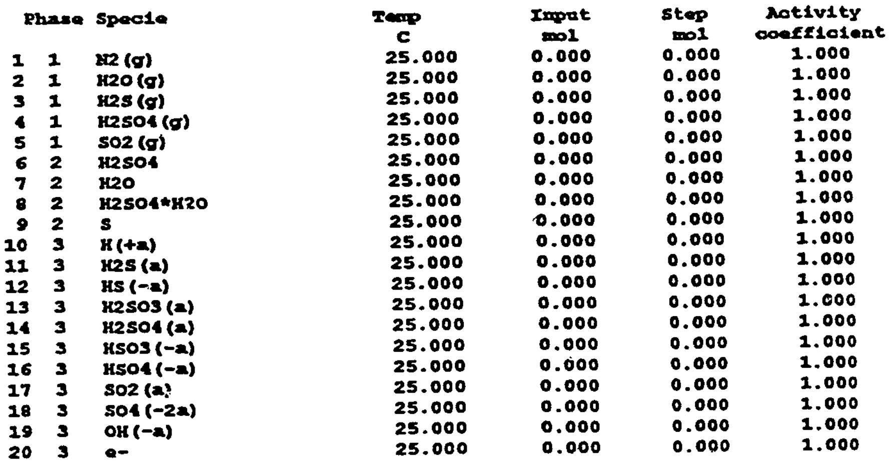
$$H_2SO_4 + H_2O = H_3O^+(a) + HSO_4^-(a) \ldots\ldots\ldots\ldots (17)$$

The third equilibrium involves the physical dissolution of the gases, H_2S and SO_2 , in acid media. Also, HSO_3(-a) would be present due to the reaction of SO_2 with H_2O. All of these aqueous species were included in the input species list. N_2 was added to the system of species at equilibrium subsequently. Water dissociation was taken into account by including the species OH(-a). Finally, electrons were added to the system to maintain electrical neutrality. Thus, the final species list used as the feed is shown in Figure 3.13.

Having selected the species for the equilibrium calculations, one should verify the HSC calculations with established data in order to ensure valid conclusions and to check the reliability of the predictions for the H_2S - H_2SO_4 system as well.

3.2.2.2 Verification of the applicability of the HSC database and calculations

For the H_2SO_4 - H_2S system, the records responsible for calculations in the HSC program taken from its main database for all principle chemicals involved are shown in Table 3.3. Hence, the selection of the species should be done carefully, not by name but by the properties required. This is evident in the case of H_2SO_4. The properties used for H_2SO_4 (a) are those of H_2SO_4 at infinite dilution; whereas, H_2SO_4 means pure sulfuric acid. The properties of acid concentrations between infinitely dilute and pure H_2SO_4 are not available in the main database The values for the specific heat coefficients A, B, C, D, etc., for these concentrations are not



```
 Phase Specie                    Temp      Input     Step    Activity
                                   C        mol       mol   coefficient
 1  1   H2(g)                   25.000    0.000     0.000     1.000
 2  1   H2O(g)                  25.000    0.000     0.000     1.000
 3  1   H2S(g)                  25.000    0.000     0.000     1.000
 4  1   H2SO4(g)                25.000    0.000     0.000     1.000
 5  1   SO2(g)                  25.000    0.000     0.000     1.000
 6  2   H2SO4                   25.000    0.000     0.000     1.000
 7  2   H2O                     25.000    0.000     0.000     1.000
 8  2   H2SO4*H2O               25.000    0.000     0.000     1.000
 9  2   S                       25.000    0.000     0.000     1.000
10  3   H(+a)                   25.000    0.000     0.000     1.000
11  3   H2S(a)                  25.000    0.000     0.000     1.000
12  3   HS(-a)                  25.000    0.000     0.000     1.000
13  3   H2SO3(a)                25.000    0.000     0.000     1.000
14  3   H2SO4(a)                25.000    0.000     0.000     1.000
15  3   HSO3(-a)                25.000    0.000     0.000     1.000
16  3   HSO4(-a)                25.000    0.000     0.000     1.000
17  3   SO2(a)                  25.000    0.000     0.000     1.000
18  3   SO4(-2a)                25.000    0.000     0.000     1.000
19  3   OH(-a)                  25.000    0.000     0.000     1.000
20  3   e-                      25.000    0.000     0.000     1.000
```

Figure 3.13 All species selected for equilibrium calculations

Table 3.3 Database for some principal S-containing species from the HSC

```
                                                              34.076 g/mol
H2S(g)
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
g    -4.900   49.160     7.020     3.680    0.000    0.000  298.150 1800.000
     0.000 g/cm3  BKK 1977          Data from MainDB.HSC File


S                                                             32.060 g/mol
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
s     0.000    7.620     3.540     5.750    0.174    0.000  298.150  368.500
s     0.096    0.261    16.337   -28.333    0.000    0.000  368.500  374.000
s     0.000    0.000     3.270     7.162    0.000    0.000  374.000  388.300
l     0.410    1.056  -493.393   828.729  270.387    0.000  388.000  440.000
l     0.000    0.000    -6.109    13.809   21.182    0.000  440.000  717.750
     0.000 g/cm3  BKK 1977
     0.000 g/cm3  BKK 1977
     0.000 g/cm3  BKK 1977
     0.000 g/cm3  BKK 1977
     0.000 g/cm3  BKK 1977          Data from MainDB.HSC File


                                                              98.073 g/mol
H2SO4(a)
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
ai -217.350    4.800   -70.040     0.000    0.000    0.000  298.150  398.150
     0.000 g/cm3  NBS 1982          Data from MainDB.HSC File


SO2(g)                                                        64.059 g/mol
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
g   -70.947   59.324     6.269    12.464    0.055   -5.641  298.150  600.000
g     0.000    0.000    13.423     0.366   -6.886   -0.024  600.000 6000.000
     0.000 g/cm3  JANAF 1985
     0.000 g/cm3  JANAF 1985        Data from MainDB.HSC File


                                                              34.076 g/mol
H2S(a)
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
ao   -9.490   28.920     0.000     0.000    0.000    0.000  298.150  398.150
     0.000 g/cm3  NBS 1982          Data from MainDB.HSC File

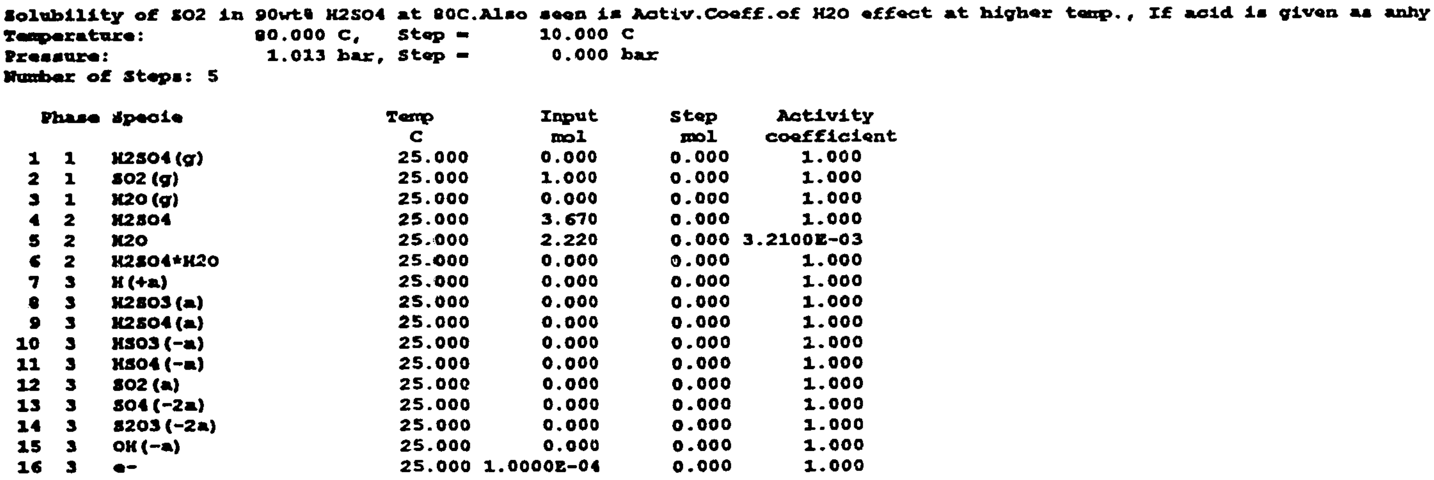

                                                              98.073 g/mol
H2SO4
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
l  -194.548   37.501    37.500     6.764   -5.608    0.000  298.150  553.000
     0.000 g/cm3  BKK 1977          Data from MainDB.HSC File


SO2(a)                                                        64.059 g/mol
   Enthalpy  Entropy   Heat Capacity                       Temperature Range
      H         S         A         B        C        D        T1       T2
   kcal/mol cal/(mol*K) cal/(mol*K)                             K        K
ao  -77.200   38.700     0.000     0.000    0.000    0.000  298.150  398.150
     0.000 g/cm3  NBS 1982          Data from MainDB.HSC File
```

available in the literature.

These intermediate concentrations of H_2SO_4, therefore, cannot be fed to the "own" database. It is imperative that the user uses H_2SO_4(a) or H_2SO_4 along with H_2O as the approximation when specifying intermediate acid concentrations. To verify whether properties of intermediate acid concentrations are taken into account by the HSC program automatically, verification of the H_2SO_4 concentration-based properties is essential. To do this, the following tests were carried out:

1. If H_2SO_4 is used as the approximation in the initial species list in the equilibrium calculations, it should give H_2SO_4(a) as the product at equilibrium. This was observed to occur in the HSC calculations.
2. H_2S reacts with H_2SO_4 and its physical solubility in acid media cannot be established conclusively by the HSC. Also, the literature does not provide reliable values of H_2S solubility in acid media due to its reactivity and the unknown kinetic behavior of the reaction of H_2S with H_2SO_4. The H_2S solubility is a function of temperature, pressure and the solution behavior. Non-ideality of solutions is approximated by solution models and the solubility parameters are not available for H_2S. However, the solubility of SO_2 in H_2SO_4 is well-established, and was used as the verification reference scale. As seen in Figure2.16, the reported solubility of SO_2 in aqueous H_2SO_4 of various concentrations, shows a hump in the temperature plot. Dissolution of SO_2 in acid was represented by including SO_2 and H_2SO_4 in the equilibrium mixture. The HSC calculation for 1 mole of pure SO_2 at 1 bar and 400 g of 90 wt% sulfuric acid at 80°C in the initial mixture, is shown in Figure 3.14. Such calculations have been done from 80 to 98 wt% acid, the rest of the conditions remaining constant. The result for the solubility is shown in Figure 3.15. When compared with Figure 2.16, Figure 3.15 shows the minima seen in the actual case. Also, the actual solubility values are comparable to those predicted by the HSC calculations. As the temperature increases, the gas solubility in the liquid decreases. Hence, any error, which may exist, due to SO_2 solubility, will be minor at temperatures above 100°C. The same behavior should be anticipated with H_2S solubility. The results were not different when only H_2SO_4 or both H_2SO_4 and H_2SO_4(a) were used in the feed.



```
Solubility of SO2 in 90wt% H2SO4 at 80C.Also seen is Activ.Coeff.of H2O effect at higher temp., If acid is given as anhy
Temperature:         80.000 C,    Step =       10.000 C
Pressure:             1.013 bar, Step =        0.000 bar
Number of Steps: 5

   Phase Specie                    Temp         Input       Step     Activity
                                     C           mol         mol     coefficient
  1  1   H2SO4(g)                 25.000       0.000       0.000       1.000
  2  1   SO2(g)                   25.000       1.000       0.000       1.000
  3  1   H2O(g)                   25.000       0.000       0.000       1.000
  4  2   H2SO4                    25.000       3.670       0.000       1.000
  5  2   H2O                      25.000       2.220       0.000 3.2100E-03
  6  2   H2SO4*H2O                25.000       0.000       0.000       1.000
  7  3   H(+a)                    25.000       0.000       0.000       1.000
  8  3   H2SO3(a)                 25.000       0.000       0.000       1.000
  9  3   H2SO4(a)                 25.000       0.000       0.000       1.000
 10  3   HSO3(-a)                 25.000       0.000       0.000       1.000
 11  3   HSO4(-a)                 25.000       0.000       0.000       1.000
 12  3   SO2(a)                   25.000       0.000       0.000       1.000
 13  3   SO4(-2a)                 25.000       0.000       0.000       1.000
 14  3   S2O3(-2a)                25.000       0.000       0.000       1.000
 15  3   OH(-a)                   25.000       0.000       0.000       1.000
 16  3   e-                       25.000 1.0000E-04       0.000       1.000
```

Figure 3.14 SO_2 solubility in 90 wt% H_2SO_4 input file

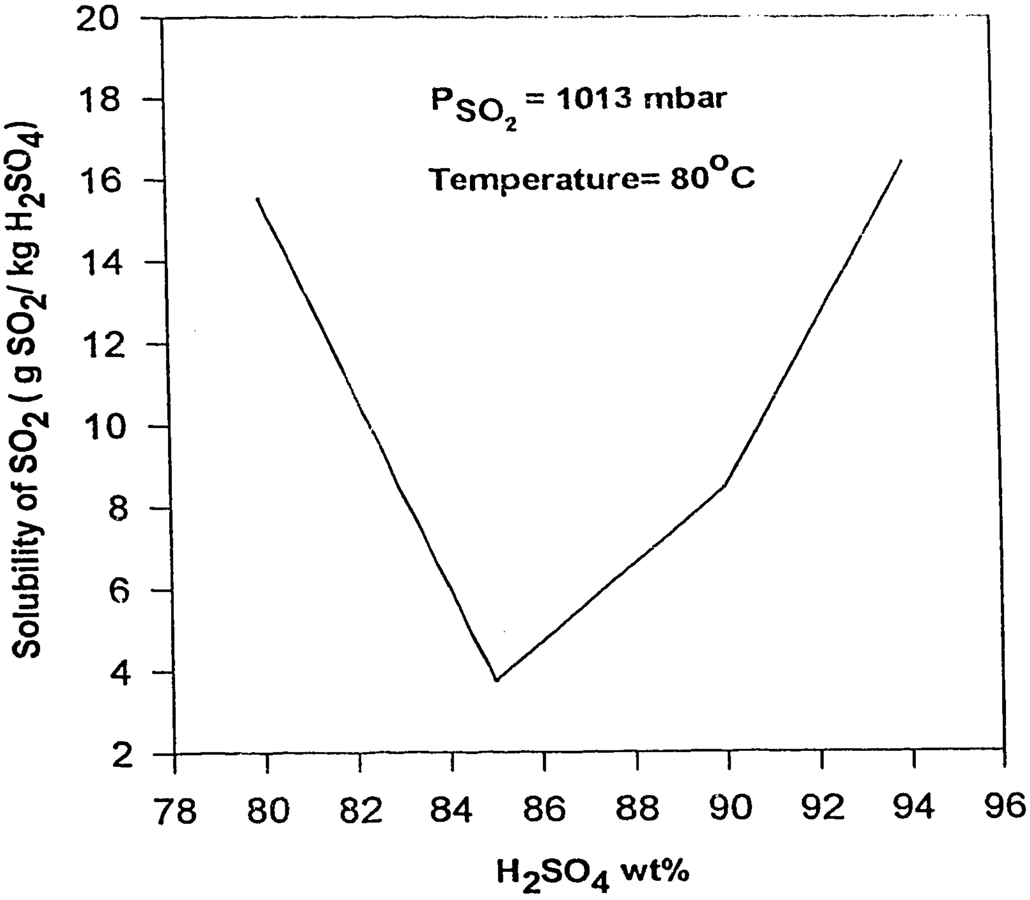


Figure 3.15 Solubility of SO_2 in 90 wt% H_2SO_4

3. In the equilibrium parametric study, which will be seen later, the use of either H_2SO_4 or H_2SO_4(a) did not affect the final results.

These observations clearly show that the HSC program can handle differences in acid concentrations. Since the acid concentrations concerned lie in the range of 80 - 98wt%, the species H_2SO_4 was used as feed in all of the equilibrium calculations.

For the sake of verification, the values of the data used by HSC program were compared with those available in the literature. For example the specific heat coefficients for H_2SO_4(a) as provided in the Journal of Physical and Chemical Reference Data (1982) are the same as those provided in the HSC database (Table 3.3). The enthalpies of reactions as calculated by the HSC for various reactions agree well with published data. For example, the heat of formation of H_2O matches its published value at 25°C (-68.315 kcal/mole). The HSC calculation capabilities are correct for this system as shown by the SO_2 solubility behavior. To prove the point further, the dissociation of H_2SO_4 was attempted using different acid concentrations. Figure 3.16 shows that the output species present are in accordance with the actual case and the major component conforms with the actual experience, e.g. for the concentrations in the range of 84-92 wt%, monohydrate of H_2SO_4 is dominant and above 80 wt% acid concentrations, the HSO_4^- and H^+ are dominant. Hence the HSC predicts H_2SO_4 dissociation fairly accurately.

When we compare Figure 2.5 with Figures 3.10-1.12, the results agree well with the stable species and pH ranges of concern. The ΔG -T plot reported and that given by the HSC program for the plausible reactions match well as seen in Figures 2.4 and 3.9. This suggests that the input values used and the calculations performed are reliable in indicating various sulfur-containing species and other chemicals of interest to the present work.

3.2.2.3 Equilibrium calculations

```
          X          Y 1          Y 2          Y 3          Y 4          Y 5          Y 6          Y 7          Y 8
Temperature     H2SO4(a)    H2SO4*H2O   H2SO4*2H2O   H2SO4*3H2O       H2O(g)     H2SO4(g) H2SO4*6.5H2O   H2SO4*4H2O
2.93150E+02  2.46090E+00  1.36210E-05  1.10730E-05  4.55430E-06  1.96640E-07  1.18020E-08  2.52350E-09  1.00000E-36
3.03150E+02  2.39650E+00  1.61940E-05  1.20420E-05  4.50810E-06  2.83620E-07  2.13220E-08  1.29910E-09  1.00000E-36
3.13150E+02  2.33060E+00  1.95210E-05  1.32440E-05  4.49490E-06  4.07440E-07  3.74920E-08  6.44220E-10  1.00000E-36
3.23150E+02  2.26750E+00  2.39120E-05  1.47640E-05  4.52400E-06  5.86050E-07  6.46630E-08  3.03570E-10  1.00000E-36
3.33150E+02  2.20140E+00  2.99060E-05  1.67380E-05  4.60440E-06  8.46940E-07  1.10500E-07  1.04270E-10  1.00000E-36

          X          Y 1          Y 2          Y 3          Y 4          Y 5          Y 6          Y 7          Y 8
Temperature          H2O        H2SO4     HSO4(-a)     H2SO3(a)        H(+a)     HSO3(-a)       OH(-a)     SO4(-2a)
2.93150E+02  4.00000E+00  1.69890E+00  1.05740E-04  5.00000E-05  5.74250E-06  6.80320E-11  4.45470E-22  1.12520E-24
3.03150E+02  4.00000E+00  1.76330E+00  1.07190E-04  5.00000E-05  7.19310E-06  4.92790E-11  4.79400E-22  9.55800E-25
3.13150E+02  4.00000E+00  1.82920E+00  1.09080E-04  5.00000E-05  9.08400E-06  3.53950E-11  4.56670E-22  7.52500E-25
3.23150E+02  4.00000E+00  1.89230E+00  1.11610E-04  5.00000E-05  1.16120E-05  2.49900E-11  3.80860E-22  5.35910E-25
3.33150E+02  4.00000E+00  1.95840E+00  1.14940E-04  5.00000E-05  1.49390E-05  1.74260E-11  2.64130E-22  3.21150E-25
```

Figure 3.16 85 wt% sulfuric acid dissociation result file

Now the strategy devised to evaluate the performance of the H_2S - H_2SO_4 system at equilibrium, using equilibrium calculation option in the HSC program, is as follows:

The purpose of these calculations was to determine the effect of various reaction system parameters on H_2S conversion and SO_2 formation. To verify their reliability, the values for the variables that were tested have been matched with those used in the actual experiments. These will be explained in the next chapter. Basically, the effects of change in temperature, feed acid concentration, feed gas composition, gas flow rate and acid flow rate were observed at a constant reactor pressure. The experimental reaction temperatures used were varied from 100°C to 150°C but, the HSC calculations were performed in the range of 30 to 200°C to verify the reaction stoichiometry and the literature reference (Snurnikov et al , 1967) as well The temperature increment has been kept small, i.e. 5°C, to minimize the extrapolation errors. The experimental system pressure had been maintained constant at 5 psig i.e. 1.36 bar but the equilibriums were calculated in the range of 5 to 5000 psig. Both the experimental and equilibrium feed acid concentrations used were in the range of 80 to 96 wt%. The experimental feed gas compositions used were 2, 4.5 and 8.9 mole% H_2S with the balance, N_2

For equilibrium calculations, H_2S compositions of 1, 2, 4.5, 9 and 15 mole% have been used. Since the thermodynamic equilibrium constant is a function of only intensive properties, the effect of extensive parameters such as the flow rates of the gas and acid on the equilibrium composition, otherwise important, becomes superfluous. Even then to facilitate a comparison between the experimental and equilibrium calculations, the volume ratio of feed gas to feed acid is kept equal to 2.73, one of the ratios used in the experiments.

Sulfuric acid is a highly hygroscopic chemical and even at high temperatures it retains water very effectively as seen in Figure 2.12. Aqueous H_2SO_4 solutions, therefore, may be highly nonideal. Since solubility is a function of temperature and solution nonideality, if nonideality is taken into account the problem is solved. The activity coefficient, which expresses the degree of nonideality, can be used by the HSC in the equilibrium calculations. These coefficient values or their correlations are required by the program. The activity coefficients for H_2O in the H_2O - H_2SO_4 system were calculated using equations (13) and (14) and vapor pressure data for H_2O over pure H_2O and various concentrations of H_2SO_4 at various temperatures. Thus data are not available for acid concentrations other than 80 and 85 wt% in the range of 80-90wt% H_2SO_4. The partial pressure (P.P.) values are shown in Table 3.4. The vapor pressure (V.P.) of water has been interpolated from Perry's Chemical Engineering Handbook, (1984). The activity coefficients were calculated as follows.

Activity, a_i = (P.P. over H_2SO_4 solution)/ (V.P. over pure H_2O)............................(13)

Activity coefficient, γ = (Activity)/ (mole fraction of H_2O)......................................(14)

The results are shown in Figures 3.17 to 3.19. The activity coefficient has a value of unity for ideal solutions. So these results show that H_2SO_4 solutions are highly nonideal. The underlying assumption in these calculations is that the vapor phase is ideal. Thus, the fugacity coefficient of the water vapor is assumed to be unity. This allows fugacity to be replaced by partial pressure of H_2O in the above calculations. This assumption should be valid since the temperature of the system is high and pressure low. Sulfuric acid has a very low vapor pressure at low temperatures as seen in Figure 2.12; hence, the nonideality of H_2SO_4 solution

Table 3.4 Water vapor pressure and partial pressure over sulfuric acid

T, °C	V. P. of water, bar	T, °C	V. P. of water, bar	T, °C	V. P. of water, bar
30.00	0.04	90.00	0.70	150.00	4.78
40.00	0.07	100.00	1.01	160.00	6.18
50.00	0.12	110.00	1.43	170.00	7.94
60.00	0.20	120.00	1.99	180.00	10.06
70.00	0.33	130.00	2.71	190.00	12.61
80.00	0.48	140.00	3.62	200.00	15.62

H_2SO_4 wt%	80.00	85.00	90.00	92.00	94.00	96.00	97.00	98.00
T, °C	Vapor	pressure	of water	over	H_2SO_4	bar		
30.00	2.53E-04	5.89E-05	1.17E-05	5.87E-06	2.75E-06	1.08E-06	5.98E-07	2.75E-07
40.00	5.31E-04	1.33E-04	2.85E-05	1.46E-05	6.96E-06	2.78E-06	1.55E-06	7.20E-07
50.00	1.06E-03	2.86E-04	6.52E-05	3.41E-05	1.66E-05	6.72E-06	3.79E-06	1.77E-06
60.00	2.04E-03	5.84E-04	1.41E-04	7.54E-05	3.72E-05	1.54E-05	8.75E-06	4.13E-06
70.00	0.00376	1.14E-03	2.90E-04	1.58E-04	7.95E-05	3.34E-05	1.92E-05	9.12E-06
80.00	0.00668	2.13E-03	0.000569	3.16E-04	1.62E-05	6.91E-05	4.00E-05	1.92E-05
90.00	1.15E-02	3.83E-03	1.07E-03	6.06E-04	3.15E-04	1.37E-04	8.01E-05	3.88E-05
100.00	1.92E-02	6.66E-03	1.94E-03	1.12E-03	5.90E-04	2.61E-04	1.54E-04	7.52E-05
110.00	3.12E-02	1.12E-02	3.38E-03	1.98E-03	1.07E-03	4.79E-04	2.85E-04	1.41E-04
120.00	4.93E-02	1.83E-02	5.71E-03	3.41E-03	1.86E-03	8.51E-04	5.11E-04	2.54E-04
130.00	7.60E-02	0.0291	9.38E-03	5.69E-03	3.15E-03	1.46E-03	8.86E-04	4.45E-04
140.00	0.115	0.0451	1.50E-02	9.23E-03	5.19E-03	2.45E-03	1.49E-03	7.57E-04
150.00	0.17	6.82E-02	2.33E-02	0.0146	8.32E-03	3.99E-03	2.45E-03	1.25E-03
160.00	0.246	0.101	3.54E-02	0.0225	0.013	6.33E-03	3.93E-03	2.02E-03
170.00	0.35	0.147	5.26E-02	0.034	0.0199	9.83E-03	6.14E-03	3.19E-03
180.00	0.489	0.208	7.66E-02	0.0502	0.0298	1.49E-02	9.41E-03	4.92E-03
190.00	0.673	0.291	0.11	0.0729	0.0438	0.0222	1.41E-02	7.44E-03
200.00	0.913	0.401	0.154	0.104	0.0631	0.0325	0.0208	1.10E-02
Water over H_2SO_4 mole fraction	0.58	0.49	0.38	0.32	0.26	0.19	0.14	0.10

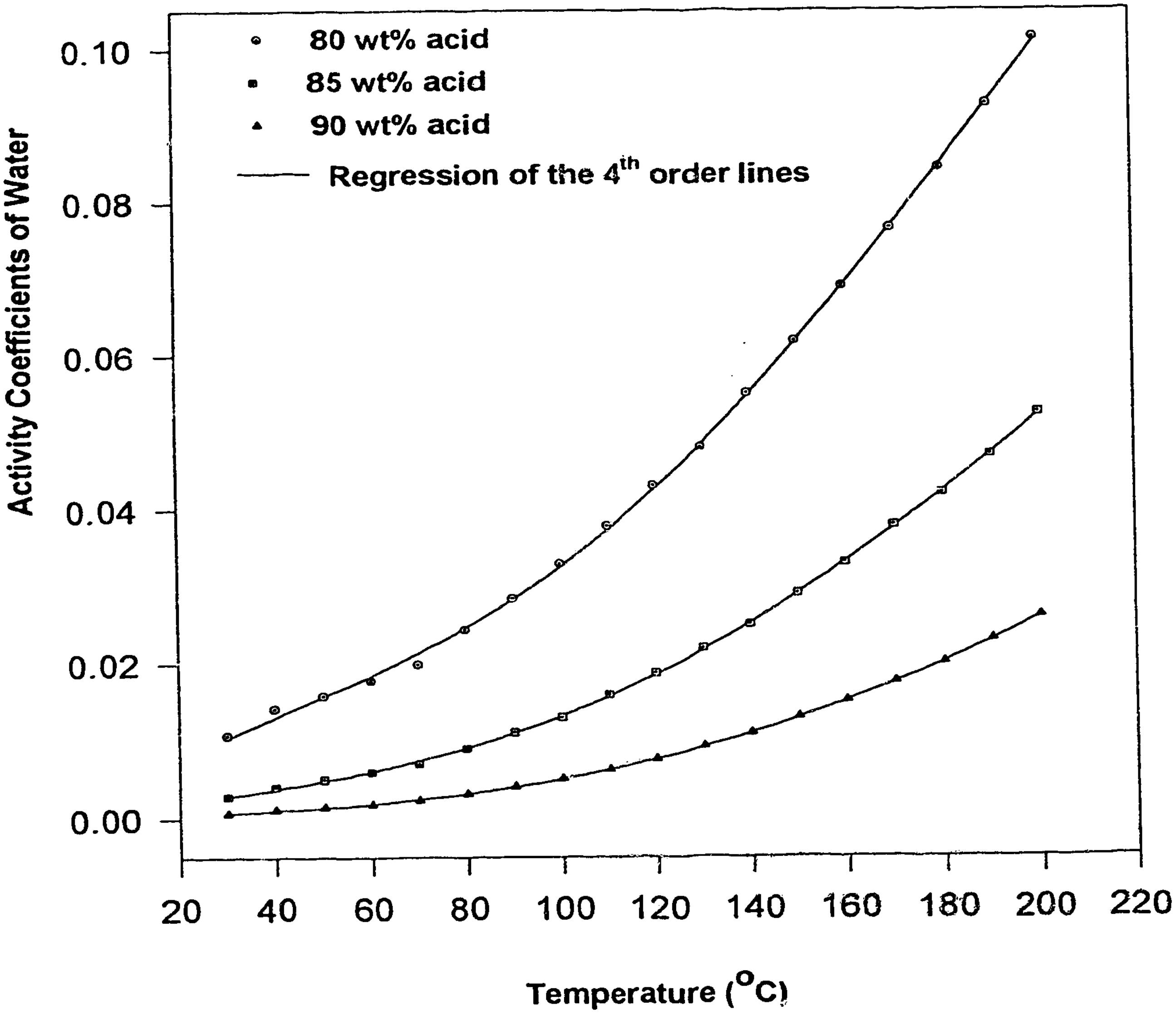


Figure 3.17 Activity coefficients of water vapor over sulfuric acid

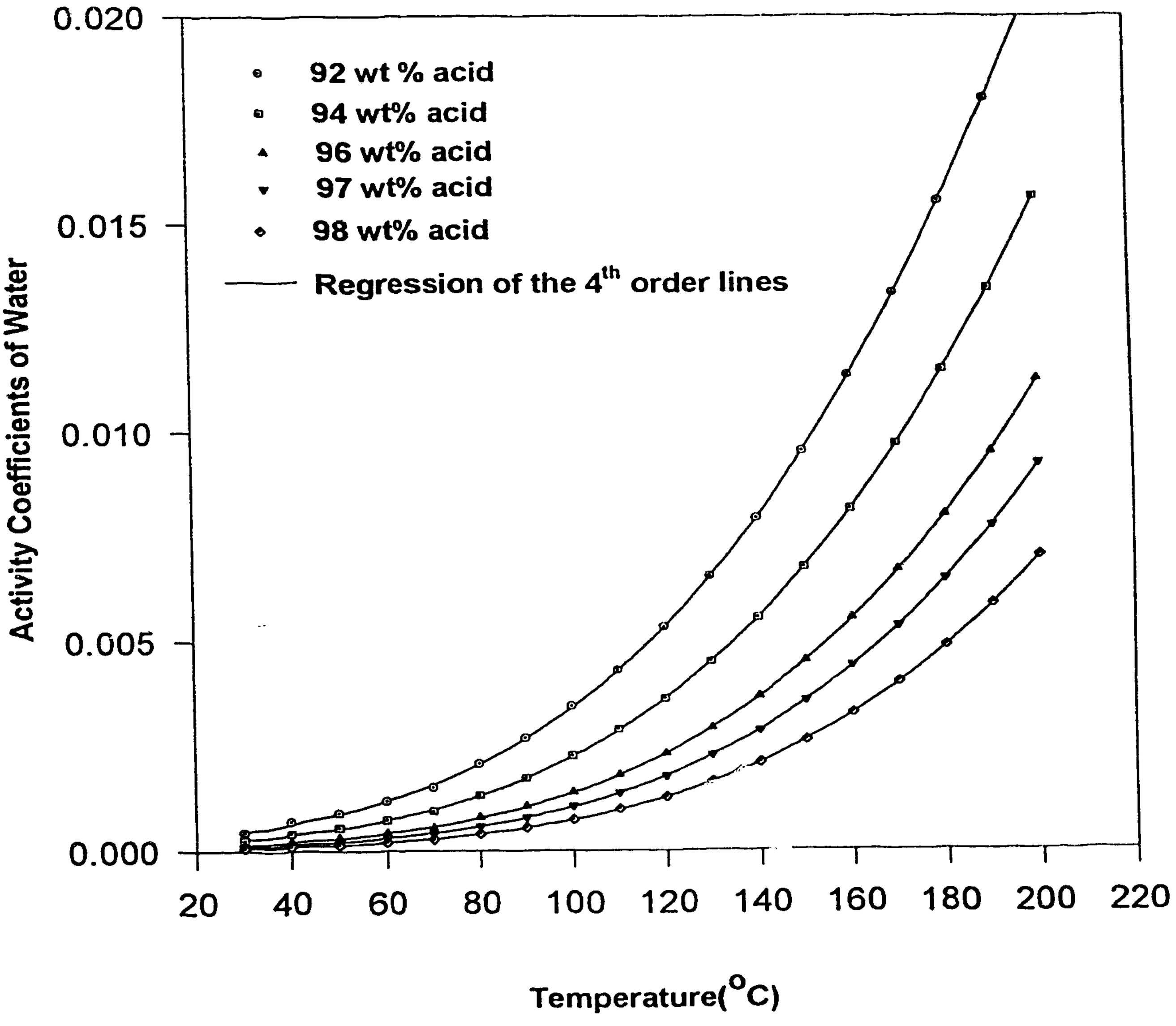


Figure 3.18 Activity coefficients of water vapor over sulfuric acid

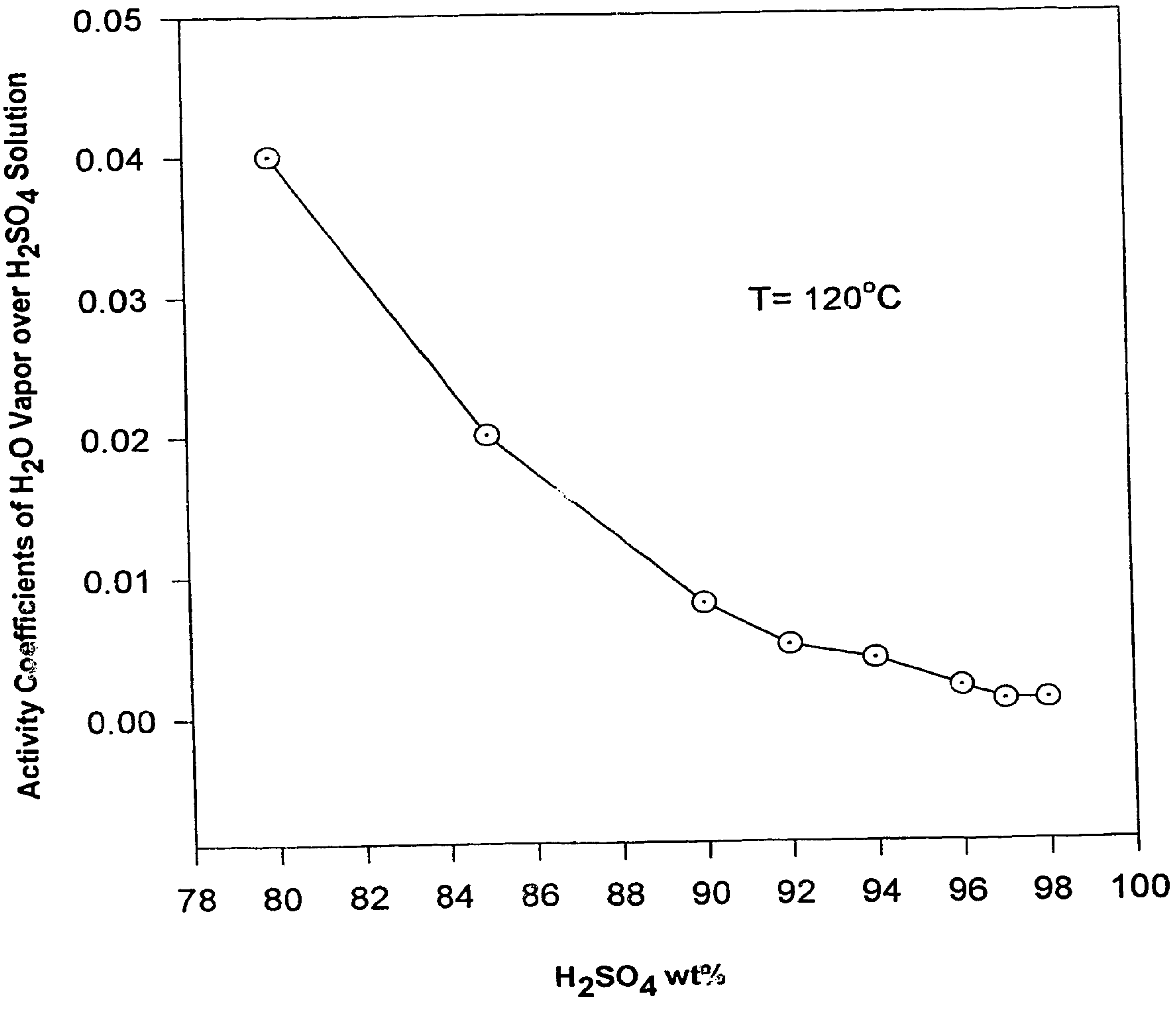


Figure 3.19 The variation in activity coefficient of H_2O vapor with H_2SO_4 concentration

with respect to acid vapor can be neglected.

It will be constructive to discuss the implications of the equilibrium results obtained, in conjunction with the experimental results. Hence this discussion of the thermodynamic calculations has been postponed to the results and discussion chapter.

The HSC equilibrium calculations performed have not been validated by manual equilibrium calulations. Also, the HSC calculation reliability has not been verified by comparing the HSC results with published experimental equilibrium results involving H_2SO_4.

Equilibrium calculations and their related simulation programs have basic limitations in that they deal only with end states. They do not take into account the kinetics of chemical reactions responsible for the changes. To simulate a chemical process without experiments will require a successful combination of thermodynamics, nonideal behavior of solutions, and the kinetics of the processes. To achieve the complete simulation of a single chemical process needs experiments, much time and computational power. Also, apart from the fact that the equilibrium picture cannot reflect the kinetic behavior of the process, the equilibrium calculations do not consider the intermediate complexes and their compositions. Various ions and complexes may possibly be present at equilibrium due to side reactions but, in the case of the H_2S-H_2SO_4 system, their existence has not been shown experimentally. This makes experimental verification of the process performance indispensable. The supplementary experimental studies involved are explained in the subsequent two chapters.

Chapter 4

Experimental Procedure

Thermochemical analysis carried out in the previous chapter for the H_2S - H_2SO_4 system predicted 100% H_2S conversion with zero SO_2 formation at high pressures and mild temperatures for acid concentrations below 90 wt%, as will be discussed in the subsequent chapter. Hence, this system holds a lot of industrial significance for acid gas sweetening. The process involving the reaction of H_2S with H_2SO_4 will be referred to as "Acid Contacting Process" in this thesis. These results combined with laboratory constraints gave us the feasible experimental variable ranges to work in. To realize the potential of this process, reliable and reproducible laboratory scale data in a flow contactor were required. The experiments were carried out with the following objectives in mind:

1. To collect reliable and reproducible data in a laboratory scale flow reactor.
2. To test the reactor performance by changing process variables one at a time.
3. To verify at the laboratory scale the zero emission of H_2S and SO_2.
4. To establish the stoichiometry of the reactions involved in this process as indicated by the HSC analysis.
5. To examine the kinetic behavior of this process.

4.1 Experimental setup

The flow diagram of the experimental system used is shown in Figure 4.1.

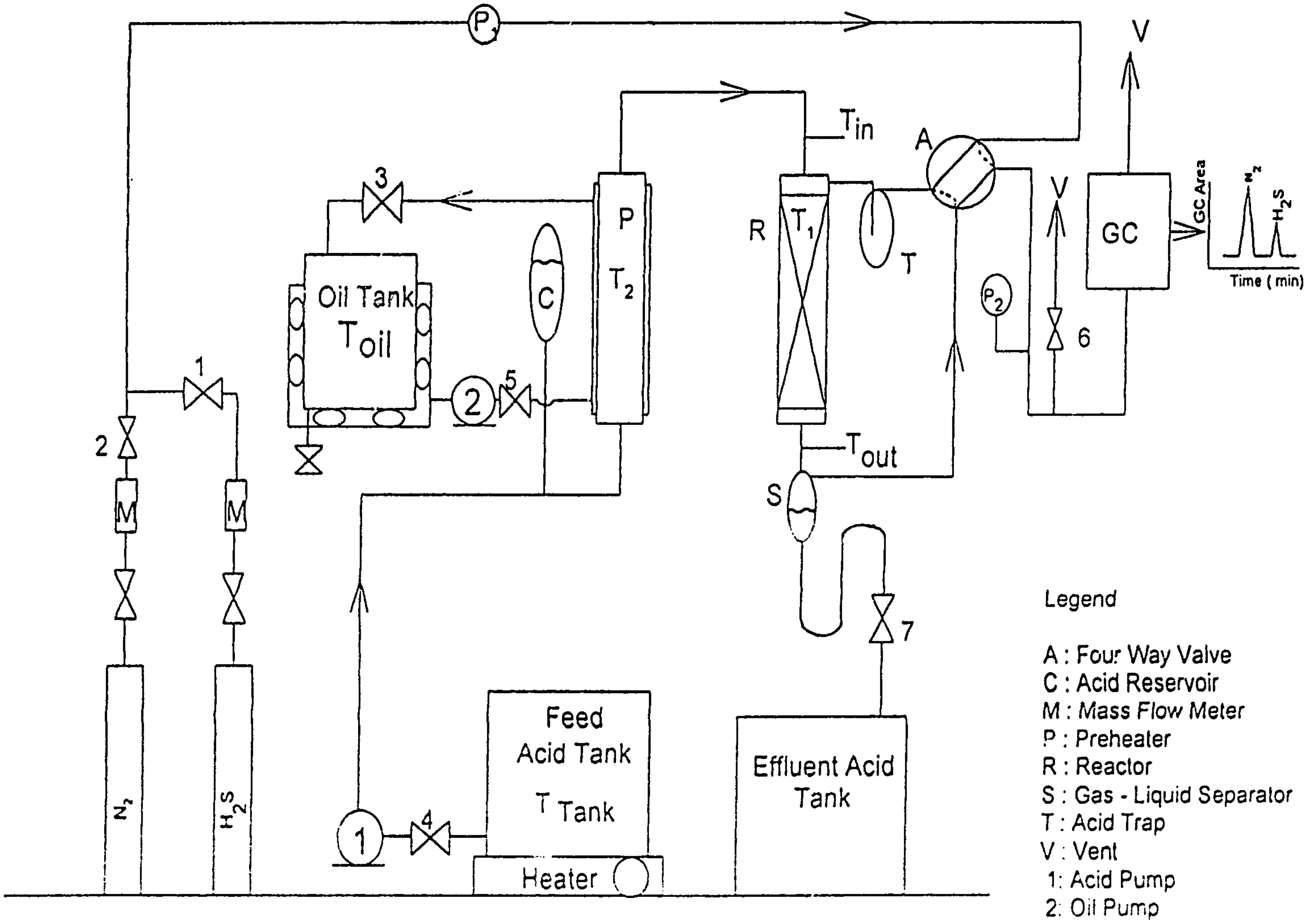


Figure 4.1 Schematic flow diagram of the acid contacting process

4.1.1 Equipment and chemicals

The principal process equipment used in the experiments included:

4.1.1.1 The reactor

The acid contacting process involves gas-liquid mass transfer with chemical reaction. In such a case a packed column may be used due to the available reliable technology. Packed columns provide excellent control of variables and good mass transfer rates by providing high interfacial areas. Liquid phase reactions that produce products that precipitate or evolve as gases are essentially irreversible. When mass transfer is accompanied by irreversible chemical reactions, cocurrent downflow packed columns do not limit the number of transfer units. In fact, they may be more advantageous than countercurrent packed columns due to the following reasons:

1. No upper limits on the gas or liquid flow rates arise due to the absence of flooding problems, resulting in higher throughputs.
2. The pressure drops are generally smaller. This can help reduce the pumping costs.
3. The interfacial areas are generally 15-20% higher than those in countercurrent packed columns. This means higher mass transfer rates.
4. As a result, the column size is usually smaller than that of the countercurrent one for the same service. This directly helps in reducing the capital costs.

Our system allowed us to use the benefits of cocurrent packed columns; and so, the experiments were carried out in a cocurrent downflow packed column. The glass column was constructed in a single piece to avoid leaks. The column packed height was 37 cm with an internal diameter of 1.5 cm. Packings used were Ceramic Raschig rings of 1/4 inch diameter. These packings provide good void fraction (0.73) and this helped prevent the sulfur plugging in the reactor. Since the column was quite small, a liquid distributor was not used. The column was jacketed and the heating (silicone) oil was circulated through the column jacket to maintain the desired column temperature.

4.1.1.2 The preheater

The preheater heated the acid, from the feed acid tank temperature to the reactor inlet temperature. It was required because the acid pump design temperature upper limit was 110°C. The preheater was made of glass and had no joints to prevent leaks. The hot silicone oil used as the heating medium passed on the shell side. The acid passed through the glass coil at the center of the shell cocurrently entering at the bottom. The preheater height was 53 cm, its diameter was 4.4 cm and the glass tube internal diameter was 1/4 inch. The glass coil diameter was 4 cm with 41 coil loops in the preheater.

4.1.1.3 Chemicals

The chemicals used in the experiments and analysis were,

1. Gases: N_2, H_2S, SO_2, calibrated SO_2 and N_2 mixture.
2. Liquids: 96 wt% H_2SO_4, distilled H_2O, standard NaOH solution (0.1 N) and silicone oil.

N_2 (prepurified, 99.99% pure) was provided by Praxair Canada Inc. Calibrated mixtures of H_2S in N_2 have a tendency to separate in the storage vessel with H_2S at the bottom and N_2 at the top due to their density difference, creating difficulties in maintaining a fixed feed gas composition. To eliminate this problem, the required feed gas mixtures containing H_2S were prepared in the laboratory by combining H_2S and N_2 from different cylinders. The H_2S (C. P. grade, 99.5 % pure) was provided by Matheson Gas Products Inc. The SO_2 required for calibration (anhydrous, 99.98 % pure) was provided by Linde. The gases were mixed to the desired proportion using calibrated mass flow meters. The gas flow rates were measured in sccm (sccm : standard cubic centimetre per minute, standard conditions imply 21°C and 1 atm). The formula used for calibration of the mass flow meters using the soap film meter is as follows.

$$P_1 v_1 / T_1 = (P_2 - P_o) v_2 / T_2 \qquad (15)$$

where, T_1 = 294.1K, P_1 = 1 atm, P_2 = room pressure, (atm), T_2 = room temperature (K), P_o= vapor pressure of water at room temperature, (atm), v_1 = standard gas flow rate (sccm), v_2 = gas flow rate at room conditions (ccm)

Sulfuric acid with a minimum assay of 96 to 98 wt% was supplied by Anachemia Canada Inc. Sulfuric acid of required concentration was prepared by adding the required amount of distilled H_2O.

Standard NaOH of 0.1 N stength used for titration of H_2SO_4 solutions was supplied by Fisher Scientific Co.

The silicone oil used for heating the acid from 100°C to the inlet temperature of the reactor while flowing through the preheater was supplied by Fisher Scientific Co.

4.1.1.4 Miscellaneous equipment

Additional equipment and control systems used in this setup were as follows:

1. An electric plate heater was used for heating to 100°C the batch of prepared acid to be used during the run. It was supplied by Fisher Scientific Co.
2. The pump used to circulate the silicone oil was supplied by Fluid Metering Inc. Its calibration is shown in Appendix C-1.
3. The control of the reactor temperatures and other process temperatures was done by the temperature control system supplied by Omron Corp.

4. The Teflon® diaphragm acid pump used for H_2SO_4 solution pumping was supplied by Cole-Parmer Instrument Co. (Model No. 7090-42). Its calibration is shown in Appendix C-2.
5. The mass flow meters and the mass flow controller used to regulate the gas flows were supplied by Sierra Instruments Inc. The calibration of the mass flow meters is shown in Appendices D-1 to D-3.
6. The pressure of the gas was measured both upstream and downstream using pressure gauges supplied by Wika Instruments Canada Ltd.
7. The pressure in the column was maintained constant using a pneumatic pressure control system supplied by Fisher Scientific Co.
8. The research control valve which acted as the control element in the pressure control loop was supplied by Badger Meter Inc. (Type 807, standard globe valve).

4.2 Process description

The prepared acid of known concentration to be used for an experimental run was stored in the 5 liter flask (Figure 4.1). It was heated up to 100°C on the electric plate heater. Additional heating of the acid was done in a preheater with cocurrent flowing hot silicone oil. The heating oil fed to the preheater was heated in a metal tank to 180°C using a electrical heating pad. The oil flow rate used was constant at 26 cc/min. The reactor and preheater were well insulated using fiber glass insulating sheets. The preheater was heated additionally with heating tapes. The packed column (reactor) was also heated with heating tapes for temperature control, primarily to replace heat losses. The acid outlet of the preheater and the acid inlet of the packed column were very close to avoid heat losses. Temperatures monitored were those at the inlet and outlet of the reactor (T_{in} and T_{out}, respectively), in the acid tank (T_{Tank}), and the external walls of the reactor and the preheater (T_1 and T_2, respectively). Temperatures were monitored using calibrated thermocouples. All acid contacting equipment was made of Teflon® and the acid flow lines were insulated using fiber glass sheets. An online acid reservoir was installed to provide acid to the reactor in between the pump strokes and to smoothen the acid flow. The gases were mixed to the desired composition by using mass flow meters and controllers before being fed to the column. The pressure in the column was maintained constant using the pneumatic pressure control system. To prevent the backflow of acid into the feed gas lines, backflow arresters were used. The same technique was used to prevent the acid going into the gas chromatograph equipment.

The gas mixture was directed to the column or to the GC for analysis, by using a four way valve. The mode in which the gas passed directly to the GC, without passing through the column was termed the bypass mode. The valve was in bypass mode when calibrating the GC or taking the feed gas blank analysis runs. The reaction product gas going to the GC for the analysis was stripped of condensed water using a water trap. As is known, H_2S and SO_2 react over water to form sulfur. Hence this measure prevented errors in gas composition calculations and also prevented possible sulfur plugging of GC lines. Gas flows were checked by using a soap film meter at the exhaust end of the GC. The acid gas mixture coming out of the reactor was separated in the gas-liquid separator. The gas was sent to the GC for analysis and then to the vent. The acid -sulfur slurry was collected in an effluent acid tank.

Apart from the fact that laboratory handling of hot, concentrated H_2SO_4 in a continuous flow manner is extremely hazardous, a number of problems were encountered and solved in running the process.

4.2.1 Problems encountered in the experiments

In determining the spent acid concentrations, the separation of sulfur from the acid by vacuum separation and the measurement of specific gravity of the resulting filtrate acid was extremely time consuming and the end results were not reliable. Hence the calculations and results were based, primarily, on the gas phase compositions. Thus obtaining excellent reproducible GC data was essential for the success of the experiments. To ensure steady-state experimental data constant inlet and outlet reactor temperatures, process pressure, and gas and liquid flow rates as well as constant flow regime in the reactor were required. The continuous observation and control of these variables by a single operator required composure and skill. The run time, typically of about 80 minutes, made it imperative to use the time efficiently to obtain several GC sample injections. The typical elution time for the last GC peak was 4.5 minutes. A number of GC injections were made and at the end of the run, they were analyzed to check for steady-state behavior. Only those observations with constant H_2S/N_2 and SO_2/N_2 were used for further calculations.

During previous studies, many errors were introduced due to a lack of steady-state operation during the experiments. Previously, the T_{in} and T_{out} differed by as much as 10°C in an individual run. Also, the pressure fluctuated by ± 2 psig about the set pressure of 5 psig. The flow rates were also not properly measured and controlled. The difference in temperatures was brought down to ±1°C around the set temperature. Also the pressure was not allowed to change. This was made possible by improving the control mechanism and proper online manual monitoring. The gas flow characteristics of the mass flow meters and acid flow characteristics of the acid pump were calibrated. The temperatures were monitored and controlled. To ensure a constant flow regime in the reactor, the acid flow rate was smoothened by adding an online acid reservoir which " breathed" acid in between the acid pump strokes and acted as a pulsation dampner.

4.3 About the experimental process variables

The HSC calculations showed that to achieve zero emission, the temperature should be low and pressure should be high. The reactions give sulfur as one of the products. To avoid plugging problems, the temperature desired was maintained above the melting point of sulfur. Also, above 150°C, the viscosity of sulfur rises sharply as seen from the Table 2.5. The thermodynamic simulations showed that above 150°C, the conditions favor formation of SO_2 rather than sulfur. This is obviously undesirable. Hence the experiments were restricted to temperatures below 150°C. Since the operations could be hazardous with the use of hot concentrated H_2SO_4 in a continuous flow system, the pressure in the system was kept slightly above ambient (5 psig).

The effects of temperature, gas and liquid contact times and gas and liquid compositions on the H_2S conversion and SO_2 formation were determined. Each parameter was varied while keeping the others constant. The effect of contact time was observed by changing gas flow rate while keeping the acid flow rate constant and vice versa, such that the G/L volumetric (sccm/ccm) ratio remained constant. The G/L ratios tried were 2.73, 1.97 and 1.37. The gas flow rate was varied between 100 and 200 sccm, the acid flow rate was varied between 50 and 100 cc/min. The upper and lower limits of the flow rates were decided by the equipment limitation and safety considerations. The inlet H_2S concentration was varied between 2 and 9 mole percent. Acid concentrations were varied between 80 wt% and 96 wt%. Below 80 wt% acid concentrations were not tried as the H_2S conversions fell to very low values and water removal did not prove effective. Also, concentrations below 80 wt% are undesirable due to the very high corrosiveness of the acid, as can be seen from Figure 2.9.

4.4 Experimental procedure

It was important to follow not only the experimental procedure carefully but also the start up and shut down procedures due to the inherent safety issues involved.

4.4.1 Start up

The following steps were always followed before each experimental run to collect reliable data:

1. Acid of particular concentration was prepared in sufficient amount that it would last for the duration of the experimental set of runs. Silicone oil was always heated to the preset value (180°C) in the metal tank.

2. The feed acid tank was heated to 100°C. The temperatures of the preheater, packed column and oil were brought to steady preset temperatures by electrical heating.

3. Then the oil flow through the system was started by opening valve 5 and starting the pump 2.

4. The system was checked for possible gas leaks.

5. It was necessary that gas lines were completely dry, otherwise H_2S and SO_2 may react outside the reactor, in the gas lines.

6. Nitrogen was passed through the entire system in bypass mode to dry and clean all gas lines. This step was carried before and after the experimental run.

7. The four way valve, A, was checked for possible plugging and cleaned.

4.4.2 During the experimental runs

The following steps were always followed during each experimental run:

1. Required amount of nitrogen was made to flow through the packed column by adjusting valve 2 and the four way valve, A (Figure 4.1). The drain valve 7 was kept closed.

2. The valve 4 was opened and the acid pump, 1, was started.

3. Once acid started coming out of the column and attained sufficient level in the gas-liquid separator, valve 7 was opened. The H_2S flow was started in required quantity by opening valve 1.

4. T_{in} and T_{out} were adjusted within ± 1° C of the required value. T_1, T_2 and T_{Tank} were monitored through out the run.

5. The pressure of the system was steadied. The gas suffered negligible pressure drop in the packed column as was observed from the upstream and downstream pressures P_1 and P_2.

6. The acid in the gas-liquid separator was brought to a steady level.

7. After the system achieved steady state with respect to the various variables, the outlet gas was analyzed using the GC.

8. The experiment was continued until enough consecutive GC readings showed steady and constant analysis of the exhaust gas or till the acid lasted, whichever came first.

9. Throughout the experiment, the variables were checked constantly to maintain steady operation.

10. Experimental runs were repeated to verify the data reliability.

A typical run lasted for about 80 min. After each run, the GC was calibrated with all gases that showed up on the chromatograph. The acid concentration was analyzed by titration. The data were entered into the datasheet. A sample datasheet is in the Appendix E. For all the runs the ambient pressure and temperature were recorded. The data used for calculations was only the steady state data. The rest of the GC readings were not considered. Raw data and processed data are shown in Appendices, F and G, respectively. The data representation insists on reproducibility and consistency which is manifested through the GC area ratios and outlet mole percentages in Appendix G.

4.4.3 Shut down

The following steps were always followed after each experimental run:

1. Acid pump 1 was switched off and valve 4 was closed.
2. Valve 1 was closed and H_2S mass flow meter was set to zero to stop the H_2S flow. N_2 flow was kept on.
3. All acid was let out of the system into the effluent acid tank.
4. System pressure was brought to ambient.
5. Once all acid got into the effluent acid tank, valve A, was adjusted to the bypass mode. All GC lines were dried.
6. T_1, T_2, and T_{Tank} were brought to ambient temperature level.

4.5 Safety precautions

Since the system was hazardous, the following precautions were always taken:

1. The exhaust fan over the experimental setup was switched on during the run to remove the gases and vapors released.
2. The H_2S and SO_2 gas cylinders were always placed under the exhaust hood.
3. To prevent acid burns a coverall supplied by Fisher Scientific Co. was used during the experiments.
4. Acid resistant rubber shoes, neoprene gloves and face shield were used.
5. A glass partition separated the operator and the main experimental setup.
6. Any H_2S leaks were monitored by the H_2S detector supplied by Bacharach Instrument Co. Its detection sensitivity is 10 ppm H_2S.
7. Ample water and a suitable base were kept handy in case of acid spills or leaks.
8. A chemical burn first aid station, supplied by Fisher Scientific Co., was also kept handy.

4.6 The chemical preparation and analysis methods

4.6.1 Gas analysis

The inlet and outlet gas was analyzed using the laboratory gas chromatograph. Its specifications are listed below.

1. GAS CHROMATOGRAPH:

Supplier: GOW MAC Instrument Co., Model 24 -150
Detector Type: Thermal conductivity type
Carrier Gas : Helium, flow rate = 30 cc/min
Oven Temperature: 120°C
Detector Temperature: 135°C

2. GC COLUMN :

To maximize the number of GC injections for a limited run time, a GC column that could separate the components N_2, H_2S, H_2O and SO_2 relatively quickly was required. After consulting the suppliers, the following column was found to meet the criteria:

Supplier: Supelco Canada Ltd.
Column Type: HayeSep DB SS column, 100/120 mesh, 10'x1/8'

The GC parameters were tuned to get the best performance. The typical time required for a complete GC analysis after injection of sample was 4.5 minutes with the GC conditions specified above.

3. INTEGRATOR:

Supplier: Hewlett Packard, model HP 3396 A

The method used for converting GC areas to mole percent was the area percent method. This method takes care of the common errors of the GC detector as the measurement is relative to the calibration of the GC. The GC calibration for SO_2 was obtained using a known gas mixture of SO_2 and N_2; whereas, in the case of H_2S the calibration mixture was prepared by mixing pure H_2S and pure N_2 to the desired extent. Calibration for water vapor was done by saturating the N_2 gas stream with water. All calibrations were done at 5 psig pressure. The analysis of the feed gas by the GC is called the blank test. A sample GC output for the product gas and the feed gas mixture is shown in Figures 4.2 and 4.3. As can be seen the total time of analysis is only about 5 minutes. The small amount of overlap between the H_2S and H_2O peaks was minimized by setting the GC conditions and integrator conditions properly. Moreover, the overlap poses no problem for acid concentrations above 88 wt%, because the acid becomes sufficiently hygroscopic that water vapor is limited. As can also be observed from the gas chromatograph, the peaks for all gases except SO_2 are sharp but the SO_2 peak tails. The later is due to strong adsorption of SO_2 on the GC column packings and the relatively small difference between the thermal conductivities of SO_2 and the carrier gas He.

With the available GC system and optimized operating parameters, the following detection limits for the various components were attained.

1. H_2S: 0.04 mole percent (400 ppm)
2. SO_2: 0.3 mole percent (3000 ppm)
3. H_2O: 0.3 mole percent (3000 ppm)

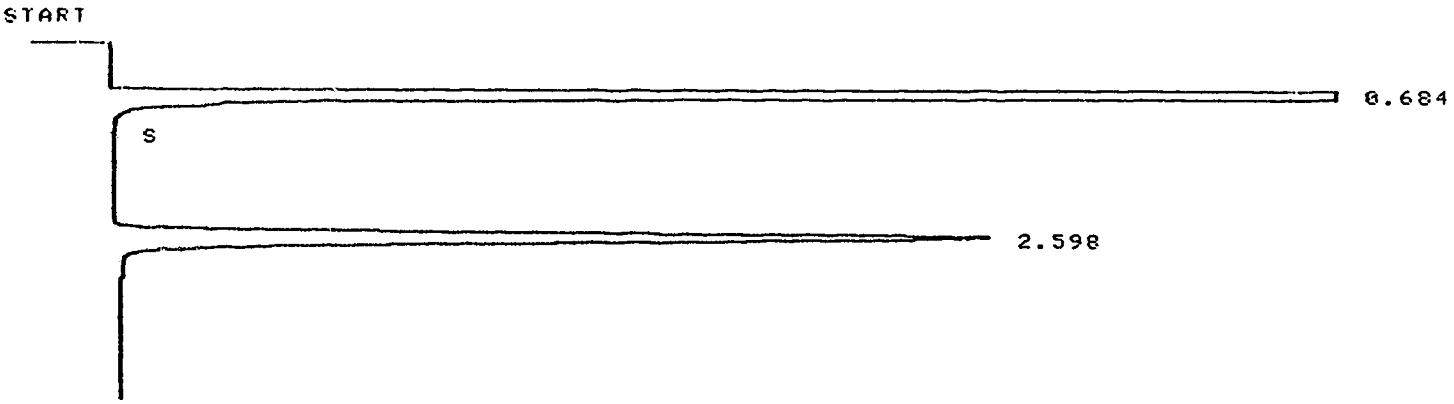


Figure 4.2 GC analysis of the feed gas mixture of H_2S and N_2

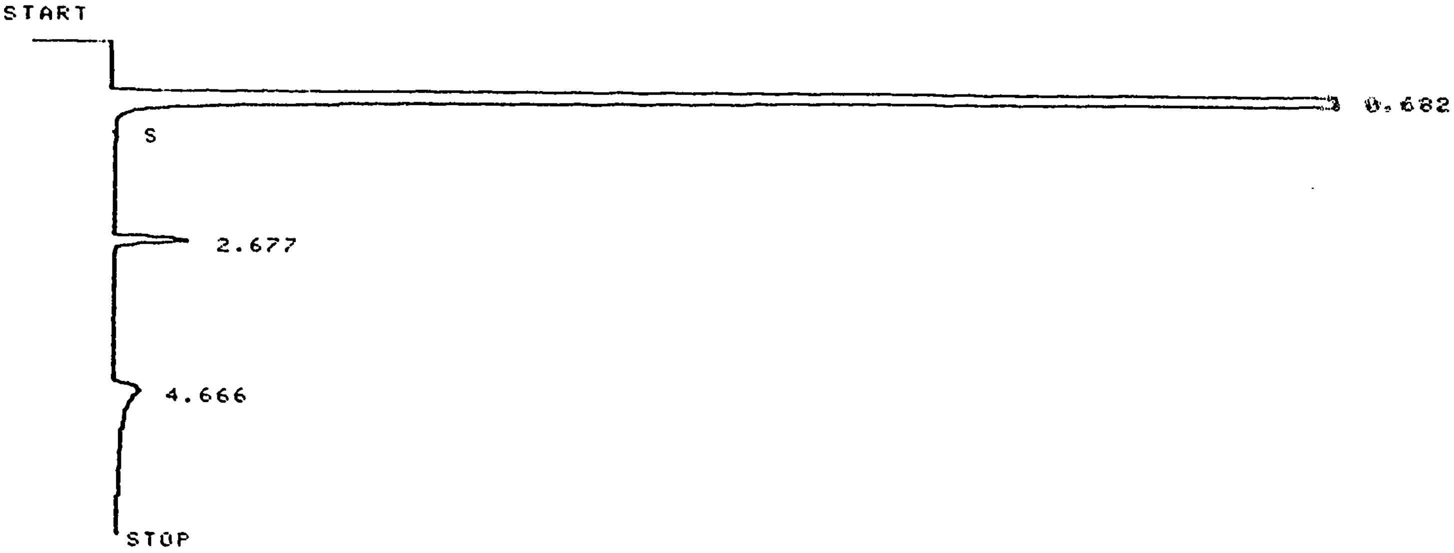


Figure 4.3 GC analysis of the product gas

4.6.1.1 Calculations

The formulae used for calculating mole percent of various gases in the exhaust are as follows:

$R.F._x = CMP_x / CGCA_x$ (16)

$MP_x = (GCA_x * R.F._x)*100 / (\Sigma\ GCA_x * R.F._x)$ (17)

where,

$R.F._x$ = Response factor of the gas x
CMP_x= The calibrated gas mole percent of gas component x used during the GC calibration
$CGCA_x$= The GC area of the gas x during calibration run
MP_x= Mole percent of the component x in the gas mixture tested (product or feed)
GCA_x= GC area of the component x in the gas mixture tested (product or feed)
$\Sigma\ GCA_x * R.F._x$ = The summation of the product of individual GC area and response factor for all gases in the gas mixture tested (product or feed)

4.6.2 Acid analysis

The feedstock H_2SO_4 concentration was analyzed by a hydrometer supplied by Cole - Parmer Instrument Co. and by titration using a standard 0.1 N NaOH solution. The accuracy of the acid concentration determined was within the first decimal point. An acid of specific desired concentration was prepared batchwise at room temperature. For the preparation of acid of such a specific concentration, calculated amounts of distilled water and feedstock acid were added to a flask of 5 liter capacity. The relevant calculations are as follows:

4.6.2.1 Preparation of 85 wt% H_2SO_4

Total final acid volume of the prepared acid = 5 liter

Acid concentration of the feedstock acid = 96.0 wt%

Specific gravities of the 96.0 wt% and 85.0 wt% H_2SO_4 at 20°C are = 1.8355 and 1.7786, respectively (Perry et al., 1984)

If , X = Volume of feedstock acid required in liter,

Y = Volume of distilled water required in liter, then

X+Y= 5 liter ....(18) and

0.85 = X*1.8355*0.96/ (X*1.8355 + Y).....................(19)

Solving these two equations

Feed stock acid required, X= 4.04 liter

Distilled water required, Y= 5-X = 0.96 liter

The prepared acid concentration was checked using the hydrometer and was analyzed by titration with standard NaOH. The indicator used was methyl orange, since H_2SO_4 is a strong acid and NaOH is a strong base. The endpoint of the titration is detected by a change in color of the solution in the flask from red to yellow. The NaOH volume was measured with a burette. The procedure for acid concentration analysis by titration and the sample calculation is as follows.

4.6.2.2 Acid titration procedure

1. Sample of acid taken = x gram
2. Make its volume to 1 liter with distilled water. Mix it well.
3. Pipette out 50 cc of the solution V_{H2SO4}. Add to clean conical flask. Add two drops of methyl orange indicator. Solution becomes red.
4. Titrate against standard 0.1 N NaOH (N_{NaOH}) from the burette.

5. Stop when last drop of NaOH just changes the color to yellow. Stir the flask to make sure that whole solution is yellow.

6. Measure amount of NaOH added . Repeat twice and take average of the NaOH required (V_{NaOH}).

4.6.2.3 Acid concentration calculation from titration

The reaction occurring during the titration is

$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2\ H_2O$..............................(20)

Usual titration equation is

$N_{H2SO4}*V_{H2SO4}= N_{NaOH}*V_{NaOH}$ (20)

Hence $N_{H2SO4} = N_{NaOH}*V_{NaOH}/V_{H2SO4} = m$ (21)

So total grams of H_2SO_4 present in 50 cc solution, n = m*98.08/2, since the molecular weight of H_2SO_4 = 98.08 g/gmole and its equivalent weight is half the molecular weight.

Hence, Total amount of H_2SO_4 present in original sample taken, o = n*1000/50 gram (22)

Hence the acid concentration in wt% = (o/x)*100 (23)

The prepared acid concentration matched the desired concentration intended in all the cases. Hence it can be concluded that the volumes of water and H_2SO_4 are additive.

With the experimental setup and the background explained, results and discussions are presented in the next chapter.

Chapter 5

Results and Discussion

Now the discussion of the experimental and equilibrium results will be presented. In each subsection of this chapter the results obtained from both the experiments and equilibrium calculations are discussed.

5.1 General discussion about the performance of the acid contacting process

The reaction equation option in the HSC predicted results as summarized in Table 3.1. These results show that:

1. Hydrogen sulfide can react with both H_2SO_4 and H_2SO_4(a) to form sulfur or sulfur and SO_2 mixture.
2. Sulfur dioxide in either gas or aqueous phase can react with H_2S to form sulfur.
3. Sulfur can not be oxidized by dilute H_2SO_4 to form SO_2, but may react with concentrated H_2SO_4.

First, thermodynamic analysis verifies the feasibility of recovering sulfur by the acid contacting process. Figure 3.9 indicated that all reactions are feasible below 150°C except reactions (9) and (10). Thus, SO_2 production is highly favored only at elevated temperatures. This undesirable condition, where sulfur recovery may not be complete, can be avoided by using relatively dilute H_2SO_4 at low temperatures. Figures 5.1 to 5.7 show the influence of H_2SO_4 concentration, temperature, pressure, and feed gas composition, respectively, on H_2S conversion and SO_2 formation in the tail gas as calculated by the program at equilibrium. The H_2S conversion was always observed to be complete for all sets. These Figures show, according to Le Chatelier's principle, that an increase in temperature results in more SO_2 formation. This suggests that SO_2 is generated in an endothermic reaction and/or is consumed in an exothermic reaction. Higher pressures favor decrease in or elimination of SO_2 formation. The inverse dependence of SO_2 formation on pressure indicates that SO_2 is formed in a reaction associated with a volume increase and/or it is consumed in a reaction associated with a decrease in volume. The effect of acid concentration on H_2S conversion and SO_2 formation shows that an increase in acid concentration increases the SO_2 formation and that the rate of reaction between H_2SO_4 and H_2S increases which produces more SO_2. The same conclusion can be drawn from the effect of inlet gas composition on SO_2 formation because increase in gas phase H_2S composition increases its liquid phase concentration thus increasing the rate of reaction between H_2SO_4 and H_2S.

This analysis verifies that the recovery of sulfur from acid gases by reaction with H_2SO_4 and the conversion of H_2S in the acid gas into sulfur completely, without production of SO_2 should be feasible. These observations are the basis for a new one-step route to zero H_2S emission sulfur recovery. For complete sulfur recovery the following overall reaction must take place.

$$3\ H_2S + H_2SO_4 = 4\ S + 4\ H_2O \qquad \text{...(6)}$$

Correspondingly, temperatures used should be less than 150°C, the system pressure used should be high and the acid concentration should preferably be less than 90 wt%. These conclusions provide the basis for planning of the experiments.

As predicted by the HSC program, contact of H_2S with concentrated H_2SO_4 resulted in formation of sulfur during the experiments. The sulfur produced in this process gave a suspension of yellow colloidal sulfur in the effluent H_2SO_4 when cooled below 120°C. The experimental results of the parametric studies on the performance of the process are shown in Figures 5.8 to 5.24. Similar data in different sets seem to agree with each other. The SO_2 formation corresponding to Figure 5.20 is always zero and so, a plot is not necessary to represent it. The Figures show error bars and the reproducibility of the data. The trends in the data will be explained in the subsequent section.

The conclusions drawn from equilibrium calculations regarding optimization of the parameters for zero H_2S and SO_2 emission are confirmed by the experimental data. The experimental results, for example, those for the effect of feed gas composition on H_2S conversion and SO_2 formation as seen in Figure 5.20 and Figures 5.18 and 5.19 for G/L = 1.37, show that zero SO_2 production and 100% H_2S conversion is possible in the laboratory even within a small contact time of the order of at the most a minute on the liquid side and half a minute on the gas side. This fact boosts the potential of the acid contacting process application in industry for sour gas sweetening.

5.2 Identification of the possible reactions

As observed from the literature, there is an ambiguity regarding the exact reactions occurring in the acid contacting process. To decide the exact stoichiometry, all possible reactions available in the literature were taken into account. These can be summarized as follows:

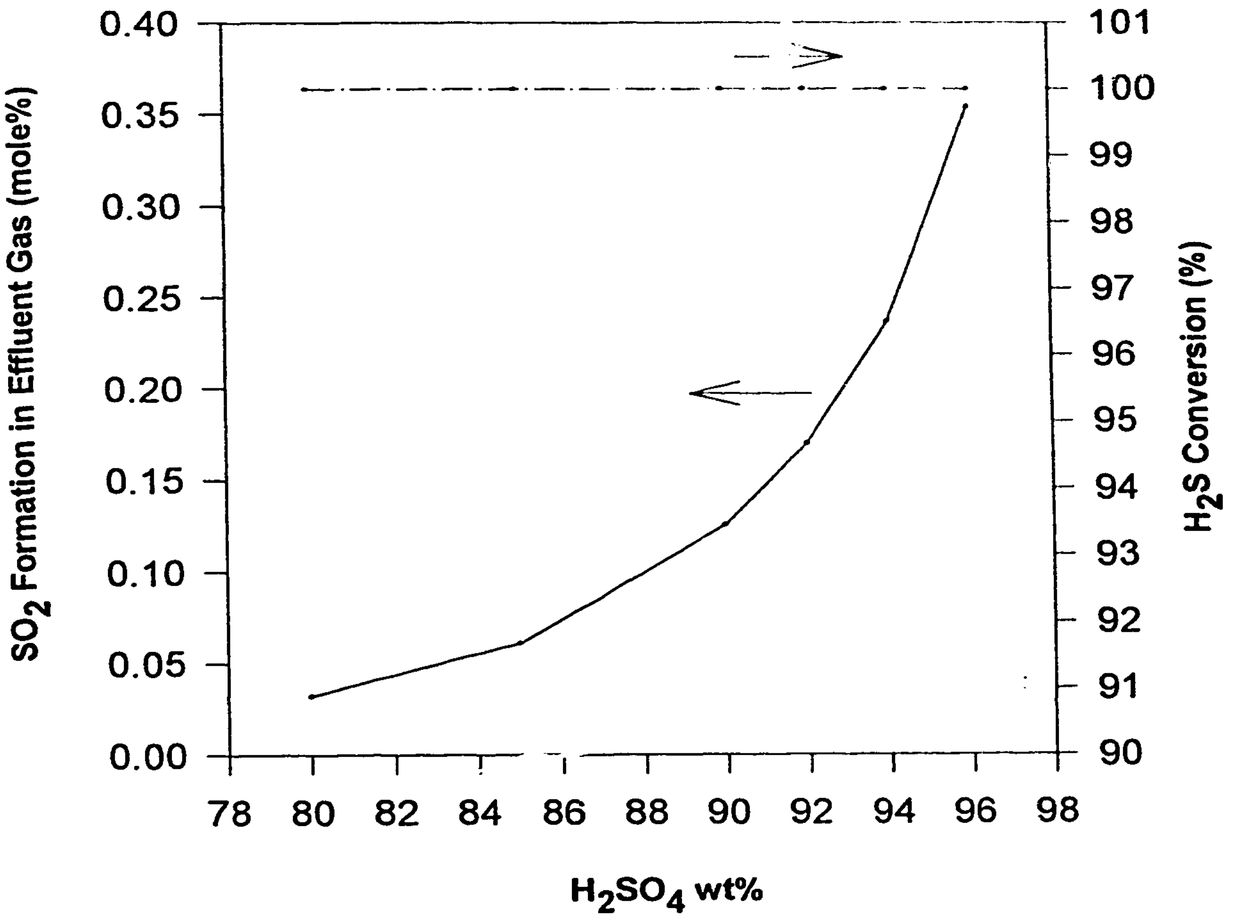
$3\ H_2S + H_2SO_4 = S + 4\ H_2O$ ....(6)

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$ ....(7)

$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$ ....(8)

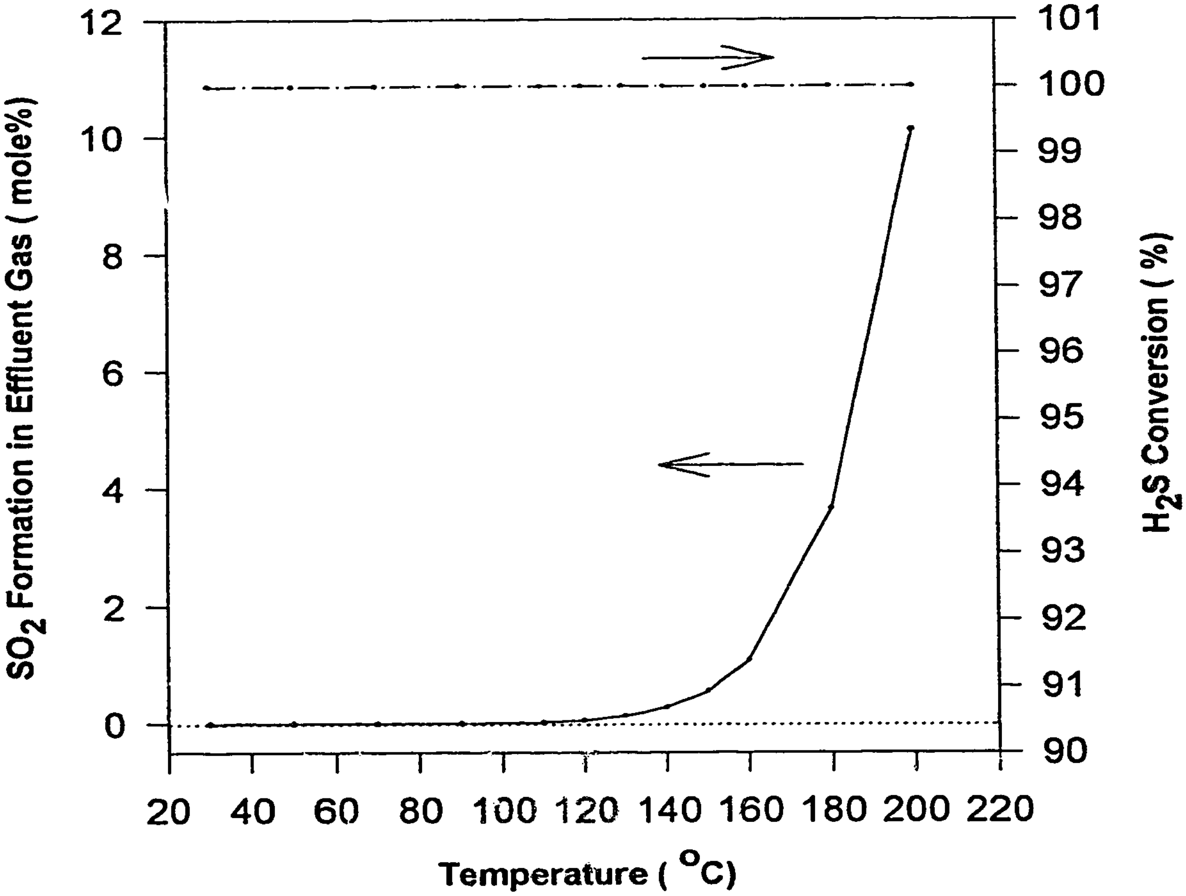
$S + 2\ H_2SO_4 = 3\ SO_2 + 2\ H_2O$ ....(9)

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$ ....(10)



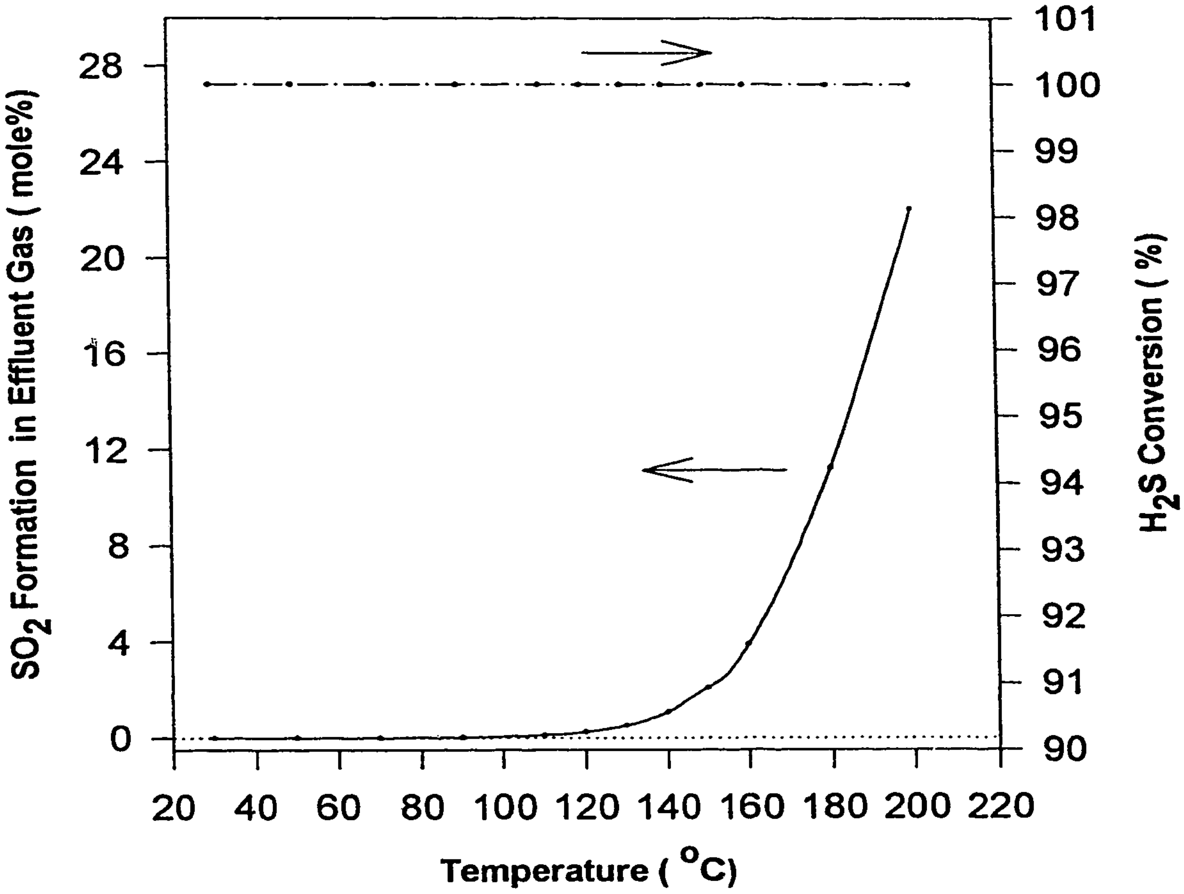
P = 5 psig, T = 120^{0}C, Feed H_2S Concentration = 9 mole%

Figure 5.1 Effect of H_2SO_4 concentration on equilibrium H_2S conversion and SO_2 formation



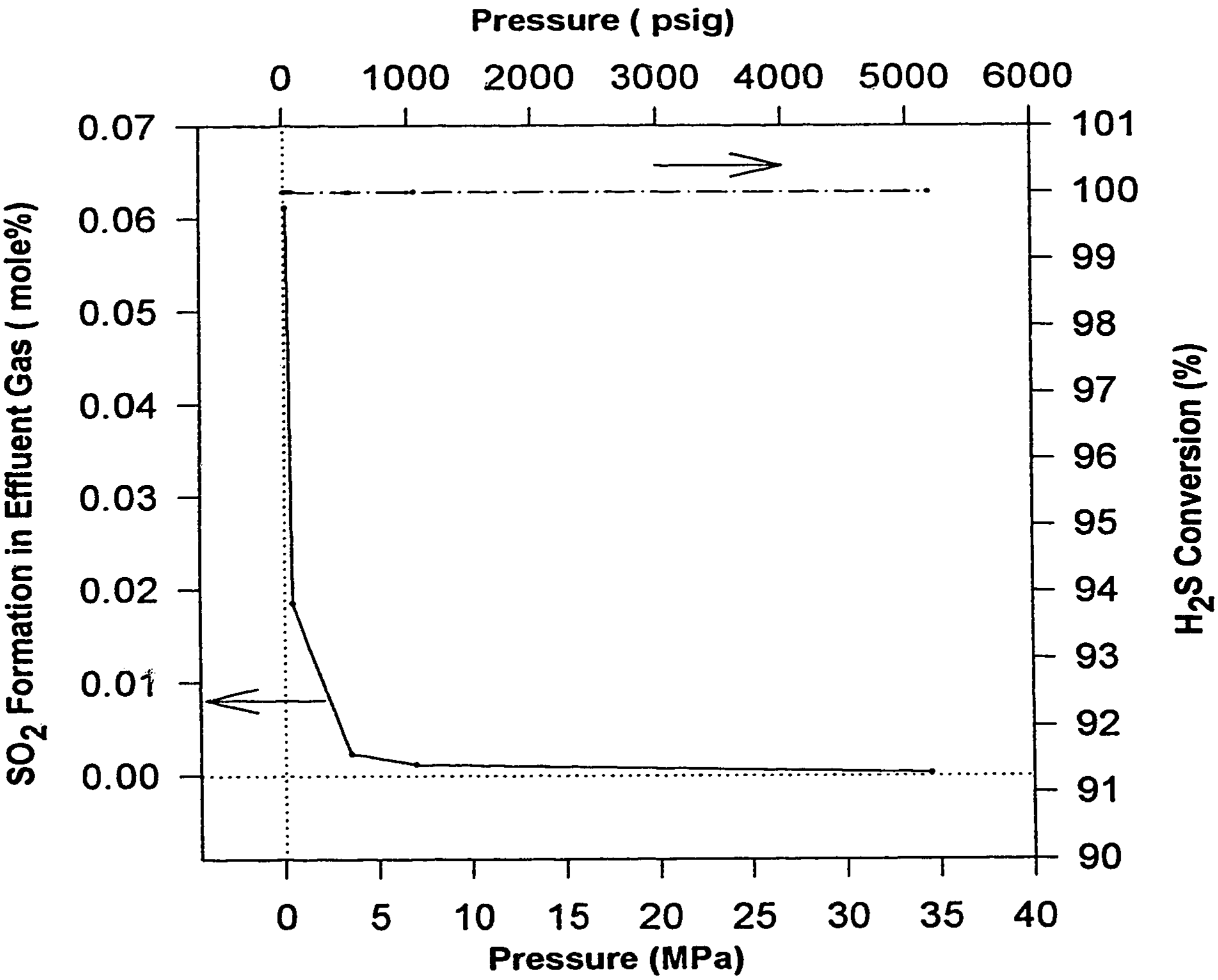
P = 5 psig, H_2SO_4 Concentration = 85 wt%, Feed H_2S Concentration = 9 mole%

Figure 5.2 Effect of temperature on equilibrium H_2S conversion and SO_2 formation



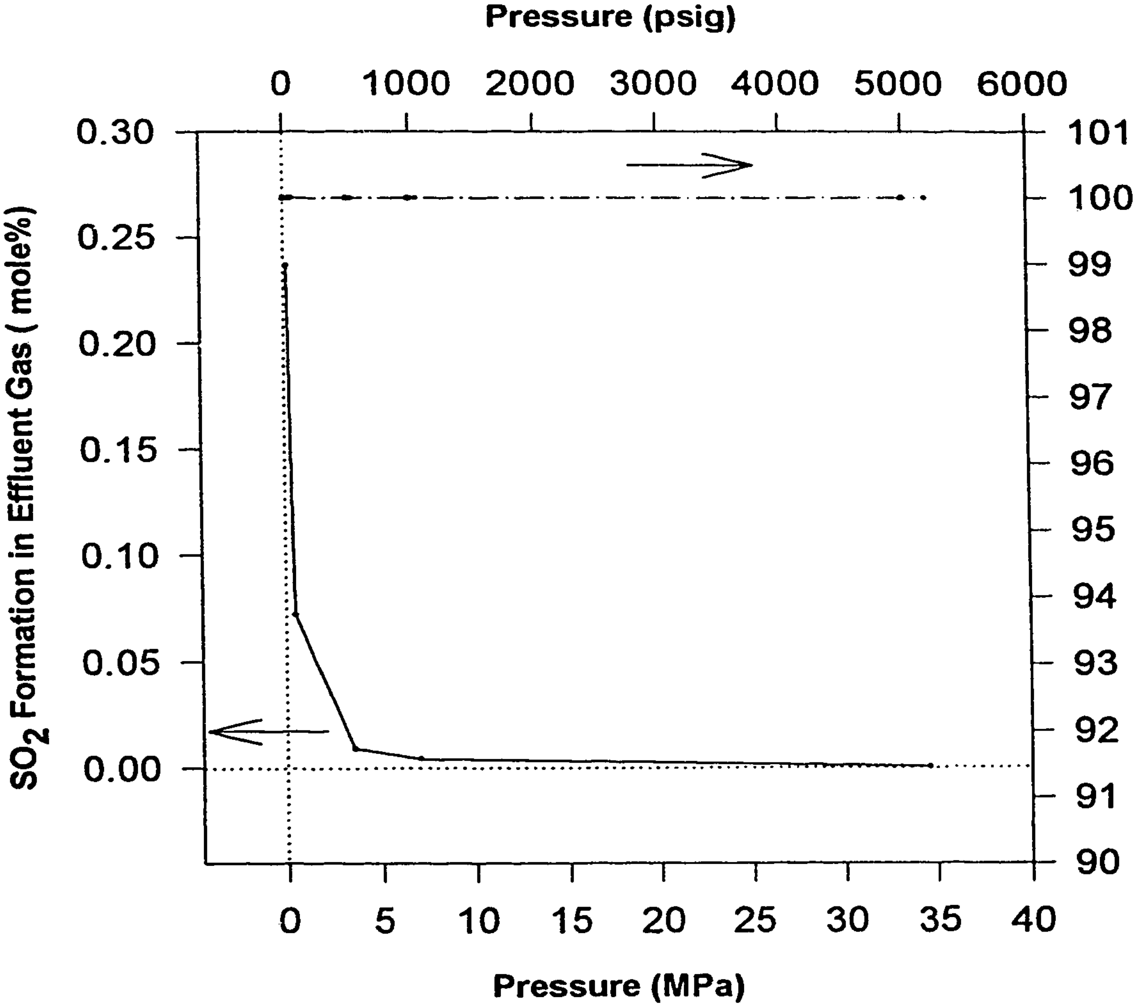
P = 5 psig, H_2SO_4 Concentration = 94 wt%, Feed H_2S Concentration = 9 mole%

Figure 5.3 Effect of temperature on equilibrium H_2S conversion and SO_2 formation



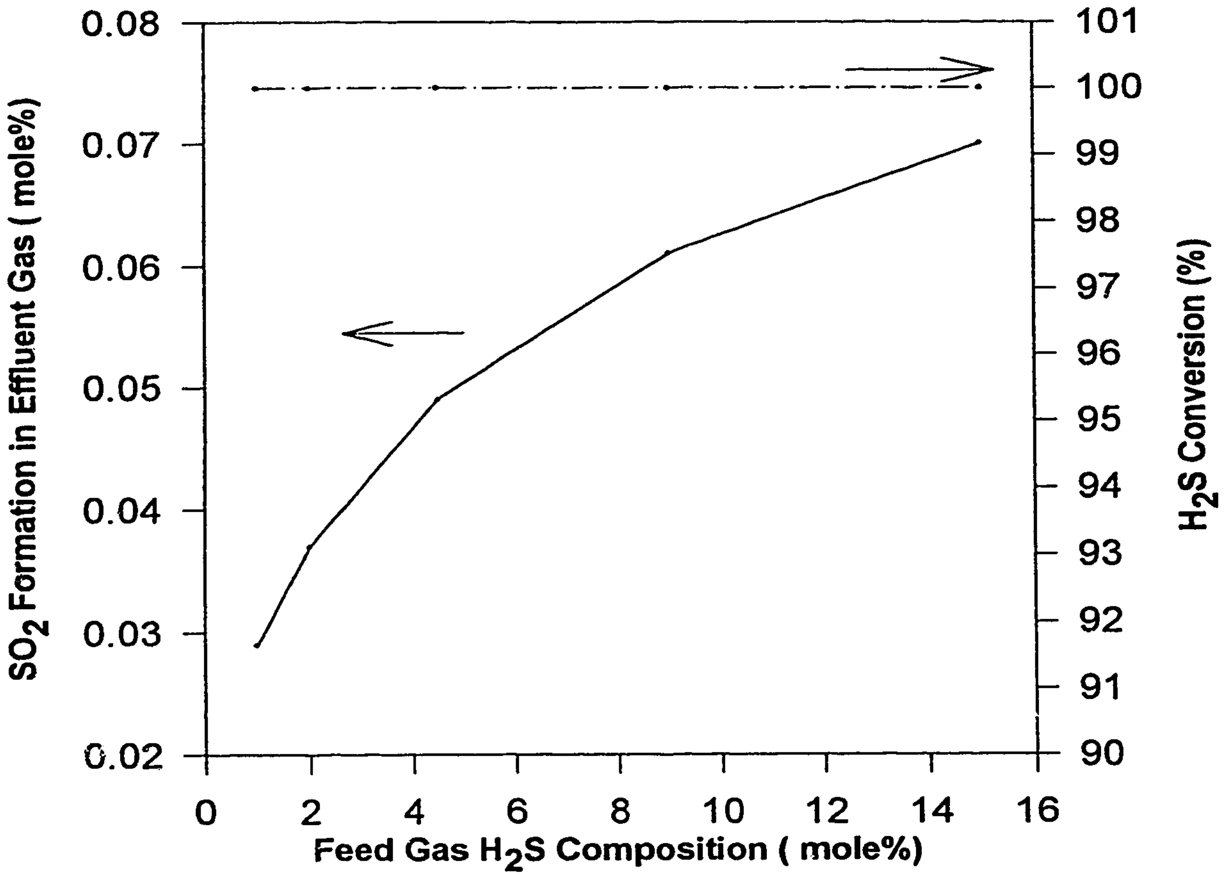
T = 120°C, H_2SO_4 Conc. = 85 wt%, Feed H_2S Concentration = 9 mole%

Figure 5.4 Effect of pressure on equilibrium H_2S conversion and SO_2 formation



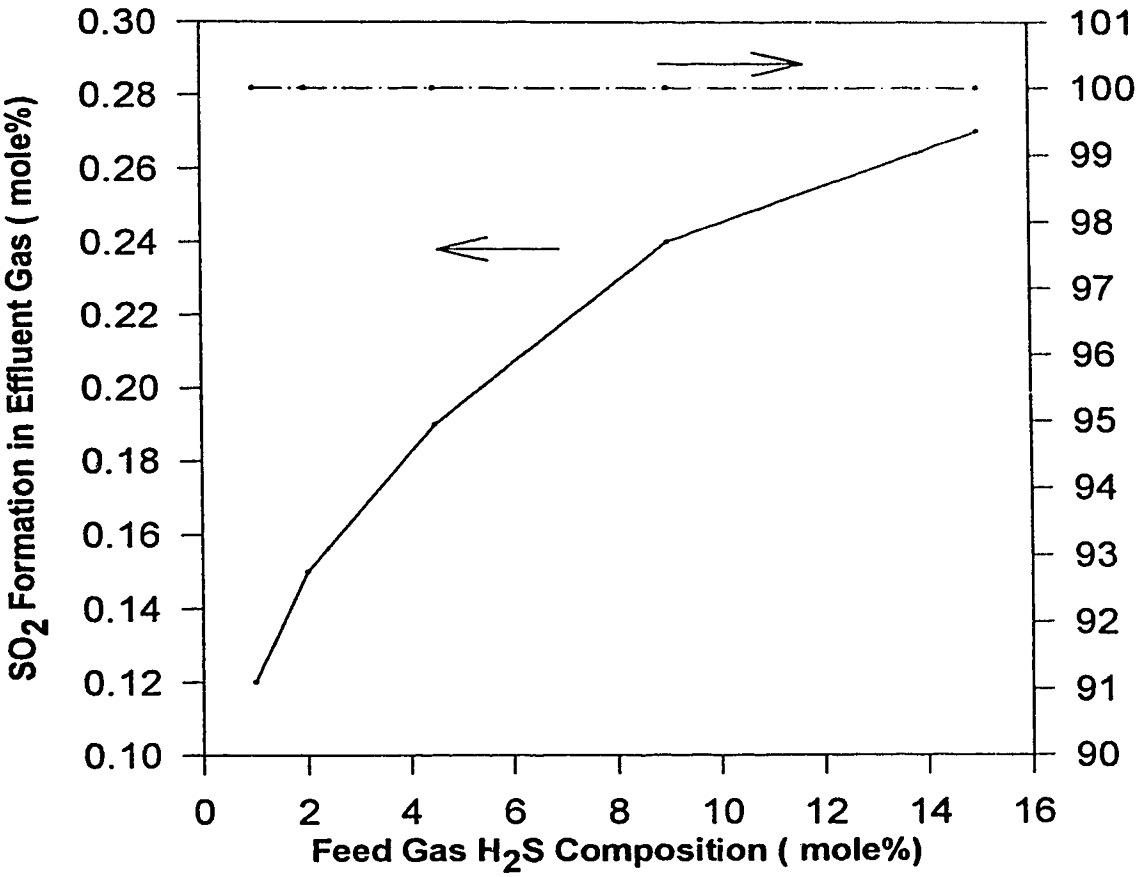
T = 120°C, H_2SO_4 Conc. = 94 wt%, Feed H_2S Concentration = 9 mole%

Figure 5.5 Effect of pressure on equilibrium H_2S conversion and SO_2 formation



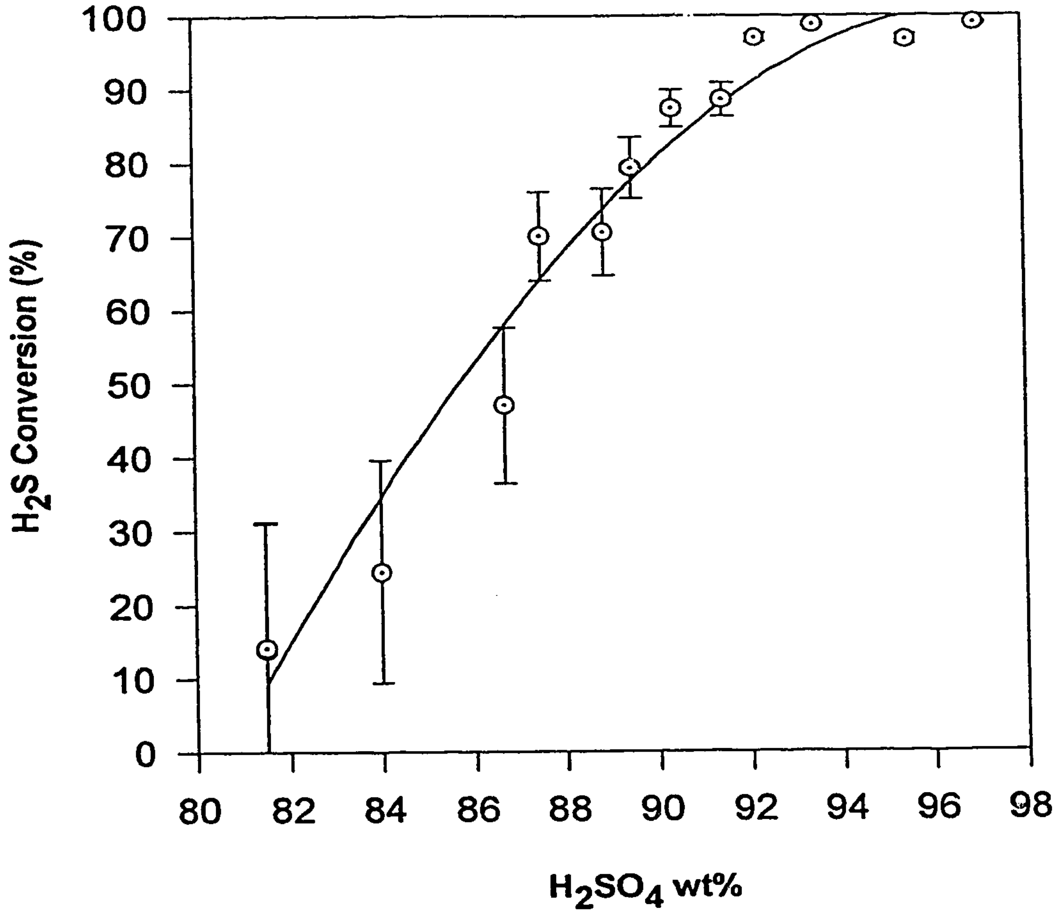
P = 5 psig, T = 120^0C, Feed H_2SO_4 Concentration = 85 wt%

Figure 5.6 Effect of feed H_2S composition on equilibrium H_2S conversion and SO_2 formation



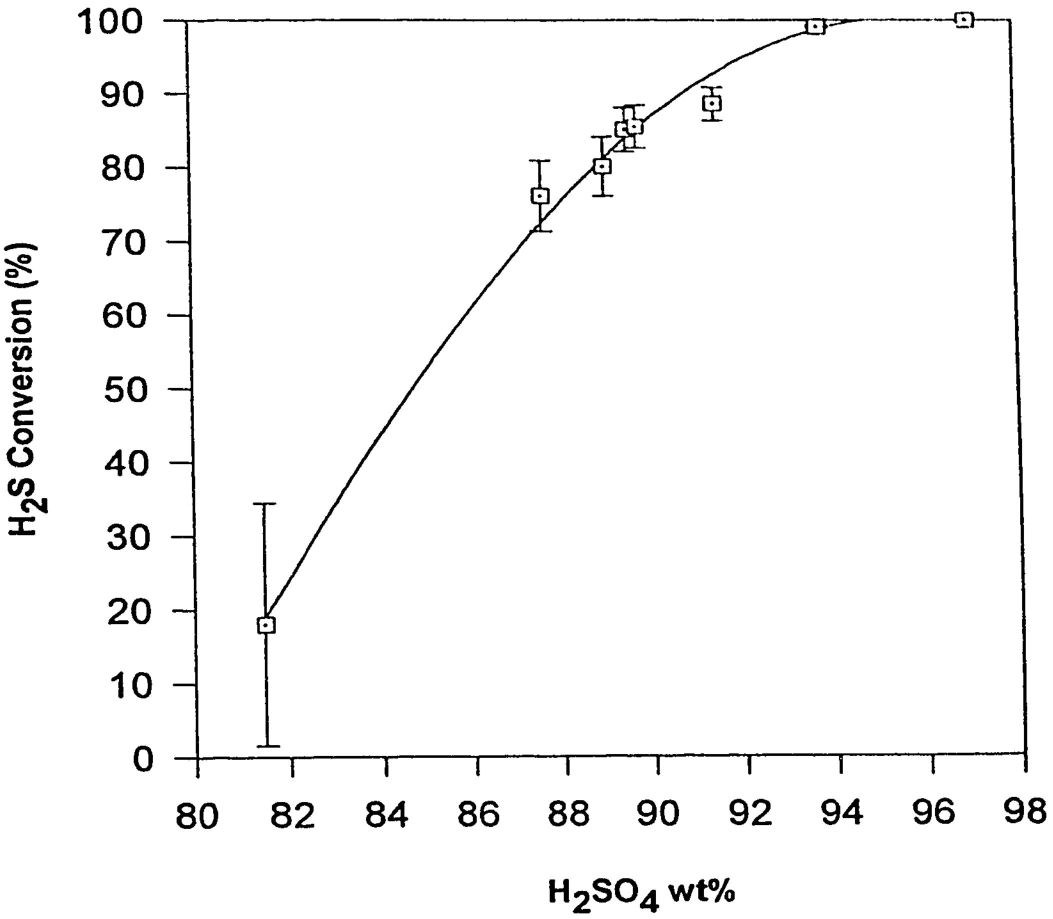
P = 5 psig, T = 120^{0}C, Feed H_2SO_4 Concentration = 94 wt%

Figure 5.7 Effect of feed H_2S composition on equilibrium H_2S conversion and SO_2 formation



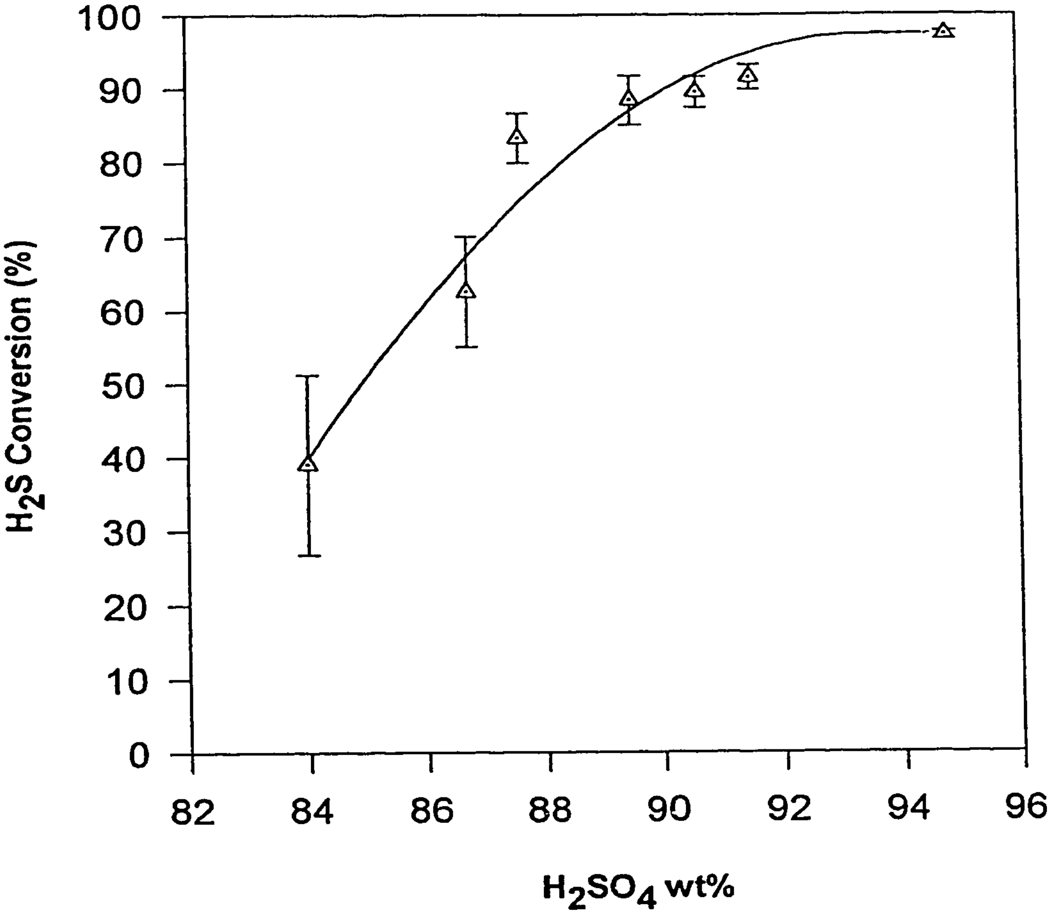
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
G= 191sccm, L= 70 cc/min, G/L= 2.73

Figure 5.8 Effect of feed sulfuric acid concentration on H_2S conversion



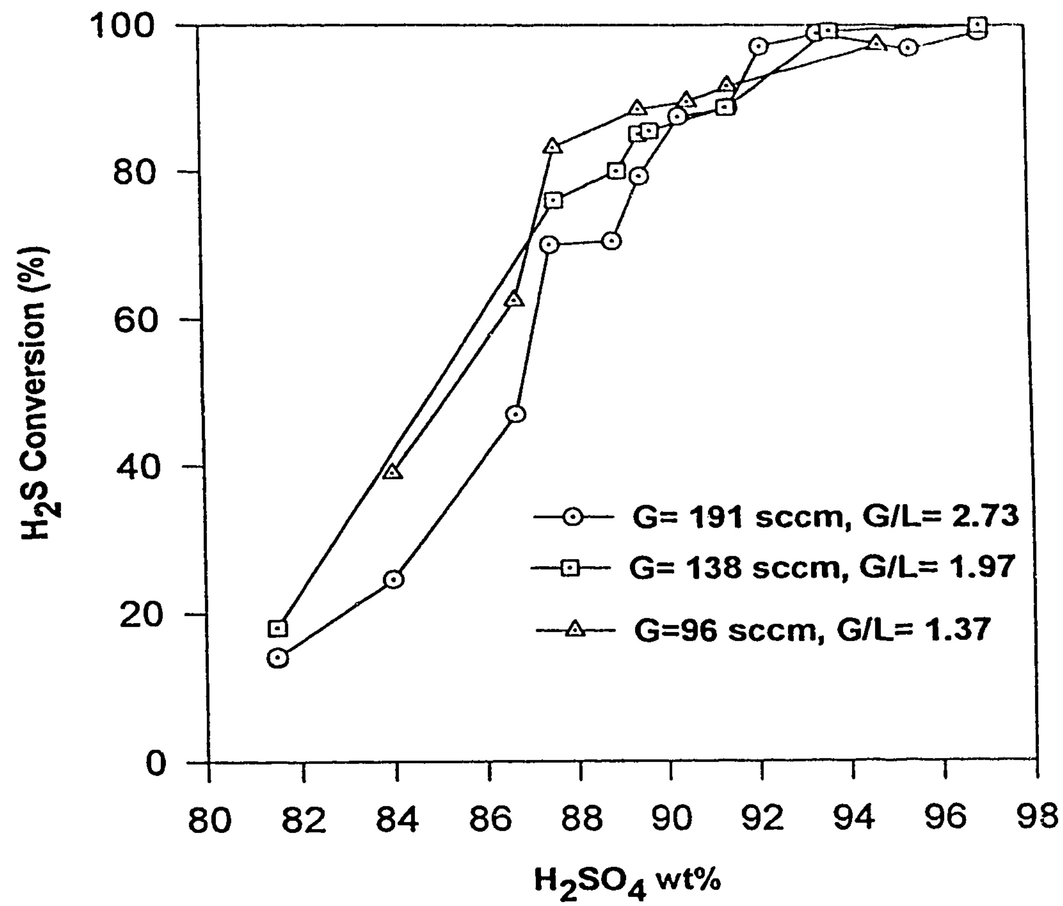
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
G= 138sccm, L= 70 cc/min, G/L= 1.97

Figure 5.9 **Effect of feed sulfuric acid concentration on H_2S conversion**



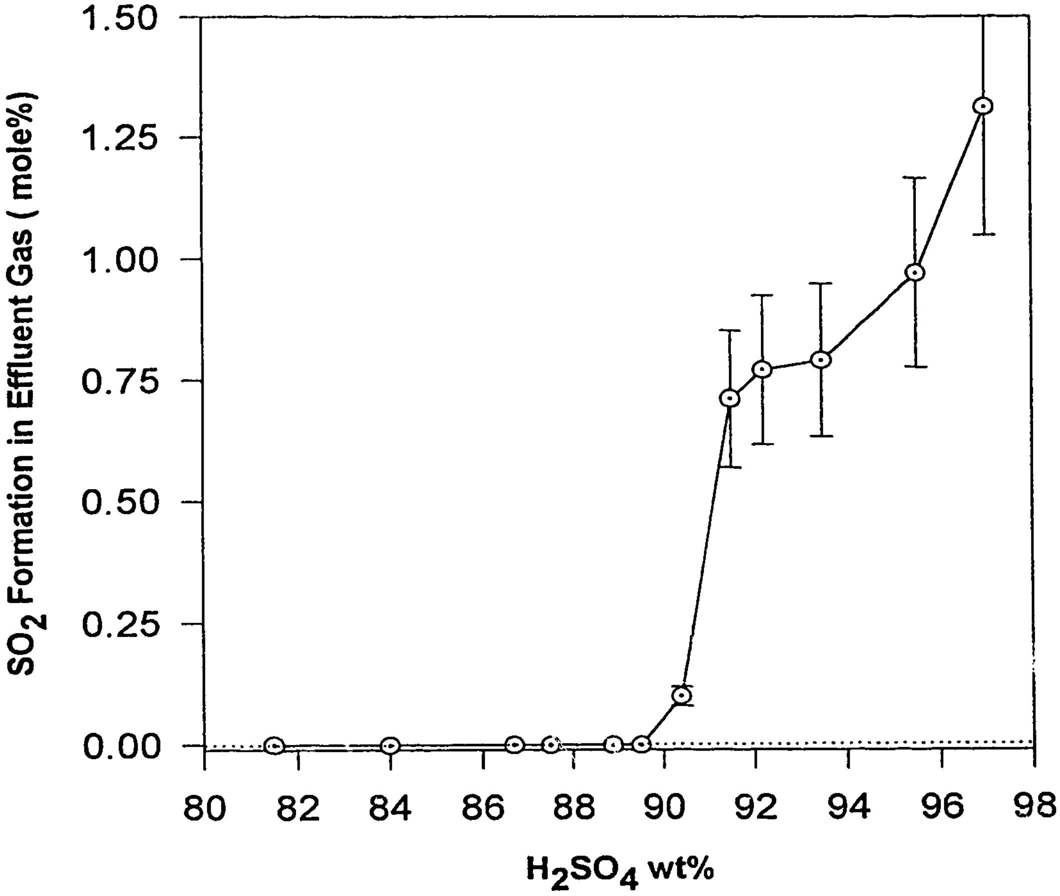
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
G= 96sccm, L= 70 cc/min, G/L= 1.38

Figure 5.10 Effect of feed sulfuric acid concentration on H_2S conversion



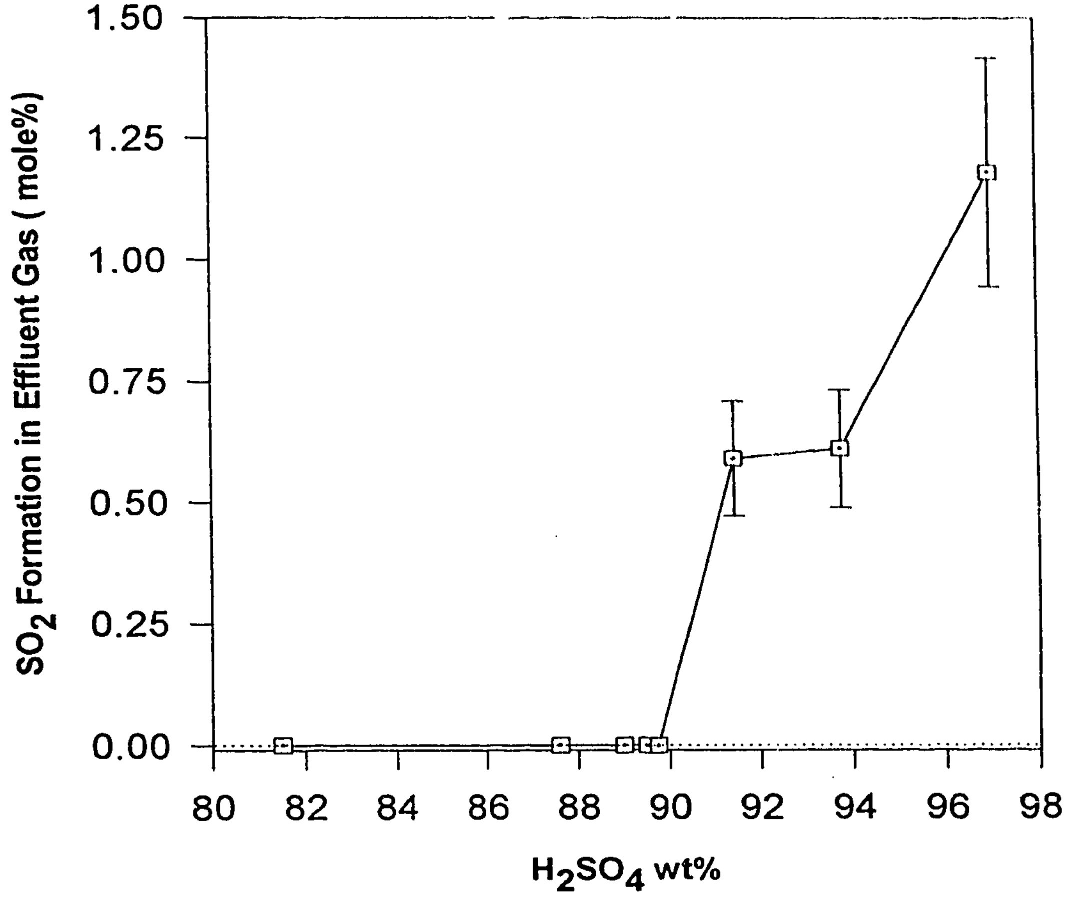
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
L= 70 cc/min

Figure 5.11 Effect of feed sulfuric acid concentration on H_2S conversion



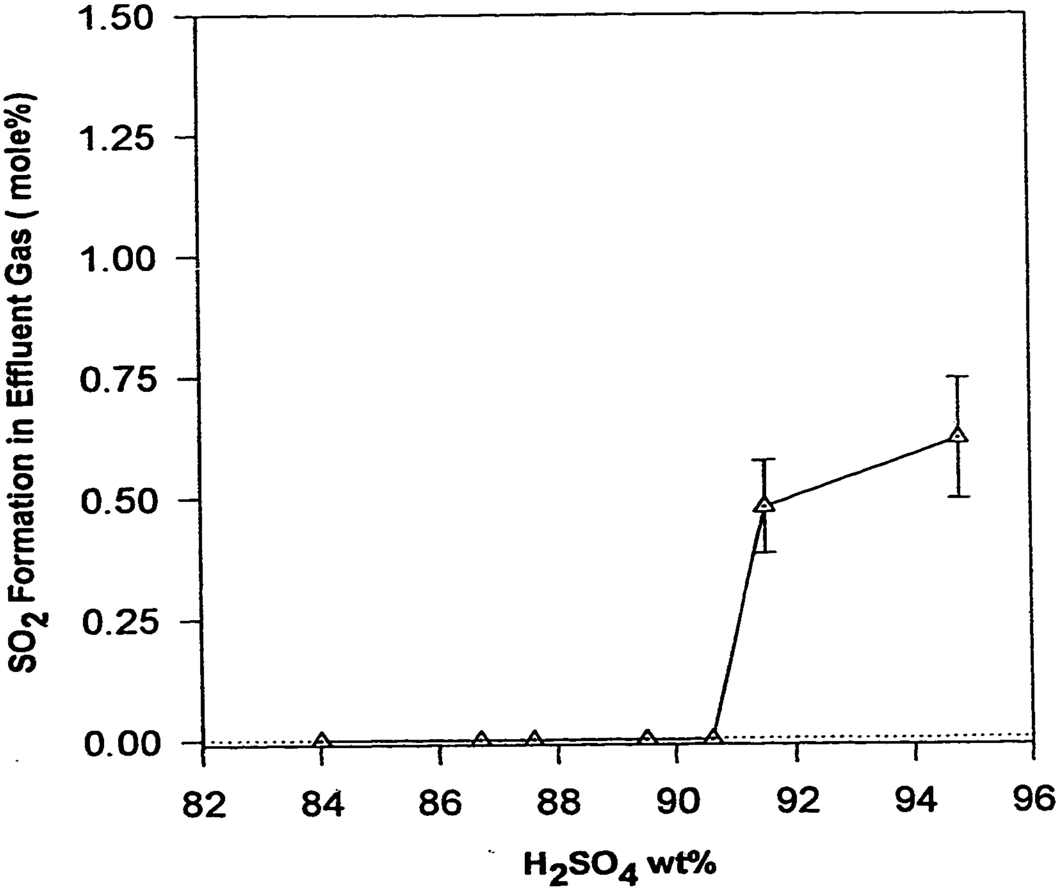
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
G=191 sccm, L= 70 cc/min, G/L = 2.73

Figure 5.12 Effect of feed sulfuric acid concentration on SO_2 formation



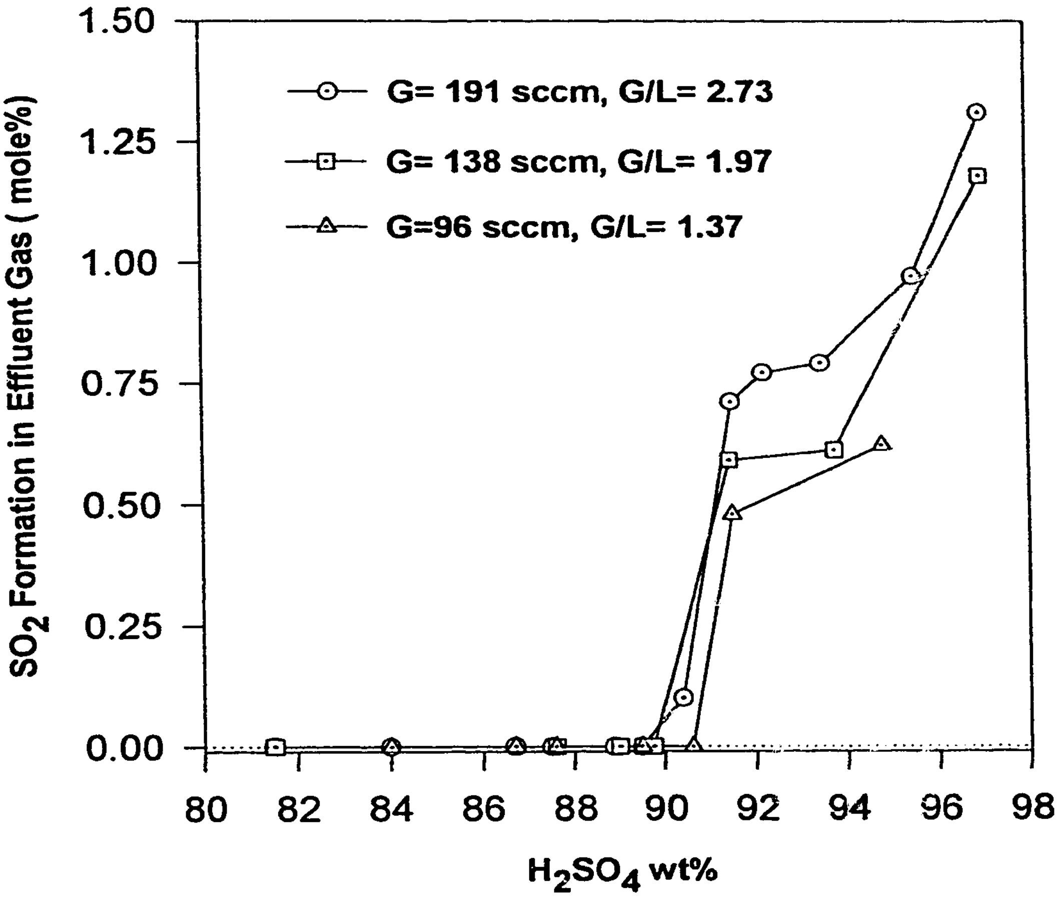
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
G=138 sccm, L= 70 cc/min, G/L = 1.97

Figure 5.13 Effect of feed sulfuric acid concentration on SO_2 formation



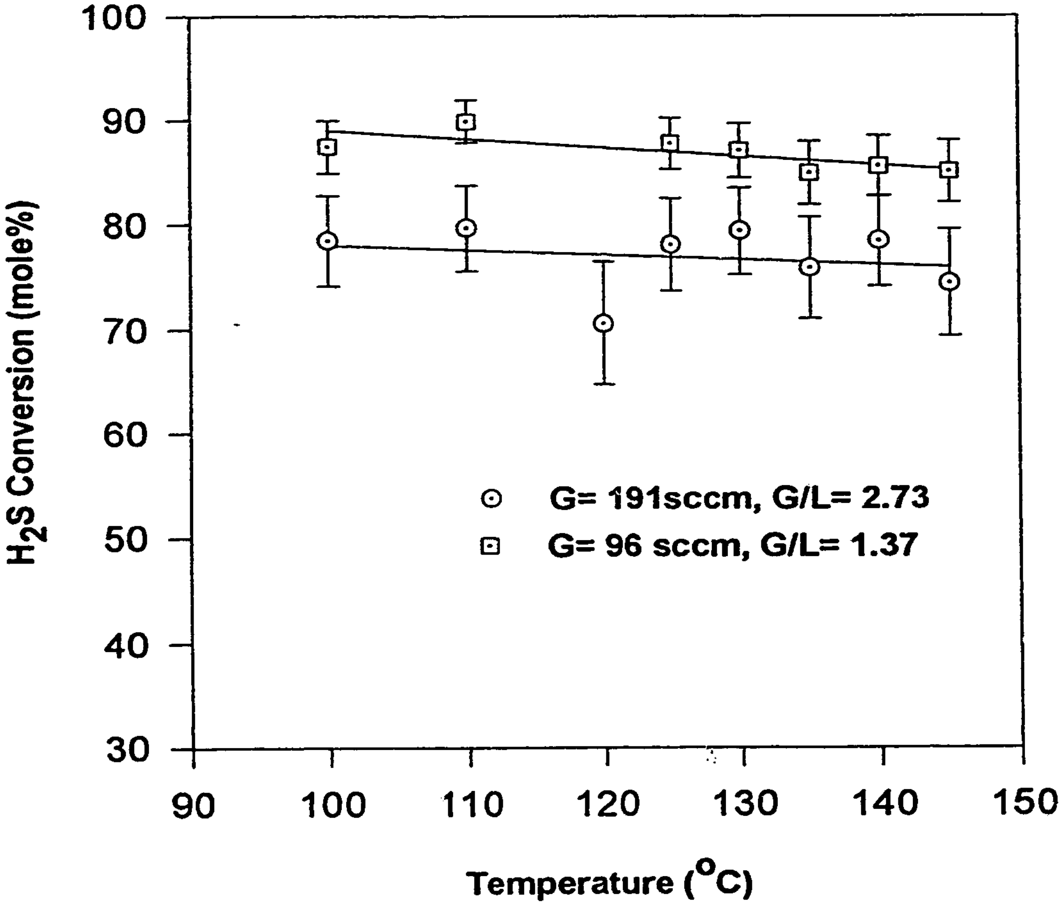
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
G=96 sccm, L= 70 cc/min, G/L = 1.37

Figure 5.14 Effect of feed sulfuric acid concentration on SO_2 formation



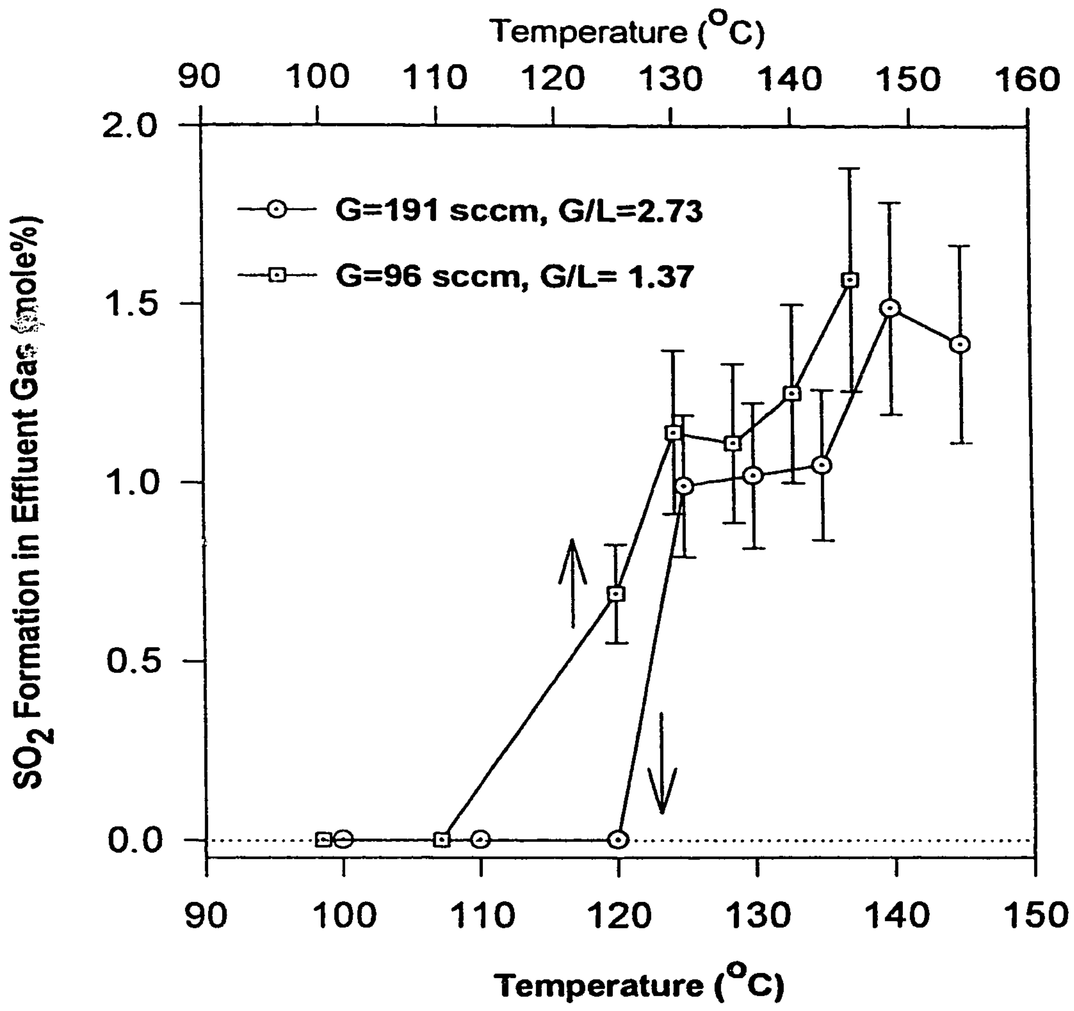
P= 5 psig, T= 120°C, Feed H_2S concentration= 9 mole%
L= 70 cc/min

Figure 5.15 **Effect of feed sulfuric acid concentration on SO_2 formation**



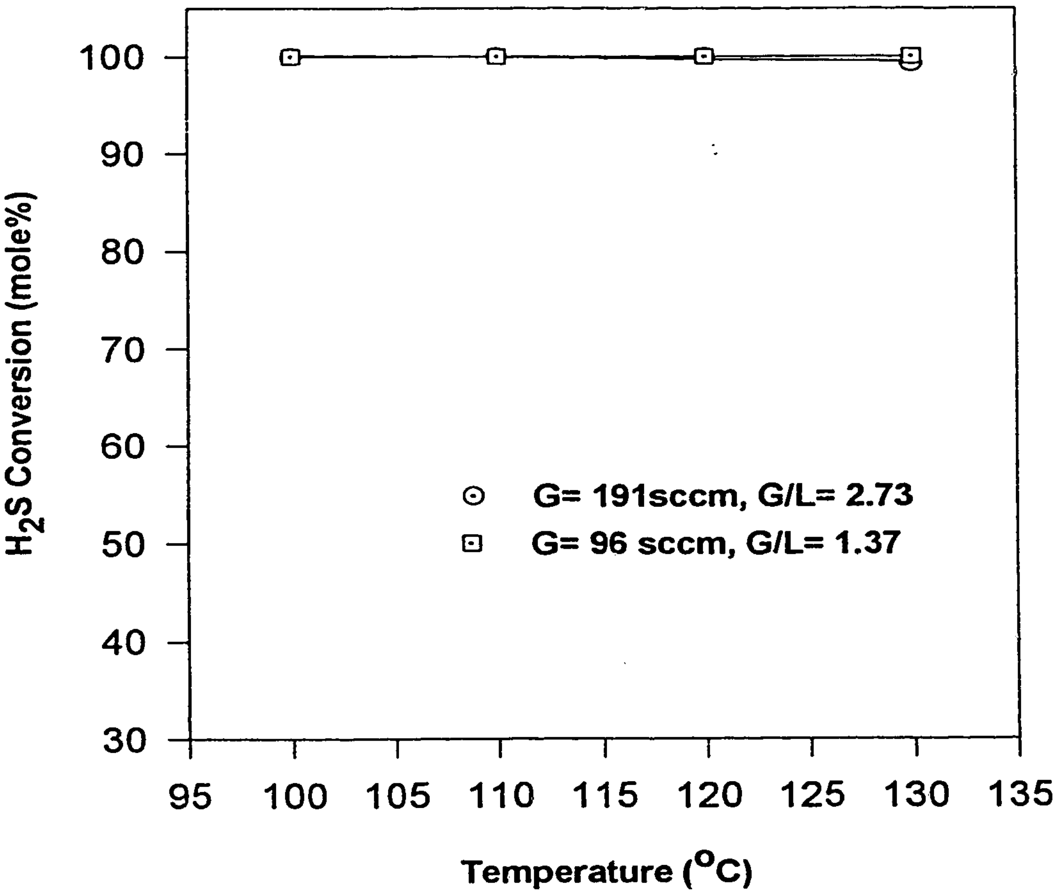
P= 5 psig, L= 70 cc/min, Feed H_2S concentration = 9 mole%, H_2SO_4 concentration= 88 wt%

Figure 5.16 Effect of temperature on H_2S conversion



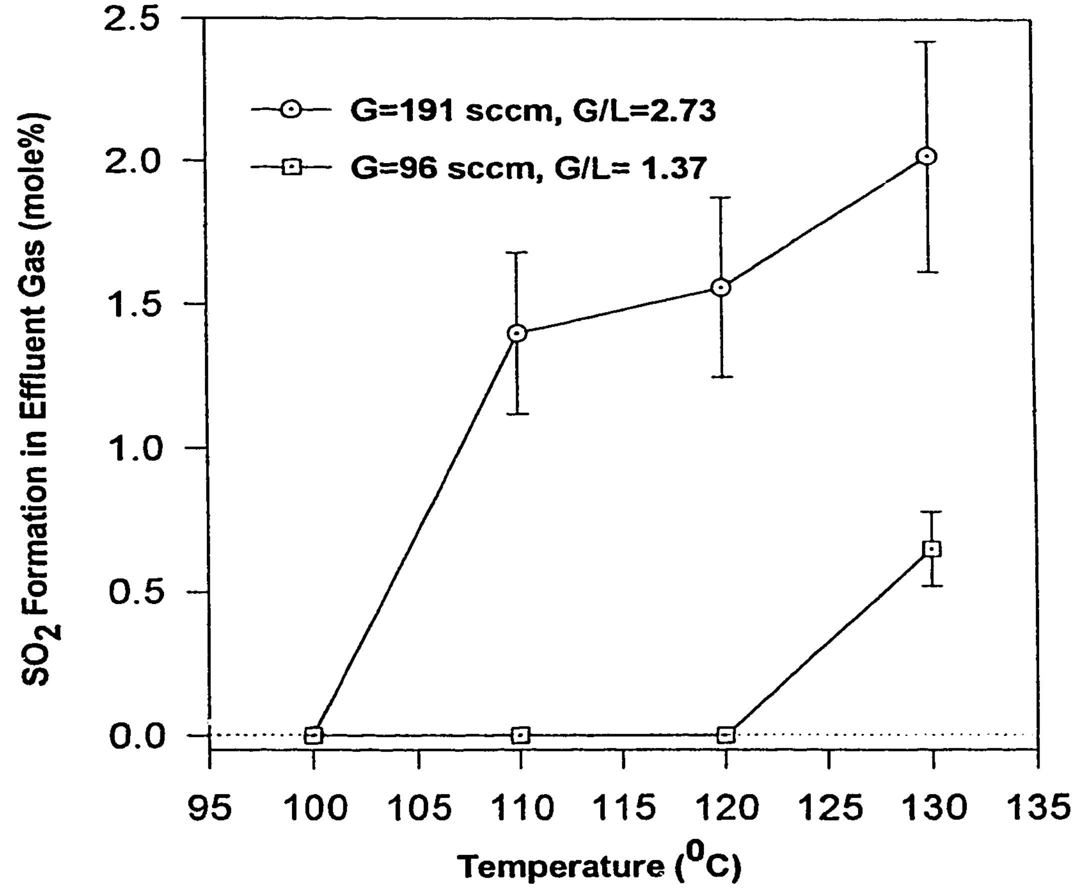
P= 5 psig, L= 70 cc/min, Feed H_2S concentration = 9 mole%, H_2SO_4 concentration= 88 wt%

Figure 5.17 Effect of temperature on SO_2 formation



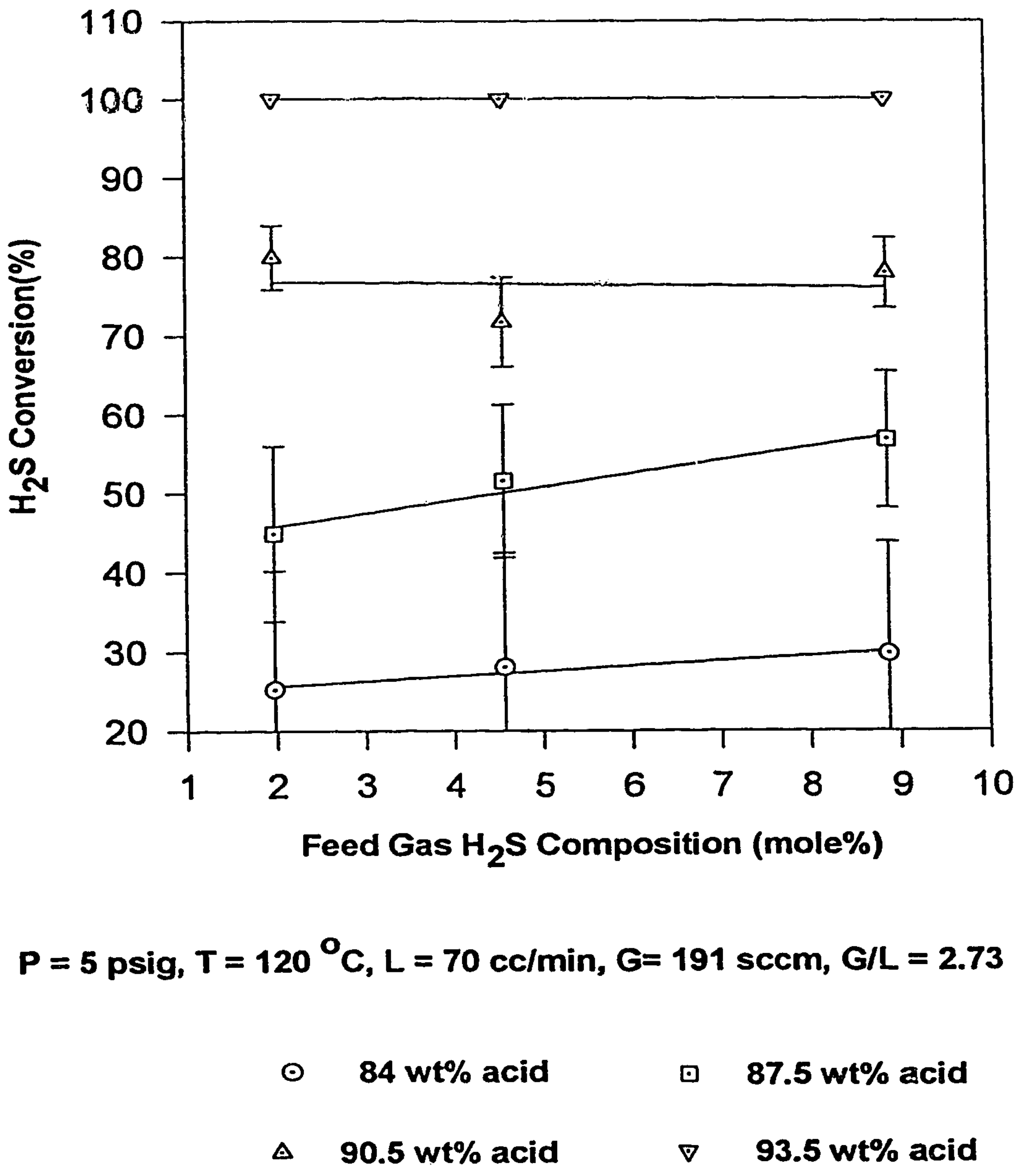
P= 5 psig, L= 70 cc/min, Feed H_2S concentration = 9 mole%, H_2SO_4 concentration= 93 wt%

Figure 5.18 Effect of temperature on H_2S conversion



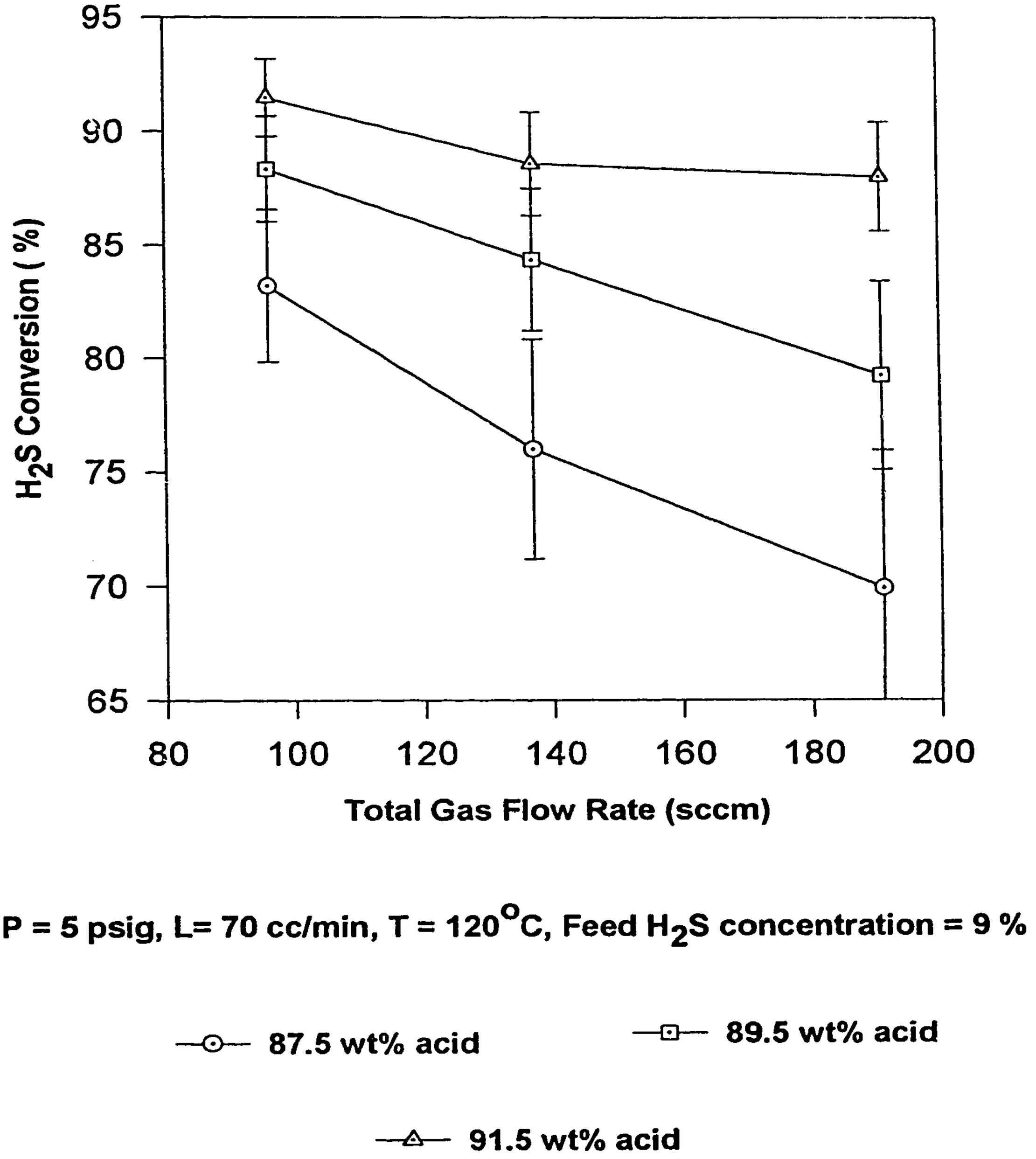
P= 5 psig, L= 70 cc/min, Feed H_2S concentration = 9 mole%, H_2SO_4 concentration= 93 wt%

Figure 5.19 Effect of temperature on SO_2 formation



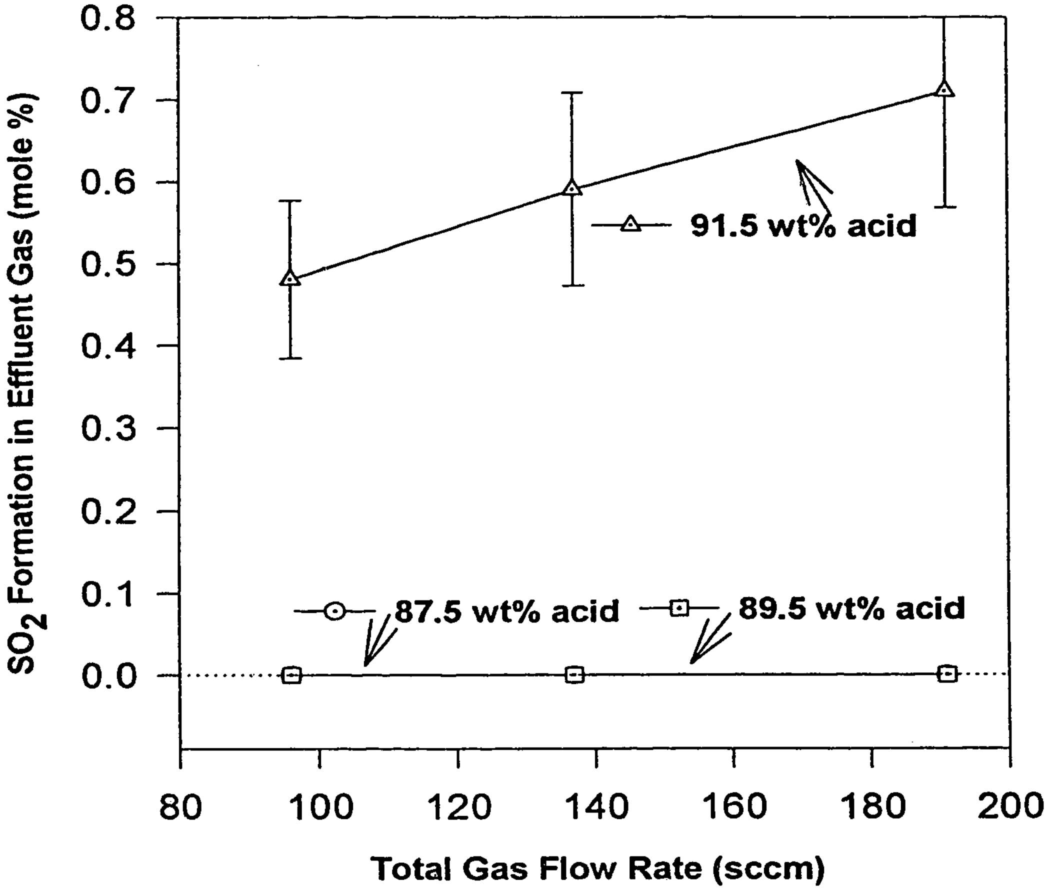
P = 5 psig, T = 120 °C, L = 70 cc/min, G= 191 sccm, G/L = 2.73

Figure 5.20 Effect of feed H_2S composition on H_2S conversion



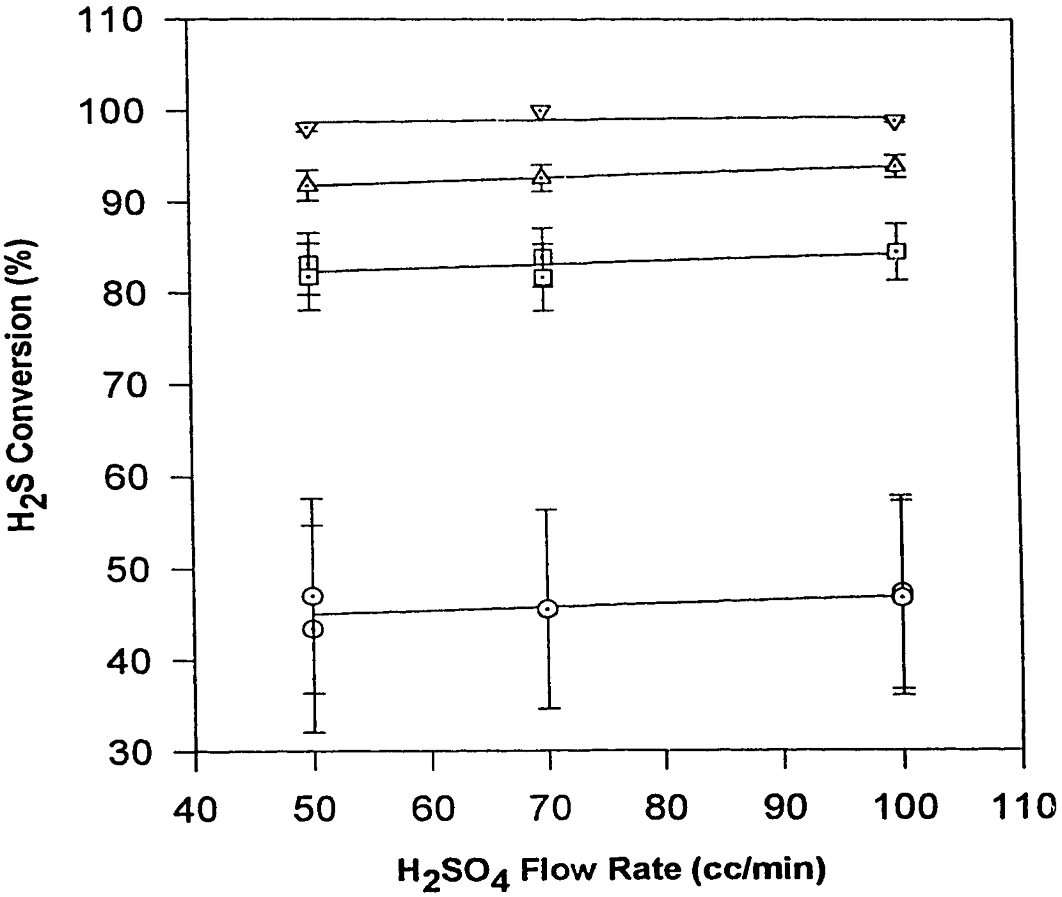
P = 5 psig, L= 70 cc/min, T = 120°C, Feed H_2S concentration = 9 %

Figure 5.21 Effect of gas flow rate on H_2S conversion



P = 5 psig, L= 70 cc/min, T = 120°C, Feed H_2S concentration = 9 %

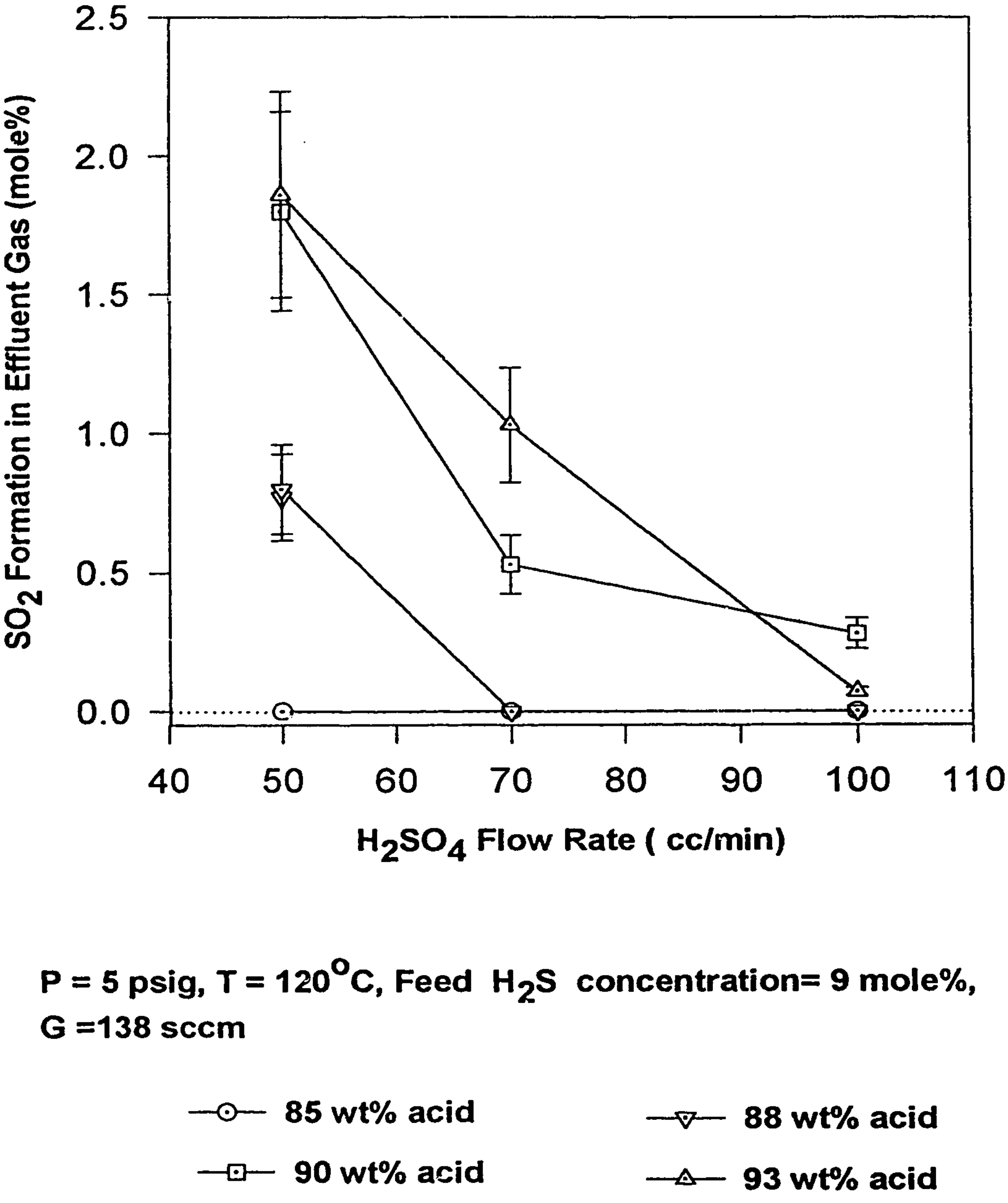
Figure 5.22 Effect of gas flow rate on SO_2 formation



P = 5 psig, T = 120°C, Feed H_2S concentration= 9 mole%, G =138 sccm

⊙	85 wt% acid	⊡	88 wt% acid
△	90 wt% acid	▽	93 wt% acid

Figure 5.23 Effect of H_2SO_4 flow rate on H_2S conversion



P = 5 psig, T = 120^{o}C, Feed H_2S concentration= 9 mole%, G =138 sccm

Figure 5.24 Effect of H_2SO_4 flow rate on SO_2 formation

As seen from the above reactions, almost all of the possible reaction mechanisms shown in the literature discuss the formation of SO_2 in the system. Table 3.1 listed the feasibility of the related reactions in the H_2S -H_2SO_4 system at 120°C. It shows that, in the case of dilute acids, the equilibrium constants for reactions (9) and (10) are very small. Also, the ΔG consideration in Figure 3.9 shows that all of the above reactions, except (9) and (10) are thermodynamically feasible at least until 150^0C. Reactions (9) and (10) become important only above 150^0C .

The Eh-pH diagrams shown in Figures 3.10 to 3.12 were constructed for the H_2S-H_2SO_4 system to examine the stability of various species at different values of the pH. These diagrams show that sulfur exists as a stable species between the H_2S and HSO_4 (-a) stability regions. The sulfur stability region appears only in the acidic range. This indicates that the interaction between H_2SO_4 and H_2S will result in the formation of stable sulfur as one of the resultant species. As the temperature rises, the pH range required for stable sulfur becomes more acidic. At about 270°C, SO_2 appears as a stable species along with sulfur at an extremely low pH. The pH of 80-98 wt% H_2SO_4 solutions lie in the range of 0-1. Hence, in such a system, sulfur has to be present as a stable species along with water.

A sample of the feed composition and the equilibrium results is shown in Table 5.1. The feed consists of 80 wt% H_2SO_4 and 9 mole percent H_2S in the gas phase. The equilibrium results are calculated in the range of 100 to 150°C at 5 psig pressure. The output shows amounts of various species, in moles, present at equilibrium at different temperatures which are represented in degrees Kelvin. These results show the presence of both sulfur and SO_2 at equilibrium. The overall reaction stoichiometry given by the HSC calculations is confirmed in Table 5.2. In all sets except that for the temperature effect, the stoichiometry conforms to the equation (6) when almost no SO_2 is formed.

$$3\ H_2S + H_2SO_4 = 4\ S + 4\ H_2O \text{..........................(6)}$$

The SO_2 formation is primarily a function of temperature. As can be seen from Table 5.3,

Table 5.1 Sample feed and equilibrium calculation results

Feed

```
Input data saved as: d:\hsc\acefecl.igi

Run for acid conc.= 80wt%, H2Smole%= 9.0mole%, T= 100-150oC, P= 5 psig
Temperature:          100.000 C,   Step =        5.000 C
Pressure:               1.360 bar, Step =        0.000 bar
Number of Steps: 11

   Phase Specie                        Temp      Input       Step    Activity
                                          C        mol        mol  coefficient
  1   1   N2(g)                      25.000    182.000      0.000      1.000
  2   1   H2O(g)                     25.000      0.000      0.000      1.000
  3   1   H2S(g)                     25.000     18.000      0.000      1.000
  4   1   H2SO4(g)                   25.000      0.000      0.000      1.000
  5   1   SO2(g)                     25.000      0.000      0.000      1.000
  6   2   H2SO4                      25.000    106.000      0.000      1.000
  7   2   H2O                        25.000    144.000      0.000      0.043
  8   2   H2SO4*H2O                  25.000      0.000      0.000      1.000
  9   2   S                          25.000      0.000      0.000      1.000
 10   3   H(+a)                      25.000      0.000      0.000      1.000
 11   3   H2S(a)                     25.000      0.000      0.000      1.000
 12   3   HS(-a)                     25.000      0.000      0.000      1.000
 13   3   H2SO3(a)                   25.000      0.000      0.000      1.000
 14   3   H2SO4(a)                   25.000      0.000      0.000      1.000
 15   3   HSO3(-a)                   25.000      0.000      0.000      1.000
 16   3   HSO4(-a)                   25.000      0.000      0.000      1.000
 17   3   SO2(a)                     25.000      0.000      0.000      1.000
 18   3   SO4(-2a)                   25.000      0.000      0.000      1.000
 19   3   OH(-a)                     25.000      0.000      0.000      1.000
 20   3   e-                         25.000 1.0000E-04      0.000      1.000
```

Output

```
d:\hsc\acefecl.gib

          X          Y 1          Y 2          Y 3          Y 4          Y 5          Y 6          Y 7          Y 8
Temperature          H2O       H2O(g)            S       SO2(g)       H2S(g)    H2SO4*H2O        H2SO4     H2SO4(g)
3.73150E+02  1.62860E+02  5.14800E+00  2.39950E+01  1.11260E-02  1.15410E-04  2.33810E-06  5.08110E-08  1.34990E-11
3.78150E+02  1.61860E+02  6.15330E+00  2.39930E+01  1.74020E-02  1.51020E-04  2.82280E-06  6.91500E-08  2.49130E-11
3.83150E+02  1.60700E+02  7.32050E+00  2.39890E+01  2.69260E-02  1.96450E-04  3.38630E-06  9.32300E-08  4.52280E-11
3.88150E+02  1.59360E+02  8.67090E+00  2.39840E+01  4.12390E-02  2.54130E-04  4.03630E-06  1.24550E-07  8.08260E-11
3.93150E+02  1.57820E+02  1.02290E+01  2.39760E+01  6.24190E-02  3.24310E-04  4.78050E-06  1.64880E-07  1.42300E-10
3.98150E+02  1.56050E+02  1.20200E+01  2.39650E+01  9.36350E-02  4.12170E-04  5.62560E-06  2.16330E-07  2.46990E-10
4.03150E+02  1.54020E+02  1.40770E+01  2.39490E+01  1.39290E-01  5.21980E-04  6.57730E-06  2.81320E-07  4.22940E-10
4.08150E+02  1.51710E+02  1.64330E+01  2.39250E+01  2.05610E-01  6.59100E-04  7.63940E-06  3.62590E-07  7.15010E-10
4.13150E+02  1.49080E+02  1.91290E+01  2.38920E+01  3.01330E-01  8.30270E-04  8.81290E-06  4.63190E-07  1.19420E-09
4.18150E+02  1.46100E+02  2.22110E+01  2.38430E+01  4.38740E-01  1.04400E-03  1.00950E-05  5.86350E-07  1.97190E-09
4.23150E+02  1.42710E+02  2.57330E+01  2.37750E+01  6.35070E-01  1.31130E-03  1.14800E-05  7.35410E-07  3.22130E-09
```

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          X          Y 1          Y 2          Y 3          Y 4          Y 5          Y 6          Y 7          Y 8
Temperature        H(+a)     HSO4(-a)     SO4(-2a)     H2SO4(a)       SO2(a)     H2SO3(a)       H2S(a)     HSO3(-a)
3.73150E+02  1.00110E+02  9.98020E+01  1.54960E-01  3.43430E-02  2.06080E-03  6.64190E-05  2.80390E-06  8.53980E-07
3.78150E+02  1.00090E+02  9.98310E+01  1.27890E-01  2.79190E-02  2.82830E-03  8.88200E-05  3.32370E-06  1.12340E-06
3.83150E+02  1.00060E+02  9.98510E+01  1.05340E-01  2.26370E-02  3.84610E-03  1.17560E-04  3.92020E-06  1.46930E-06
3.88150E+02  1.00040E+02  9.98640E+01  8.66000E-02  1.83060E-02  5.18370E-03  1.54060E-04  4.60130E-06  1.91090E-06
3.93150E+02  1.00010E+02  9.98680E+01  7.10560E-02  1.47680E-02  6.91230E-03  1.99560E-04  5.33030E-06  2.46660E-06
3.98150E+02  9.99780E+01  9.98610E+01  5.81950E-02  1.18840E-02  9.14330E-03  2.56160E-04  6.15130E-06  3.16790E-06
4.03150E+02  9.99370E+01  9.98420E+01  4.75770E-02  9.54130E-03  1.20010E-02  3.25980E-04  7.07410E-06  4.04910E-06
4.08150E+02  9.98840E+01  9.98060E+01  3.88260E-02  7.64260E-03  1.56370E-02  4.11390E-04  8.10990E-06  5.15150E-06
4.13150E+02  9.98110E+01  9.97480E+01  3.16300E-02  6.10770E-03  2.02290E-02  5.15020E-04  9.27080E-06  6.52480E-06
4.18150E+02  9.97110E+01  9.96590E+01  2.57210E-02  4.86980E-03  2.59910E-02  6.39750E-04  1.05700E-05  8.22850E-06
4.23150E+02  9.95710E+01  9.95300E+01  2.08770E-02  3.87370E-03  3.31750E-02  7.88690E-04  1.20230E-05  1.03330E-05
```

Table 5.2 Stoichiometry in the absence of SO_2 at the equilibrium

Conditions	H_2S consumed per mole H_2SO_4 consumed	S produced, per mole H_2SO_4 consumed	SO_2 produced, per mole H_2SO_4 consumed	H_2O produced per mole H_2SO_4 consumed
T=120 C, Feed H_2S = 9mole%				
Acid concen.: 85wt%				
P= 5 psig	2.91	3.88	0.02	3.94
P= 50 psig	2.94	3.92	0.00	3.92
P= 5000 psig	2.95	3.93	0.00	3.94
Acid concen.: 94wt%				
P= 5 psig	2.80	3.71	0.08	3.78
P= 50 psig	2.89	3.84	0.03	3.87
P= 5000 psig	2.93	3.90	0.00	3.92
T=120°C, P =5 psig, Feed gas H_2S = 2 mole%				
Acid concen.: 85 wt%	2.70	3.58	0.05	3.29
Acid concen.: 94 wt%	2.41	3.14	0.18	3.35

Table 5.3 Stoichiometry with increase in temperature

Conditions	H_2S consumed per mole H_2SO_4 consumed	S produced per mole H_2SO_4 consumed	SO_2 produced per mole H_2SO_4 consumed	H_2O produced per mole H_2SO_4 consumed
Feed H_2S= 9mole%, P =5 psig, Acid concen.=85 wt%				
100°C	2.89	3.86	0.00	3.86
120°C	2.92	3.88	0.01	3.90
140°C	2.81	3.71	0.09	3.80
160°C	2.41	3.11	0.29	3.41
180°C	1.60	1.90	0.71	2.62
200°C	0.78	0.56	0.12	1.80
Feed H_2S= 9mole%, P =5 psig, Acid concen.: 94 wt%				
100°C	2.85	3.80	0.01	3.77
120°C	2.78	3.68	0.08	3.76
140°C	2.36	3.04	0.28	3.33
160°C	1.51	1.80	0.66	2.46
180°C	0.75	0.66	1.02	1.67
200°C	0.40	0.13	1.22	1.36

as the temperature increases the reaction stoichiometry shifts from (6) to (10) through (7). The effect is more pronounced at higher acid concentration of 94 wt%.

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$....................(7)

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$.....................(10)

Also for the system consisting of feed sulfur (5 mole) and H_2SO_4 (191.3 moles of 90 wt%), the HSC calculations show that sulfur reacts with H_2SO_4 to generate SO_2 at higher temperatures (Table 5.4). The temperatures are shown in degree Kelvin and various species are quantified in terms of moles. This observation supports the occurrence of reaction (10) at higher temperatures.

Table 5.4 The HSC program results for the system of 90 wt% H_2SO_4 and S

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          X           Y 1           Y 2           Y 3           Y 4           Y 5           Y 6           Y 7           Y 8
Temperature           H2O        H2O(g)        SO2(g)             S        H2S(g)    H2SO4*H2O         H2SO4     H2SO4(g)
3.73150E+02  7.10680E+01  9.53670E-01  2.63570E-02  4.98920E+00  5.01460E-06  1.80320E-07  2.06810E-08  1.31980E-11
3.83150E+02  7.07040E+01  1.34570E+00  6.29380E-02  4.97530E+00  8.37060E-06  2.63310E-07  3.82000E-08  4.38070E-11
3.93150E+02  7.02470E+01  1.86170E+00  1.43210E-01  4.94560E+00  1.34250E-05  3.76050E-07  6.81900E-08  1.36160E-10
4.03150E+02  6.96990E+01  2.53090E+00  3.11340E-01  4.88480E+00  2.06870E-05  5.25970E-07  1.17880E-07  3.98360E-10
4.13150E+02  6.90810E+01  3.38920E+00  6.49090E-01  4.76480E+00  3.07550E-05  7.21560E-07  1.97690E-07  1.10270E-09
4.23150E+02  6.84400E+01  4.48430E+00  1.29690E+00  4.53770E+00  4.36140E-05  9.72630E-07  3.22220E-07  2.90180E-09
4.33150E+02  6.78550E+01  5.88410E+00  2.47310E+00  4.13010E+00  5.75870E-05  1.29100E-06  5.11300E-07  7.29700E-09
4.43150E+02  6.74080E+01  7.69010E+00  4.45440E+00  3.45020E+00  6.74220E-05  1.69090E-06  7.90870E-07  1.76230E-08
4.53150E+02  6.70660E+01  1.00400E+01  7.40590E+00  2.44640E+00  6.33900E-05  2.18660E-06  1.19260E-06  4.10490E-08
4.63150E+02  6.63950E+01  1.30470E+01  1.08720E+01  1.27810E+00  3.97050E-05  2.77620E-06  1.74850E-06  9.22840E-08
```

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          X           Y 1           Y 2           Y 3           Y 4           Y 5           Y 6           Y 7           Y 8
Temperature      HSO4(-a)        SO2(a)      SO4(-2a)     H2SO4(a)     H2SO3(a)      HSO3(-a)        H2S(a)        OH(-a)
3.73150E+02  1.19050E+02  5.95670E-03  1.84850E-01  4.09660E-02  3.63780E-05  4.677[illegible]E-07  1.48650E-07  1.87950E-12
3.83150E+02  1.19100E+02  1.10700E-02  1.25650E-01  2.69990E-02  6.42150E-05  8.02600E-07  2.05690E-07  2.63630E-12
3.93150E+02  1.19090E+02  1.[illegible]630E-02  8.47360E-02  1.76090E-02  1.08520E-04  1.34150E-06  2.74990E-07  3.57360E-12
4.03150E+02  1.19000E+02  3.[illegible]430E-02  5.67110E-02  1.13710E-02  1.75960E-04  2.18580E-06  3.54750E-07  4.69380E-12
4.13150E+02  1.18780E+02  5.61920E-02  3.76710E-02  7.27240E-03  2.74440E-04  3.47740E-06  4.42850E-07  5.88800E-12
4.23150E+02  1.18350E+02  8.94040E-02  2.48290E-02  4.60510E-03  4.11000E-04  5.38580E-06  5.27730E-07  7.43490E-12
4.33150E+02  1.17540E+02  1.35730E-01  1.62240E-02  2.88530E-03  5.87540E-04  8.06600E-06  5.84230E-07  9.00150E-12
4.43150E+02  1.16190E+02  1.93810E-01  1.04970E-02  1.78670E-03  7.91700E-04  1.15240E-05  5.70100E-07  1.06430E-11
4.53150E+02  1.14190E+02  2.53730E-01  6.72000E-03  1.09290E-03  9.81140E-04  1.53130E-05  4.42960E-07  1.23060E-11
4.63150E+02  1.11850E+02  2.92560E-01  4.26820E-03  6.62320E-04  1.07210E-03  1.81290E-05  2.28360E-07  1.39360E-11
```

The electron transfer consideration shows reaction (7) to be the most feasible reaction because S^{-2} in H_2S gets oxidized to S and S^{+6} in acid gets reduced to S^{+4}, although the acid may convert the S^{-2} of H_2S into S^{+4} at high concentrations due to the enhancement in its oxidizing power. So the possibility of reaction (10) is strong only in case of systems with high acid concentrations (more than 90 wt%) and high temperatures (above 200°C).

We can decide the number of independent chemical reactions feasible in the system consisting of H_2S, SO_2, S, H_2SO_4 and water according to Duhem's rule for reacting systems (Smith and Van Ness, 1975). First, we write down all reaction equations of formation of the compounds present in the system from their respective constituent elements. These are as follows:

$H_2 + S = H_2S$..........................(21)
$H_2 + 1/2\ O_2 = H_2O$..................(22)
$S + O_2 = SO_2$..........................(23)
$H_2 + S + 2\ O_2 = H_2SO_4$...........(24)

Then we combine these equations to eliminate all the elements which cannot be present in the system at equilibrium. The HSC calculations clearly show that H_2 and O_2 cannot be present in the system at equilibrium. Hence after eliminating these two elements by the combination of the equations above, we find the number of independent chemical reactions feasible in the above system is two. One such elimination procedure is as follows:

We eliminate H_2 from the equations (21) and (24) by combining them with equation (22). This leaves three equations as follows.

$S + H_2O = H_2S + 1/2\ O_2$....................(25)
$S + 3/2\ O_2 + H_2O = H_2SO_4$.................(26)
$S + O_2 = SO_2$....................................(23)

Then we eliminate O_2 from these equations. This results in the following two independent chemical reaction equations which are the maximum possible number of independent chemical reactions in the above system.

$3\ S + 2\ H_2O = 2\ H_2S + SO_2$.................(27)

$4\ S + 4\ H_2O = 3\ H_2S + H_2SO_4$.............(28)

In the set of five reactions (6 to10) mentioned above, any two of the reactions can be used as algebraic equations to generate a third reaction equation. Also any effort to solve a set of three or more reaction equations in this system results in an inconsistency. This makes the fact very clear that only two independent reactions are possible in this system.

The Wackenroder reaction has been shown to occur quickly when H_2S and SO_2 are exposed to aqueous surfaces even at low temperatures by Tiwari, (1976). Also this reaction is thermodynamically feasible at 120°C. Hence one of the two independent reactions is the Wackenroder reaction. So the other reaction must be the one which yields SO_2. Reaction (7) and (10) are the possibilities. This makes two reaction sets feasible.

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$.......... $\Delta H = +ve$.......(7)

$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$..................$\Delta H = -ve$........(8)

or

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$............$\Delta H = +ve$.......(10)

$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$....................$\Delta H = -ve$.......(8)

If the HSC calculations in Table 5.4 are considered, they show that, reaction (9) should also be treated as an independent reaction. Thus, overall three independent reactions appear in the system. To satisfy this, the number of species in the system must be 6. This is possible only if we include excited state sulfur (S') as the hypothetical additional species formed as the intermediate. Its existence is very short-lived. It quickly reacts with H_2SO_4 to give SO_2. Thus, reaction (2) is thought to proceed through sulfur formation which is then oxidized to SO_2 by the highly oxidizing, concentrated H_2SO_4 at higher temperatures. This gives rise to the following system of reactions:

$$H_2S + H_2SO_4 = (1\text{-}y)\ S + y\ S^* + SO_2 + 2\ H_2O \text{.................... (7)}$$

$$2\ H_2S + SO_2 = 3\ S + 2\ H_2O \text{.. (8)}$$

$$y\ S^* + 2y\ H_2SO_4 = 3y\ SO_2 + 2y\ H_2O \text{.................................... (9)}$$

At lower temperatures, the rate of formation of S^* is slow and most of the sulfur is in its ground state. The overall reaction is then (6). As the temperature increases, more and more S^* is formed and eventually all of it is in the S^* form thus giving the overall reaction as (10).

Experimental verification and analysis is important to discriminate between the models concluded from the HSC results analysis. As seen from Figures 5.8 to 5.11, the effect of acid concentration on H_2S conversion shows that conversion increases as the acid concentration is increased. Up to about 90 wt% acid concentration SO_2 is not observed in the exhaust gas. At higher acid concentrations, H_2S conversion is almost complete and SO_2 starts to appear in the products as well. Thus, it can be concluded that SO_2 appears in the product gas only when H_2S conversion is almost complete; hence, SO_2 is either produced and/or consumed in the reaction involving H_2S. At higher gas contact times H_2S conversion is higher and SO_2 formation is less. As a result, SO_2 can be deemed to be the intermediate product in the system of reactions. This inference is also supported by the conclusions from the experiments involving, 1. reaction between H_2S and SO_2 over water and 2. Reaction between H_2S, SO_2 and H_2SO_4. Experiment 1 showed the formation of sulfur and experiment 2 gave higher H_2S conversions than those attained with only H_2S as the feed under similar conditions. Hence, these experiments showed that the Wackenroder reaction really occurs in the acid contacting process. Therefore, in any reaction model proposed the Wackenroder reaction has to be taken into account.

Regarding the theory of excited state sulfur, although detection of S^* as an intermediate was not possible in the present work, in the experiments involving a slurry of H_2SO_4 of concentration more than 90 wt% and sulfur as the feed liquid stream and N_2 as the feed gas stream, no SO_2 was observed in the effluent gas at temperatures between 120^0 C and 150^0C. This shows that elemental sulfur in the solid or liquid state does not react with H_2SO_4 to produce SO_2 in the temperature range of interest in this process. Also, the HSC conclusions regarding the reaction of sulfur with H_2SO_4 are only valid at temperatures above 150^0C. The acid concentrations required for this are high as well. Moreover the HSC results represent only the equilibrium picture and the kinetic aspects of different reactions can change the results appreciably if only a small time is allowed for the reactions to occur.

Electron transfer considerations, equilibrium constants and literature sources, as well, clearly suggest that the reaction (7) is the most likely reaction between reactions (7) and (10). Analysis of the equilibrium data, according to Le Chatelier's principle, can be successfully done by equations (7) and (8). Hence, in the temperature range of interest to the acid contacting process, the reactions occurring in the acid contacting process can be conclusively established to be,

$$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O \ldots\ldots\ldots\ldots\ldots \Delta H = +ve \ldots\ldots\ldots\ldots (7)$$

$$2\ H_2S + SO_2 = 3\ S + 2\ H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \Delta H = -ve \ldots\ldots\ldots\ldots (8)$$

One limitation of the experiments is that this conclusion can not be proven by our experimental material balance calculations since the calculations were based solely on the gas phase composition.

The extents of each of these reactions can be analyzed to verify the material balance at equilibrium. If the H_2S consumed in reaction (7) is α and that consumed in reaction (8) is β, then the corresponding amounts of various species consumed or produced are as shown in Table 5.5. To calculate α and β, the quantities of H_2S consumed and SO_2 produced are considered. The results are shown in Table 5.6 and

Table 5.5 **Amounts of various species consumed or produced according to reactions (7) and (8)**

H_2S consumed, moles	SO_2 produced, moles	H_2SO_4 consumed, moles	S produced, moles	H_2O produced moles
$\alpha+\beta$	$\alpha-\beta/2$	α	$\alpha+1.5\beta$	$2\alpha+\beta$

5.7. For achieving zero SO_2 formation i.e for the overall reaction to be reaction (6), 66.67% of the total H_2S should be consumed in reaction (8), the balance being consumed in reaction (7). This is verified in these tables below 150°C. As the temperature increases the extent of reaction (7) i.e. α increases to the point that SO_2 produced exceeds the H_2S consumed. The effect is more pronounced at high acid concentration as seen Table 5.8. Thus, at high temperatures the stoichiometry followed could be that of reaction (10) and (8). Similar to Table 5.5, Table 5.8 shows the amounts consumed or produced for reactions (10) and (8). The underlined values of α and β in Table 5.7 represent extents of reactions (10) and (8) respectively. Such a material balance is not possible in the case of a mechanism involving $S^{\cdot}$ due to unknown y.

5.3 Regime of operation

The acid contacting process involves the phenomenon of gas-liquid mass transfer with chemical reactions. An idea about which transfer rate is controlling should prove useful in scale up and better understanding of the process kinetics. Also parameters improving the transfer constants of the absorption rate controlling step will help achieve the process in a much shorter contactor. As seen before, the acid contacting process is defined by two reactions and all the observed phenomena should be explained by these two reactions.

Table 5.6 Extents of the reactions (7) and (8) in the absence of SO_2

Conditions	H_2S consumed, moles	H_2SO_4 consumed, moles	S produced, moles	SO_2 produced, moles	H_2O produced, moles	α percent	β percent
T=120 C, Feed H_2S = 9mole%							
Acid concen.: 85wt%							
P= 5 psig	18.00	6.18	23.96	0.12	24.08	33.80	66.20
P= 50 psig	18.00	6.12	23.98	0.05	24.01	33.30	66.70
P= 5000 psig	18.00	6.10	24.00	0.01	24.01	33.30	66.70
Acid concen.: 94wt%							
P= 5 psig	18.00	6.43	23.84	0.49	24.30	35.20	64.80
P= 50 psig	18.00	6.23	23.95	0.19	24.13	34.10	65.90
P= 5000 psig	18.00	6.14	23.97	0.06	24.04	33.60	66.40
T=120°C, P =5 psig, Feed gas H_2S = 2mol							
Acid concen.: 85wt%	4.00	1.48	5.31	0.08	4.87	65.30	34.70
Acid concen.: 94wt%	4.00	1.66	5.22	0.30	5.56	61.80	38.20

Table 5.7 Extents of the reactions (7) and (8) with increasing temperature

Conditions	H_2S consumed moles	H_2SO_4 consumed moles	S produced moles	SO_2 produced moles	H_2O produced moles	α percent	β percent
Feed H_2S= 9mole%, P =5 psig, Acid concen.=85 wt%							
100°C	18.00	6.22	24.00	0.02	24.00	33.44	66.56
120°C	18.00	6.17	23.95	0.12	24.08	33.77	66.22
140°C	18.00	6.41	23.81	0.55	24.38	35.38	64.62
160°C	18.00	7.47	23.25	2.13	25.49	41.22	58.78
180°C	18.00	11.20	21.32	7.99	29.33	62.95	37.05
200°C	18.00	22.84	12.85	25.60	41.10	42.66	57.33
Feed H_2S= 9mole%, P =5 psig, Acid concen.: 94 wt%							
100°C	18.00	6.30	23.97	0.10	23.78	33.71	66.29
120°C	18.00	6.47	23.83	0.49	24.31	35.17	64.83
140°C	18.00	7.64	23.29	2.15	25.41	41.28	58.72
160°C	18.00	11.90	21.38	7.90	29.24	62.61	37.39
180°C	18.00	23.93	15.89	24.3	40.20	41.11	58.89
200°C	18.00	44.46	5.77	54.63	60.46	78.56	21.44

Table 5.8 **Amounts of various species consumed or produced according to reactions (10) and (8)**

H_2S consumed, moles	SO_2 produced, moles	H_2SO_4 consumed, moles	S produced, moles	H_2O produced moles
$\alpha+\beta$	$4\alpha-\beta/2$	3α	1.5β	$4\alpha+\beta$

5.3.1 Analysis of the experimental data

We can analyze the data in Figures 5.8 to 5.24 to determine the step controlling the overall transfer process as follows:

Figures 5.8 to 5.11 show the effect of H_2SO_4 concentration on H_2S conversion. As can be seen H_2S conversion progressively increases to 100% at around 93 wt% H_2SO_4. This shows that reaction (7) is kinetics controlled and is in the slow reaction regime at acid concentrations below roughly 90 wt%. This is in agreement with the fact that only above 90 wt% concentration, H_2SO_4 becomes a strong oxidant. The effect of gas contact time on H_2S conversion is visible only at lower acid concentrations and is shown in Figure 5.21. We see that the H_2S conversion increases with the contact time. Also, Figure 5.23 shows that the H_2S conversion is independent of the acid flow rate from 80 to 93 wt% acid concentrations and that the liquid distribution is satisfactory in the column. SO_2 should not be observed in the exit gas for the lower acid concentrations below roughly 90 wt% acid as shown in all the graphs for SO_2 formation at lower acid concentrations. The data in Figure 5.20 are also in agreement with the fact that the H_2S conversion increases with feed gas composition at the lower acid concentrations. When the gas phase H_2S mole percent increases, $H_2S(a)$ also increases and this is reflected in increasing H_2S conversions. These arguments suggest that reaction (7) is in the slow regime for the lower acid concentration range (less than 90 wt%).

At higher acid concentrations, the H_2S conversion is almost complete and SO_2 appears in the gas phase which indicates that reaction (7) becomes either fast or instantaneous. The data do not distinguish between these two possibilities. Figure 5.23 shows that increasing the acid flow rate slightly increases the H_2S conversion. At high acid concentrations, the H_2S conversion is almost complete and so, no trend is evident. Such is the case with the effect of gas composition on the H_2S conversion as seen in Figure 5.20. Figure 5.21 is slightly contradictory because the H_2S conversion drops slightly with an increase in gas flow rate. The presence of SO_2 in the gas phase at high acid concentrations, as seen in Figures 5.12 to 5.15, shows that reaction (8) cannot be instantaneous. The SO_2 formation increases with increasing gas velocity as seen in Figure 5.22 and in Figure 5.15; however, the data in Figure 5.24 for various acid contact times are confusing. Nevertheless, it is abundantly clear that at high acid concentrations, (more than 90 wt%) reaction (7) must be falling in the fast reaction regime.

For 88 wt% acid, the effect of temperature as shown in Figures 5.16 and 5.17, indicates that the H_2S conversion remains almost steady but above 120°C, SO_2 formation increases rapidly as the temperature increases. Reaction (7) is likely to be mass transfer controlled, i.e the rate of reaction (7) is likely to be fast since the H_2S conversion is almost constant and independent of temperature. This conclusion agrees with the earlier conclusion that the rate of reaction (7) is fast at higher acid concentrations. The decrease in the solubility of SO_2 could be responsible for observing an increasing SO_2 with temperature.

5.3.2 Analysis of the acid contacting process from the theory

Analysis of the acid contacting process kinetics from theory can improve the understanding of the basic processes involved and also confirm the experimental observations. The absorption steps involved in the case of the acid contacting process can be summarized as follows:

1. Diffusion of H_2S from bulk gas phase to the gas-liquid interface.
2. Diffusion of H_2S into the bulk acid from the interface.
3. Liquid phase reaction (7) to give sulfur, SO_2(a) and water. Molten sulfur is formed in a separate liquid phase.
4. SO_2(a) reaction with H_2S(a) to give sulfur and H_2O by reaction (8).
5. SO_2(a) diffusion from the acid phase to the gas-liquid interface.
6. Desorption of SO_2(a) from interface to the gas phase.
7. Desorption of H_2O from acid phase.

Thus, the acid contacting process involves simultaneous absorption-desorption with two consecutive, two step reactions (Astarita, (1965), Shah and Sharma, (1976), Doraiswamy and Sharma, (1983) and Kastanek et al., (1992)). The available literature regarding the two-step parallel-consecutive reactions with absorption-desorption do not describe the situation encountered in the present case. In the literature analyzing such two reaction systems but without desorption of the intermediate product, the second reaction is assumed to be slow. This situation is different from that in the present case because the Wackenroder reaction is proven to be fast. Also desorption of SO_2 in the acid contacting process makes this system different from similar systems reported without desorption. Apart from this, reported systems consider only one product reactions. In the present case sulfur and water are also formed as the products. Hence, the analysis of the acid contacting process for determination of the reaction regimes is important.

Some of the salient features of the acid contacting process can be described as follows:

1. The Wackenroder reaction is proven to proceed at a fast rate (Tiwari, 1976). Reactions can occur almost entirely near the gas -liquid interface under the right conditions. In that case, hindrance to the mass transfer process due to sulfur near the interface needs to be considered. Sulfur viscosity is not a concern below 150°C. Also above 120°C, i.e the melting point of sulfur, the difference between the specific gravities of sulfur and H_2SO_4 is almost negligible. Sulfur formed in the process at 120°C is in the liquid phase. This

combined with turbulent dispersed liquid phase in a trickle flow, should make the hindrance of sulfur to the mass transfer process at the interface negligible.

2. Reaction (8), i.e. the Wackenroder reaction, is thought to proceed through ionization of both H_2S and SO_2 in water. Its rate constant is pH-dependent (Tiwari, 1976). It is reported to proceed at a very fast rate on aqueous surfaces even at mild conditions but is slow in other nonaqueous media (Andreev et al., 1970). Also, dry H_2S and SO_2 do not react. Thus, water is the essential medium of reaction and acts as a catalyst for the Wackenroder reaction. Hence, at high acid concentrations, the Wackenroder reaction may be inhibited. If SO_2 is generated in situ in the aqueous medium where H_2S is also present, as in the case of the acid contacting process, the Wackenroder reaction proceeds at a fast rate at the plane where SO_2 is generated. Also, if reaction (8) is slow, then SO_2 would always appear in the gas phase due to finite SO_2 concentration at the gas-liquid interface. This is not the case as seen from experiments. Hence reaction (8) should be very fast or instantaneous at low acid concentrations.

3. Reaction (8) occurs when SO_2 is generated by reaction (7) and hence the H_2S concentration profile is already established as shown in Figure 5.25. But it will compete with reaction (7) for H_2S. Hence reaction (8) may make the H_2S profile sharper. If reaction (8) is faster than reaction (7), it is self regulatory since it consumes H_2S to a zero level as soon as SO_2 is generated.

4. Although reactions involving desorption are generally reversible, those involved here are irreversible because sulfur transfers out of the reaction phase and SO_2 is an intermediate product.

5. Water desorption adds a degree of compexity to the situation. But the present study is not interested in desorption rates of water. The H_2SO_4 concentrations used in the experiments were high and the hygroscopicity of H_2SO_4 eliminated desorption of water to a large extent. Also, the reactions occuring in the acid phase are irreversible irrespective of the desorption of water, and the acid concentrations were independent of water loss as well. Hence water desorption phenomenon could be neglected to simplify the analysis.

6. Desorption of SO_2 can be classified as non-bubbling (Doraiswamy and Sharma, 1983), since it can be assumed that the liquid phase is never saturated with SO_2 due to reaction (8).

For the purpose of regime determination the acid concentration remains almost constant from the top to the bottom of the column in the experiments; whereas, the H_2S concentration actually becomes very small at the exit of the column. Also, the feed gas H_2S concentration is small in the experiments. The SO_2 concentration on the other hand is zero in the feed and has its maximum value, if at all, at the exit. Thus, major absorption process occurs near the top of the column and the rest of the column is needed for cleanup to the required specifications. The effect of this on reaction (7) is that for most of the column height except that near the top, it must be kinetically controlled. Similarly, reaction (8) is definitely kinetically controlled throughout most of the column because of the very low percent of H_2S in gas phase and SO_2 coming out of the liquid phase. Thus the effect of various parameters controlling the regimes is clear only due to the factors controlling the reactions near the top portion of the packed column.

For the acid contacting process, the column is presumed to operate in the trickle-flow regime in which liquid trickles along the packings and is the dispersed phase. Using the simplest phase contact theory: the two-film theory, we can make a convenient pictorial representation of the process showing the steady-state concentration profiles in space coordinates under different situations. Figures 5.25(a) and 5.25(b) show its application to the acid contacting process.

Thus we can satisfactorily explain the experimental observations on the basis of reported facts and basic understanding. Therefore, we can conclude that for lower acid concentrations (below 90 wt%), reaction (7) is slow and for high acid concentrations it is either fast or instantaneous. Reaction (8) is instantaneous at lower acid concentrations. Although reaction (8) it is reported to be fast, it may actually be slow at very high acid concentrations due to lack of water. Since reaction (8) is slower than reaction (7), and reaction (7) is fast enough at high acid concentrations (above 90 wt%), SO_2 will appear in the gas phase. The SO_2 formation will then be controlled by the same factors that control the reaction (7). As a result, SO_2 generation may have secondary importance when compared to the H_2S consumption. That is why the SO_2 curves are joined pointwise to

bring out the apparent trends; whereas, the H_2S curves are represented by regression lines in most cases. Figures 5.25(a) and 5.25(b) depict these conclusions.

5.3.2.1 Recommendations

Thus looking at all the choices, we can make a wish list of the conditions to optimize the transfer process with respect to reactions (7) and (8). But in any case, since reactions occur in the liquid phase, the interfacial area needs to be kept at the maximum value possible. Hence the contactor that disperses acid so as to achieve maximum acid interfacial area needs to be selected. Normally, packed columns with proper packings and packing materials provide such conditions.

The regime in which the column will have the smallest height will be the regime where reaction (7) is fast and reaction (8) is instantaneous. Sufficiently high acid concentrations to keep reaction (7) in the fast regime and at the same time reaction (8) in the instantaneous regime need to be found. High acid concentrations are unfavorable to reaction (8) kinetics. Even then, the acid concentrations can be increased to keep reaction (8) fast as long as reaction (7) is fast as well. Therefore, the acid concentration to be used should be about 90 wt%. The temperature should be such that sulfur does not add to the mass transfer resistance due to its phase behavior or its viscosity. Hence, the process temperature needs to be in the range of 120°C to 150°C. Reaction (8) kinetics will obviously be improved by an increase in pressure due to increased $SO_2(a)$ concentration. The same is the case with feed gas H_2S composition in case of reaction (7). The gas and liquid flow rates then can be increased to achieve better efficiencies within limits so that

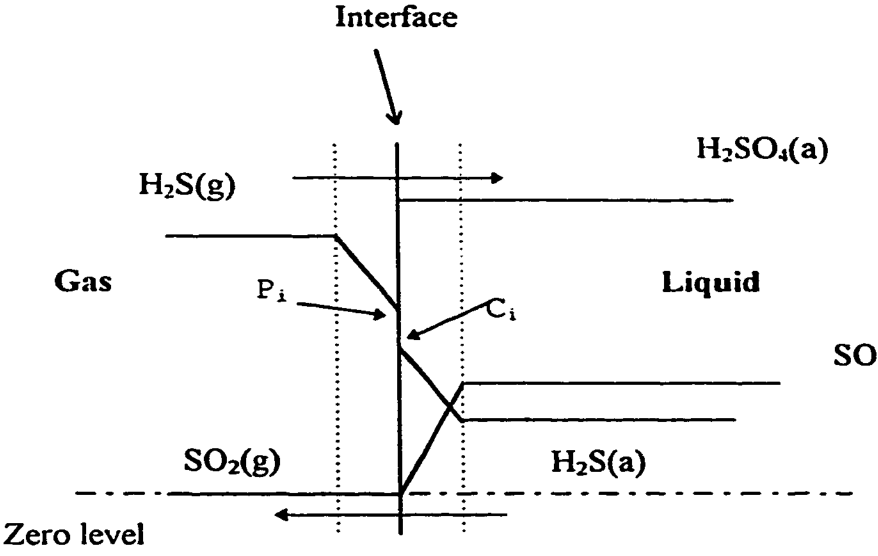

Figure 5.25(a) **Two film depiction of the acid contacting process below 90 wt% acid**

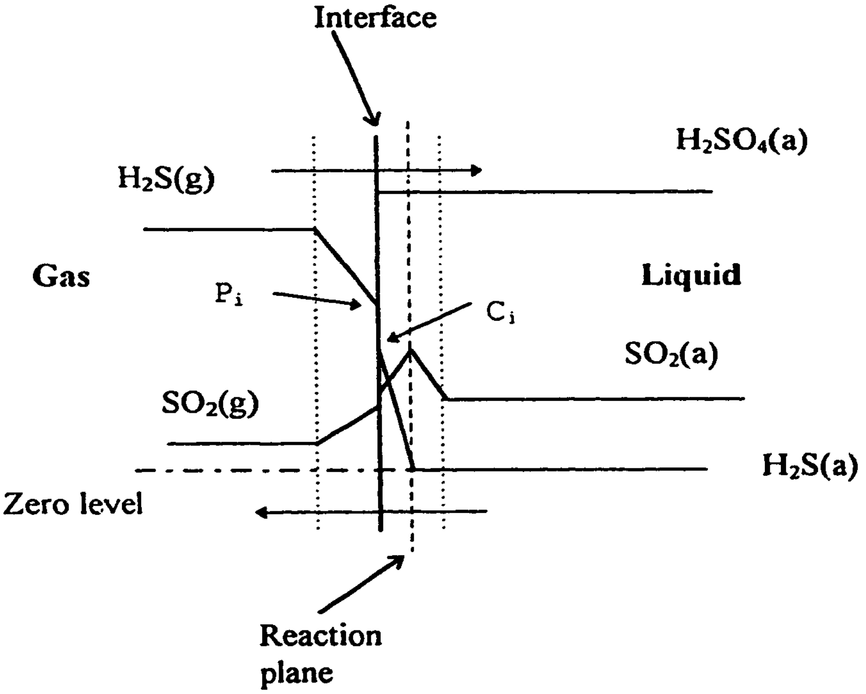

Figure 5.25(b) **Two film depiction of the acid contacting process above 90 wt% acid**

the acid recycle system does not prove costly. This situation is probably the best choice.

However, SO_2 formation in the effluent gas is still observed and if it is undesired, then the only option is to keep reaction (7) sufficiently slow so that SO_2 does not appear in the gas phase. Low acid concentrations and lean feed gas will help achieve this. In this case, the whole process becomes contact-time dependent and the longer the column, the better the performance.

From the data gathered using a very simple column, it is really not possible to confirm quantitatively which reaction regimes are dominant or which step is the controlling step in the gas absorption process. Material balances were not possible to confirm these conclusions. Hence, the above is our best view of the phenomena based upon certain assumptions.

Since this is the first time that data on the performance of the acid contacting process have been collected, the validity of the data gathered needs to be addressed.

5.4 Validity of the HSC and experimental data

As seen in chapter 3, the HSC provides a reliable database as well as capabilities for prediction of the equilibrium compositions. The crosscheck done on the H, S, C data and other published values, e.g. those of SO_2 solubility, etc. bear testimony to this fact. The HSC can handle solution nonideality, which is a major consideration in the acid contacting process and holds the advantage of speed and convenience; however, experimental verification of the HSC calculations is needed. To date, data on the acid contacting process have not been reported except for the ΔG vs. T diagram for the various reactions involved and the Eh-pH diagrams. Even this limited evidence favors the HSC program as is clear from Figures 3.9 and 2.4 and Figures 3.10 to 3.12 and 2.5. More data will, of course, be welcome to further prove the point. The results of the parametric study show that HSC can be used for nonideal inorganic systems with a fair degree of confidence and accuracy. The HSC equilibrium calculations seem to be free of random error due to the absence of scatter in the results obtained. Also the material balances agree well as seen from Tables 5.6 and 5.7. Hence this work suggests that the HSC results are reliable and representative of the equilibrium picture.

As can be seen in Appendices, F and G, the experimental data are reproducible lying well within the error bar. Most of the data points have been repeated and the difference in two repetitions is not more than 2 to 3%. The data from the various sets are consistent as well and also, when compared with the HSC results, they show consistency. At conversions less than 100%, experimental SO_2 formations are larger than those shown at equilibrium. This fits the reaction model perfectly and generates credibility. When the values of experimental SO_2 formations for 100% H_2S conversions for maximum gas liquid contact time were tested, a reasonable match with those given by the HSC calculations within the errors of the system was observed as seen in Table 5.9. But, as seen in chapter 4, the SO_2 detection sensitivity of the analytical instruments can influence such a comparison. The results also show that, within a small contact time of the order of a minute on the liquid side and half a minute on the gas side, excellent results regarding performance of this process have been achieved. Hence given enough contact time and efficient gas-liquid contact, zero H_2S emission by the acid contacting process is technically feasible.

Verification of the results given by the GC, which is the most important analytical instrument in the experimental studies, was done by using the water mole percent in the exit gas. As shown in chapter 4, the gases fed to the GC were stripped of any condensible moisture. Hence the moisture held by the gas is equivalent to the lesser of the saturation value (vapor pressure) at that ambient temperature or the partial pressure of water over acid of that particular concentration. This comparison of representative data, in Table 5.10, shows a difference between these values of water mole percentages. This may be because of the limited detection limit of the GC and possible adsorption of water on the tubing within the experiment. On the other hand, the water mole percent for the same temperature and acid concentrations in the different sets is nearly the same (Table 5.11). The GC acid gas detection limits are satisfactory and the peak separation is good. For SO_2, industrially, 500 ppm is the emission limit. So the laboratory scale detection limit for SO_2 of 3000 ppm is tolerable. There is a small overlap of H_2S and H_2O peaks at acid concentrations below 88wt%, but at lower acid concentrations, the H_2S conversions are less and the H_2S peak area is large. Hence the small error due to overlap is further reduced. So it can be concluded that the error in this principal analytical instrument was negligible and it can be said with confidence that the GC operation is devoid of any serious flaws.

We do have some notable limitations on the experimental data applicability. The experimental results were gathered in a very simple reactor column. The column was not characterized in terms of the interfacial area and flow regime. The temperature along the column was not

Table 5.9 SO_2 formation comparison between experimental and the HSC data when H_2S conversion is almost complete

Run number	Conditions	Experimental SO_2 Formation, mole%	Equilibrium SO_2 Formation, mole%
59	T=120°C, P=5 psig Feed H_2S conc. = 9 mole%, L = 70cc/m, G= 138sccm, Acid conc. = 94 wt%	0.41- **0.61**-0.74	0.36
115	T=130°C, P=5 psig Feed H_2S conc. = 9 mole%, L = 70cc/m, G= 138sccm, Acid conc. = 94 wt%	0.52-**0.65**-0.78	0.51

Table 5.10 Water mole percent comparison between experimental values and provided values in the literature

Acid Concentration wt%	Literature Value of Water Mole Percent at 120°C Over Sulfuric Acid	Experimental Value of the Mole Percent of Water Appearing in Exhaust Gases
85	1.35	0.2
90	0.42	0.004

Table 5.11 Water mole percent at the same acid concentrations and temperatures in various experimental sets

Run Number	Water Mole Percent in Exhaust Gas
45B and 49	0.4 each
80 ans 81	0.2 each
121B and 124B	0.1 each
135 and 136	0.21 each

monitored although this could be neglected because the contact time was quite small in the short column. The column was not designed to provide a particular gas-liquid contact pattern. It was designed to provide the acid and gas certain contact times in a continuous flow manner. Also, since the experimental results were based on gas phase calculations, a precise interpretation involving liquid phase calculations, e.g. reaction stoichiometry, was not possible. This confirmation should be considered in future work.

To prove the range of variation in the data due to experimental limitations, an error analysis was carried out. Generally, the experimental results are a function of several experimental variables. The cumulative effect of errors in the measurement of these variables may result in an overall error in the experimental results. The results of the experiments were represented by including an estimate of this error. Typically the error is shown as the error bar bounding the calculated results. In the acid contacting experiments, the results are shown as percent H_2S conversion and percent SO_2 formation. The following is a list of the system variables on which these results depend:

A. Gas side:

1. Mass flow meter tolerances and calibrations, 2. Pressure gauge sensitivity, 3. System pressure variation, 4. Gas-liquid contacting inside the reactor, 5. Temperature variation in the reactor and the ambient temperature, 6. Condensation of water vapor along the lines, 7. GC sensitivity, 8. GC detection limit and separation of gas components.

B. Liquid side:

1. Acid pump calibration and resulting acid flow variations, 2. Acid concentration, 3. Change in acid concentration along the column, 4. Acid phase dispersion on the packings, 5. Temperature distribution along the column.

Thus the number of variables are many and unfortunately an error estimation in case of the most important variables is difficult due to experimental limitations and other constraints. Moreover, the kinetics of the reactions involved and mass transfer parameters such as interfacial area are unknown. This makes it impossible to relate the variations in many system variables to the results; hence, only a rough estimate of the possible errors in the final results is possible. Typically in a packed column with sulfur systems, the data variation is ±10 to 15% (Doraiswamy and Sharma, 1983). The percentage area method used in the case of GC eliminated the common GC inaccuracies, since the product mole percentages were calculated with respect to the calibrated gas GC areas. The cumulative instrument error, in the case of the analytical instruments we employed was therefore less than 2 to 3%. Hence, an error of ±15 to 20% was assumed in the unprocessed data gathered, shown in the experimental results of Figures 5.8 to 5.24. The data in Figure 5.11 is joined point wise rather than by the regression lines to avoid interference between various plots.

5.5 Intellectual property rights and proprietary issues

Since the acid contacting process has not been developed for sour gas purification previously, it deserved a consideration for protection through patent application. From this view point the essential differences in this process and some closely resembling references are brought out next so as to make the acid contacting process standout as novel.

The reactions involved in the acid contacting process as such are not new. They were known for almost one and half centuries (Bussy and Buigne, 1864, Wood, et al., 1924, Milbauer, 1937 and Stashchuk, et al., 1970). The kinetics of the reaction between H_2S and H_2SO_4 have not been studied and the exact reactions involved in this process have not been established. This acid contacting process has never been appplied to gas purification.

The patent by Torrence (1975) perhaps deserves close scrutiny. He has patented a process, with the objective to remove oxides of sulfur from flue gas streams. The reactions involved use carbon as an adsorbent for sulfur oxides and as a catalyst for oxidizing sulfur oxides to SO_3 and to retain adsorbed H_2SO_4 formed from reaction of the SO_3 with water vapor. Sulfuric acid is reduced by reaction with H_2S to give a sulfur and SO_2 mixture. Even this reaction requires carbon as a catalyst. In our case no such catalyst is needed. Only liquid water is needed as the medium of reaction. Our reaction system involves an additional reaction called the Wackenroder reaction which converts SO_2 to sulfur. This reaction is not possible on charcoal, as tested in our laboratory, thus obviating any chance of it being employed in Torrence's patent. Hence the objective as well as the reactions underlying the phenomena are totally different. We have studied the effect of acid concentration on optimizing the conditions for maximum sulfur recovery. Torrence studied the effect of temperature alone on the H_2SO_4 reduction and on the resultant S-SO_2 mixture composition. He used very high temperatures in his process (570°F and up) whereas we have used very moderate temperatures (250°F to 300°F) in our studies. Definitely, recovery of sulfur was not an objective for him as sulfur would have proved a strong poison for his carbon-catalyzed process; whereas, utility of carbon in our process is unwelcome. Hence the two processes are dissimilar and have different objectives. Our process is novel and only it has the potential for a one-step H_2S absorption and sulfur recovery from lean sour gases.

5.6 Socio -economic potential

Acid contacting process should be applicable in the following areas:

1. It can remove water vapor from gases. Thus it has the utility in the Claus plants for additional sulfur recovery by improving Claus plant performance through shifting the equilibrium to the right.

2. For gases containing a relatively small percentage of H_2S (up to 10 mole%) this process should prove economical as compared to conventional processes described in chapter 2. This is because other liquid phase oxidation processes require costly reagents and down stream oxidization of the reduced reagents. The acid contacting process requires cheaper feedstock and should have a simpler process flow diagram because of a simple acid recycle system. The

gases that can be processed by the acid contacting process include lean natural gases, various off gases etc.

3. The process offers one step gas sweetening and sulfur recovery. Since the technology of hot, concentrated H_2SO_4 handling already exists, this process should be attractive to the sour gas processing industry.

4. This process offers a practical way to treat the natural gas at well head pressures since high pressure is beneficial to the performance of this process. The gas coming from the wells can be sweetened at the well head prior to entering the distribution system.

Chapter 6

Summary and Recommendations

6.1 Summary

A new one step process for sulfur recovery called as 'the Acid Contacting Process" has been developed on a laboratory scale. The process involves a one step conversion of H_2S to the value added sulfur and SO_2 by reaction with concentrated H_2SO_4. The oxidative and hygroscopic behavior of concentrated H_2SO_4 has been used in this process. Complete conversion of H_2S without SO_2 formation can be achieved under certain conditions.

> Now is not the time to think of what you do not have.
> Think of what you can do with what there is.
>
> Ernest Hemingway

This had been the guiding principle throughout the work carried out in this thesis. The data and interpretations represent the best of what could have been achieved in the limit of the available equipment. But even then the data collected have signal merits. It is very reproducible. Most of the data points have been repeated and the difference in two repetitions is below 2 to 3%.

A cause effect analysis of the process in a continuous flow system using a cocurrent downflow packed contactor brought out the performance of the process in terms of the H_2S removal efficiency and SO_2 formation in relation to various process variables. The process variables investigated experimentally were, 1. Feed acid concentration, 2. Feed gas composition, 3. Temperature 4. Gas contact time and 5. Acid contact time.

The applicability of the data is restricted to only judging the performance of the process and the data are too limited to build a quantitative kinetic expression. The trends shown by the data have wider meaning than their absolute values. In this respect research carried so far will work as the proof of the performance of the acid contacting process .

Figures 5.18, 5.19 and 5.20 show that zero SO_2 formation with complete H_2S conversion is possible by the acid contacting process in the laboratory. Thus for such a short contact time; of the order of a minute on the liquid side and half a minute on gas side at the most, excellent results regarding performance of this process were achieved. This shows that given enough contact time and efficient gas-liquid contact, zero emission of H_2S and SO_2 is industrially feasible. Hence the most obvious outcome of this research is the success of the acid contacting process and appreciation of its potential for industrial application. The optimum conditions for zero emission of H_2S and SO_2 could be experimentally achieved by

1. Using acid concentration less than or about 90 wt%.
2. Using low temperature preferably between 120°C and 150°C.
3. Increasing feed gas H_2S mole % moderately
4. Maximizing gas contact time and
5. Minimizing liquid phase contact time

Equilibrium simulations support these conclusions. Also the HSC equilibrium simulations show that this goal of zero acid gas emission is favored at high pressures.

The stoichiometry of the process was defined by the following redox reactions:

$$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O ...... \Delta H_{120C} = 23.9\ \text{kcal/mole} ...... (7)$$

$$2\ H_2S + SO_2 = 3\ S + 2\ H_2O .... \Delta H_{120C} = -51.8\ \text{kcal/mole} .... .(8)$$

As can be seen this process has inherent ability to achieve zero emission since SO_2 is the intermediate product. Depending upon the acid concentration, the process seemed to be kinetically controlled or in the fast regime as far as reaction (7) is concerned. Reaction (8) was observed to be either in the instantaneous or fast reaction regime. The later regime is likely at high acid concentrations due to less water being available since water acts as the medium of reaction for reaction (8).

In the course of evaluation of this process, an indirect fallout is the test on the performance of the HSC simulation software. As has been found, the HSC is very reliable in terms of database and the calculation capabilities for inorganic chemicals. Its limitations are no more than those of the manual equilibrium calculations. It, however, holds several advantages over manual calculations due to speed, convenience and versatility.

6.2 Future course

Successful research gives birth to questions besides solutions. Likewise, several venues of potential research have come up. They must be pursued in earnest to exploit this process fully. Research in two parallel directions is required. One for applied development and the other for fundamental understanding. Applied objectives include:

1. Better analysis of the data collected needs to be done. This includes the waste acid concentration determination and accurate measurement of the sulfur formed. To achieve reliable data in this respect, a representative sample of the acid coming out of the reactor needs to be collected. This may be done by installing an online acid sample valve to draw a proper sample. This will help determine the reaction stoichiometry, reaction regimes etc. from material balance point of view. Also the perfect separation of water and H_2S peaks in GC output at low acid concentrations needs to be achieved. Currently the peaks overlap slightly. This may need the replacement of the GC column and reoptimization of the GC conditions for the new column.

2. Pilot plant evaluation is very important for development of quantitative relationships and scale up. Since the type of column used in the laboratory worked nicely, similar but well characterized columns should be used in a pilot plant. Different contacting devices like a stirred cell which minimizes the concentration of the intermediates are worth a try.

3. Effect of various other acid gases on the performance of this process and applicability of this process in removal of other acid gases need to be seen. This includes gases such as COS, CS_2, CO_2 etc.

4. Kinetics of the reactions involved in the acid contacting process need to be established.

5. Quick sulfur recovery from the product acid slurry is needed. The sulfur produced is CS_2 insoluble and high grade. Its value needs to be tapped. Apart from that the acid thus cleaned can be recycled. There is also a requirement to find the right feed acid concentration at which water balance occurs in such a way that concentration of the acid at exit is the same as that of feed acid. This will allow substantial savings in as much as the make-up H_2SO_4 requirement and processing of the spent acid are concerned.

6. Industrial feasibility of the process is possible through cost analysis. The cost comparison between other liquid phase redox processes and the acid contacting process would need pilot scale performance of this process. Hence such feasibility studies must be undertaken as soon as a pilot scale data become available. In this respect, the acid contacting process may face competition from processes such as the LO-CAT process. The acid contacting process may hold an advantage over other such processes due to the possibility of a cheaper recycling operation apart from cheaper reagents. In the acid contacting process, H_2SO_4 is consumed unlike other redox processes where the reagents are reduced. Therefore, acid recycling in the acid contacting process should involve only a makeup acid addition process instead of expensive large oxidization units as used in other liquid redox processes.

Fundamental development will, definitely, abate the applied objectives. The following should be undertaken in this direction:

1. Reaction steps involved at high temperatures need to be established. Excited state sulfur may be a possibility which may be formed as an intermediate in this process and its effect on the performance of the process should be understood.
2. There can be several intermediate elementary steps involved in the two overall reactions we have identified. There can be several intermediates. The rate constant, k_c of the Wackenroder reaction depends on acid concentration in the range of 80 - 98wt% acid. Existence of intermediates has been proved in this reaction. The proper understanding of such complexes can improve the performance of this process. Hence understanding the mechanism of these reactions is important.
3. Confirmation of HSC data by experiments will improve confidence in this software as well as the calculations performed.

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Appendix

A

Chemical reactions involved in this thesis

$H_2S + 1/2\ O_2 = S + H_2O$ ……(1)

$H_2S + 3/2\ O_2 = SO_2 + H_2O$ ……(2)

$2\ H_2S + SO_2 = 3/n\ S_n + 2\ H_2O$ ……(3)

$H_2S + CO_2 = CO + H_2O + 1/2\ S$ ……(4)

$CO + H_2O = CO_2 + H_2$ ……(5)

$3\ H_2S + H_2SO_4 = 4\ S + 4\ H_2O$ ……(6)

$H_2S + H_2SO_4 = S + SO_2 + 2\ H_2O$ ……(7)

$2\ H_2S + SO_2 = 3\ S + 2\ H_2O$ ……(8)

$2\ H_2S^* + SO_2 = 2\ S^* + S + 2\ H_2O$ ……(8a)

$S + 2\ H_2SO_4 = 2\ H_2O + 3\ SO_2$ ……(9)

$H_2S + 3\ H_2SO_4 = 4\ SO_2 + 4\ H_2O$ ……(10)

$3\ Na_2SO_3 + 2\ S^* + S = 2\ Na_2S^*SO_3 + Na_2S_2O_3$ ……(11)

$H_2S + SO_2 = H_2S_2O_2$ ……(12)

$H_2S_2O_2 = H_2SO_2 + S$ ……(13)

$H_2SO_2 + H_2S = H_2S_2O + H_2O$ ……(14)

$H_2S_2O = S_2(2S) + H_2O$ ……(15)

$H_2S + SO_2 + 1/2\ O_2 = H_2S_2O_3$ ……(16)

$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$ ……(17)

$HSO_4^- + H_2O = H_3O^+ + SO_4^{2-}$ ……(18)

$H_2S(a) = H^+(a) + HS^-(a)$ ……(19)

$H_2SO_4 + 2\ NaOH = Na_2SO_4 + 2\ H_2O$ ……(20)

$H_2 + S = H_2S$ ……(21)

$H_2 + 1/2\ O_2 = H_2O$ ……(22)

$S + O_2 = SO_2$ ……(23)

$H_2 + S + 2\ O_2 = H_2SO_4$ ……(24)

$S + H_2O = H_2S + 1/2\ O_2$ ……(25)

$S + 3/2\ O_2 + H_2O = H_2SO_4$ ……(26)

$3\ S + 2\ H_2O = 2\ H_2S + SO_2$ ……(27)

$4\ S + 5\ H_2O = 3\ H_2S + H_2SO_4$ ……(28)

Appendix

B

Equations and formulae involved in this thesis

$$\frac{d[H_2S]}{dt} = -k_c A_i [H_2S][SO_2] \tag{1}$$

$$C_p = A + B \bullet 10^{-3} \bullet T + C \bullet 10^{5} \bullet T^{-2} + D \bullet 10^{-6} \bullet T^{2} \tag{2}$$

$$H^0(T) = H_f(298) + \int_{298}^{T} C_p(T)dT + \sum H_{tr} \tag{3}$$

$$S^0(T) = S^0(298) + \int_{298}^{T} (\frac{C_p}{T})dT + \sum \frac{H_{tr}}{T_{tr}} \tag{4}$$

$$G^o = H^o - T \bullet S^o \tag{5}$$

$$R \bullet \ln X_i = 1.987 \bullet \ln(1/55.51) = 7.981 \text{ cal/mole} \bullet K \tag{6}$$

$$aA + bB = cC + dD \tag{7}$$

$$\begin{aligned} \Delta H_r &= \Sigma\, \nu_i H_i (\text{ Products}) - \Sigma \nu_i H_i (\text{Reactants}) \\ &= (c^* H_C + d^* H_D) - (\, a^* H_A + b^* H_B) \end{aligned} \tag{8}$$

$$\begin{aligned} \Delta S_r &= \Sigma\, \nu_i S_i (\text{ Products}) - \Sigma\, \nu_i S_i (\text{Reactants}) \\ &= (c^* S_C + d^* S_D) - (\, a^* S_A + b^* S_B) \end{aligned} \tag{9}$$

$$\begin{aligned} \Delta G_r &= \Sigma\, \nu_i G_i (\text{ Products}) - \Sigma\, \nu_i G_i (\text{Reactants}) \\ &= (c^* G_C + d^* G_D) - (\, a^* G_A + b^* G_B) \end{aligned} \tag{10}$$

$$K = \frac{[a_C]^c [a_D]^d}{[a_A]^a [a_B]^b} \tag{11}$$

$$\ln(K) = \Delta G / (-RT) \tag{12}$$

$$\text{Activity, } a = (\text{P.P. over } H_2SO_4 \text{ solution}) / (\text{V.P. over pure } H_2O) \tag{13}$$

$$\text{Activity coefficient, } \gamma = (\text{Activity}) / (\text{mole fraction of } H_2O) \tag{14}$$

$$P_1 v_1 / T_1 = (P_2 - P_o) v_2 / T_2 \tag{15}$$

$$R.F._x = CMP_x / CGCA_x \tag{16}$$

$$MP_x = (GCA_x * R.F._x) * 100 / (\, \Sigma\, GCA_x * R.F._x) \tag{17}$$

$$X + Y = 5 \text{ liter} \tag{18}$$

$$0.85 = X * 1.8355 * 0.96 / (\, X * 1.8355 + Y) \tag{19}$$

$$N_{H2SO4} * V_{H2SO4} = N_{NaOH} * V_{NaOH} \tag{20}$$

$$N_{H2SO4} = N_{NaOH} * V_{NaOH} / V_{H2SO4} = m \tag{21}$$

$$o = n * 1000/50 \text{ gram} \tag{22}$$

$$\text{Acid concentration in wt\%} = (o/a) * 100 \tag{23}$$

Appendix

C

Calibration of the process pumps

The pumps used for oil and acid pumping were calibrated to find the flow rates at set pump controllers. The temperatures used during calibration were same as those used during the actual experiments. Temperature of oil used during calibration was 180°C and that of acid used was 100°C. Pressure used during the acid pump calibration was same as the pressure used during the experiments i.e. 5 psig.

The flow rates were measured several times and the average of them was used as the final value. The volumes of the acid and oil collected during flow measurements were adjusted properly.

C-1 Oil pump

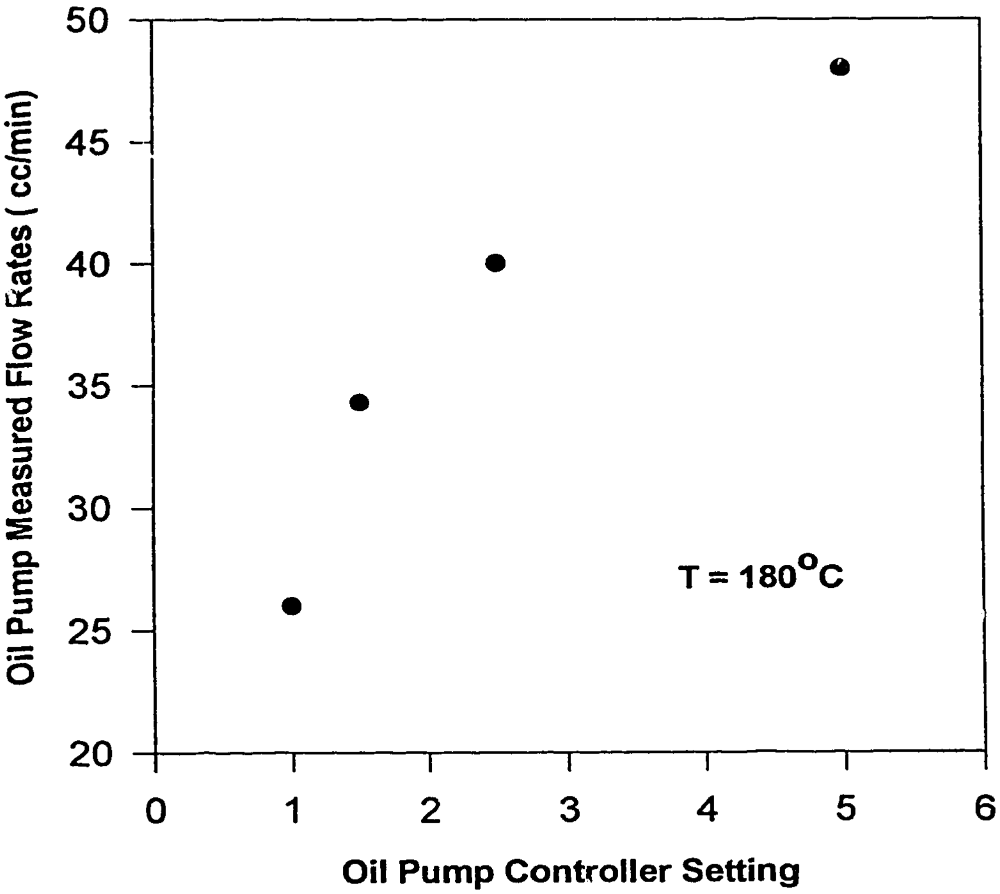
T= 180°C

Controller setting	Average flow rate, cc/min
1	26
1.5	34.3
2.5	40
5	48

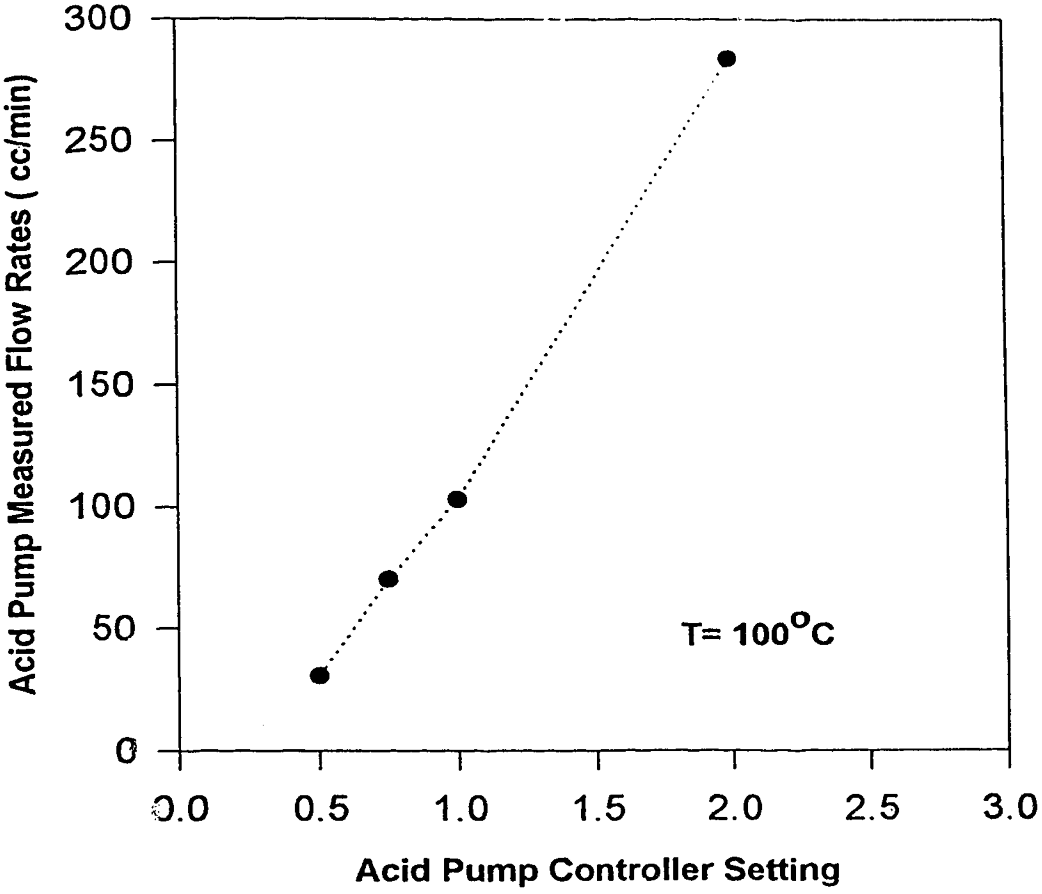
C-2 Acid pump

T = 100°C, P = 5 psig

Controller setting	Average flow rate, cc/min
1	30.71
1.5	70.19
2.5	103.18
5	283.93



Appendix C-1 Oil pump calibration



Appendix C-2 Acid pump calibration

Appendix

D

Calibration of the mass flow meters

The mass flow meters were calibrated during each run in order to find the exact response factors for various gases used.

They were calibrated in order to find the actual flow only once.

The amount of gas flowing was measured by the soap film meter several times and the average of the flow rate was used as the actul flow rate corresponding to the set flow rate reading.

The volumes measured were corrected for the partial pressure of the water vapor by using the formulae mentioned on page 76 in chapter 4.

The standard conditions are 21.1°C and 760 mm Hg.

D-1 N_2 mass flow meter

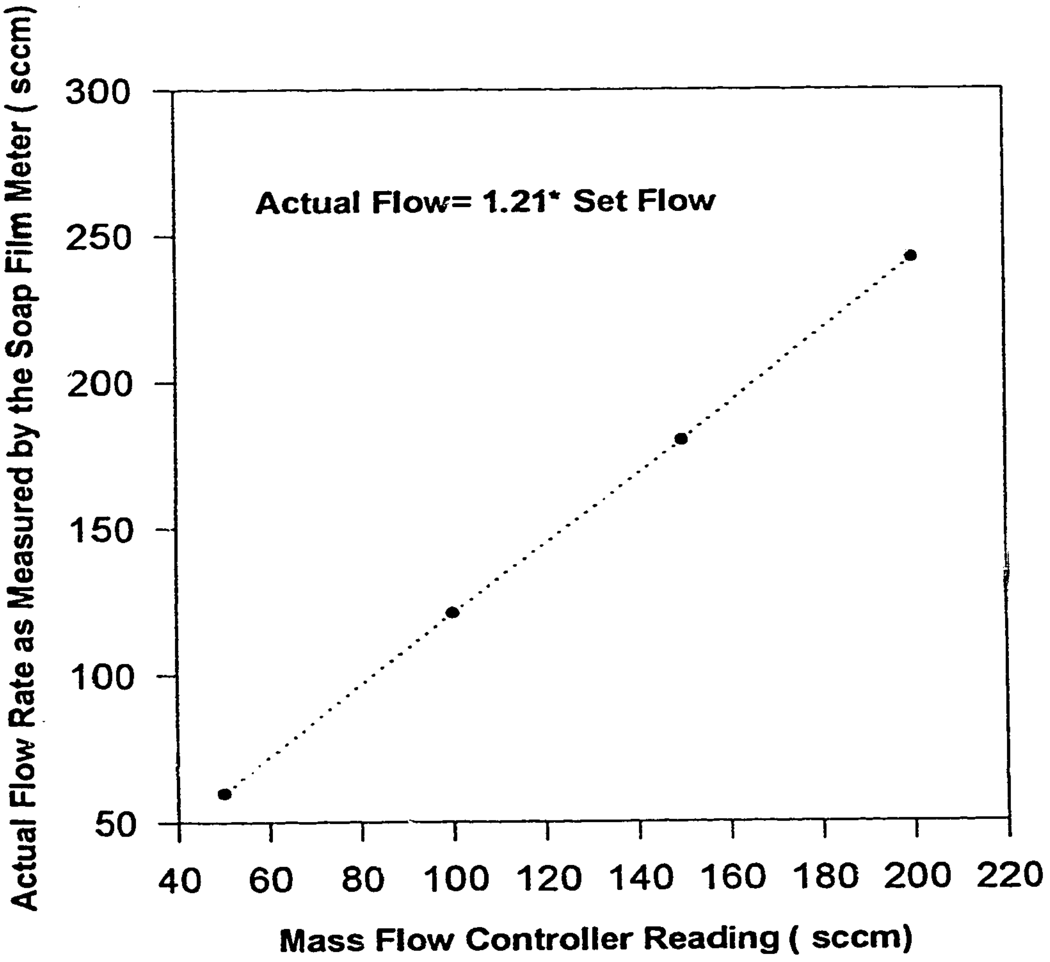
Mass Flow Meter Setting	Actual Average Flow Rate, Standard cc/min
50	60
100	121
150	180
200	242

D-2 H_2S mass flow meter

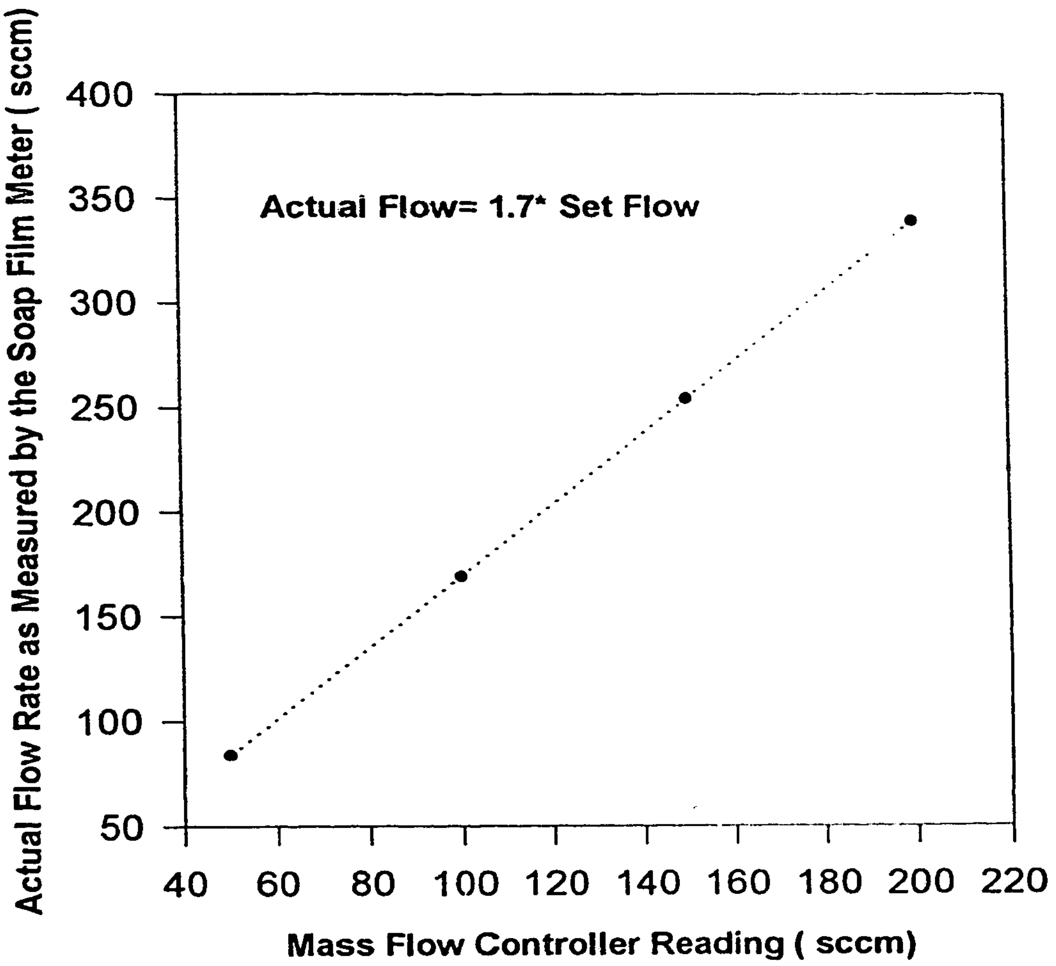
Mass Flow Meter Setting	Actual Average Flow Rate, Standard cc/min
50	84
100	169
150	254
200	339

D-3 SO_2 mass flow meter

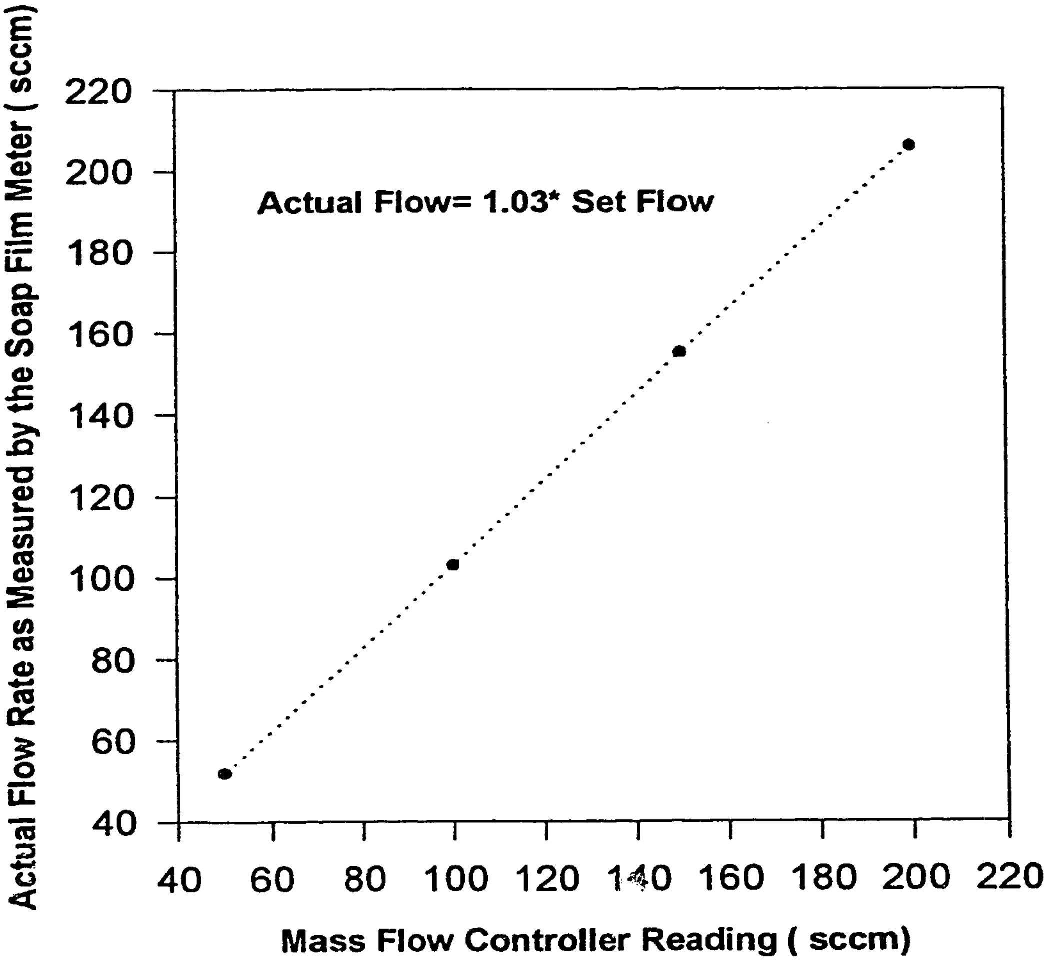
Mass Flow Meter Setting	Actual Average Flow Rate, Average cc/min
50	52
100	103
150	155
200	206



Appendix D-1 N_2 mass flow meter calibration



Appendix D-2 H_2S mass flow meter calibration



Appendix D-3 SO_2 mass flow meter calibration

Appendix

E

Sample data sheet used during each experimental evaluation

EXPERIMENTAL DATA SHEET

DATE 19.11.94 BY Mohan, Qinglin
RUN NO. 81

ROOM T 21 C
ROOM P 692 mm Hg

CYLINDER DELIVERY PRESSURE
i) He 70 psig
ii) N2 30 psig
iii) H2S 30 psig
iv) SO2 40 psig

PURPOS To get reproducible intermediate points on the conversion- acid concentration plot.

RUN CONDITIONS

ACID VOLUME TAKEN FOR THE BATCH = 4.5 lit
INLET ACID CONCENTRATION = 0.04 N, wt% = 84
OUTLET ACID CONCENTRATION = 0.07 N, wt% = 83.53

ACID FLOW RATE = 70.00 cc/min -0.75
TOTAL GAS FLOW RATE = 191.19 sccm
G / L RATIO = 2.73 scc/cc

T in = 120 C
T out = 120 C
P in = 3.5 psig P out = 5 psig

OIL FLOW RATE = 26 cc/min -1
T1 = 140 C
T2 = 138 C

GC CONDITIONS

Column = Hay Sep - DB
Bridge Current = 180 mA
Oven T = 120 C
Detector T = 135 C
Attenuation = 4

He flow rate = (cc/mi 30
He pressure = (psig) 70

FEED GAS ANALYSIS

Component	GC area average	MFM setting sccm	Actual Flow sccm	Actual mole %	R.F.
H2S	135742.3	10	16.96	8.87	6.53E-05
SO2	0	0	0	0	4.93E-05
N2	1230462	144	174.2256	91.13	7.41E-05
H2O	0	0	0	0	6.97E-06

PRODUCT GAS ANALYSIS
DETAILED OBSERVATIONS

T in	T out	GC AREA IN PRODUCT GAS				H2S:N2	H2O:N2
C	C	H2S	SO2	N2	H2O	RATIO	RATIO
120	120	104304	0	1239274	28719	0.08	0.02
120	120	101010	0	1254337	31730	0.08	0.03
120	120	100438	0	1261004	25829	0.08	0.02
120	120	111471	0	1257734	29775	0.09	0.02
121	120	104305.8	0	1253087	29013.25	0.08	0.02

AVERAGE

	MOLE % IN RODUCT GAS			
	H2S	SO2	N2	H2O
	6.89	0.00	92.91	0.20
	6.61	0.00	93.17	0.22
	6.55	0.00	93.27	0.18
	7.23	0.00	92.56	0.21
AVERAGE	6.82	0.00	92.98	0.20

RESULTS BASIS IS 100 MOLES PER MINUTE OF FEED GAS

H2S IN = 8.87 moles/min H2S OUT 6.68 moles/min

SO2 IN = 0.00 moles/min SO2 OUT 0.00 moles/min

H2S CONVERSION 24.64 %

SO2 SELECTIVITY 0.00 %

H2SO4 CONSUMED 0.00 gm/gm H2S introduced
0.01 gm/gm H2S reacted
0.85 gm/100g S produced

CALCULATIONS

N2 IN = N2 OUT = 91.13 moles /min
TOTAL GAS MOLES OUT= 98.01 moles/min
H2S OUT= 6.68 moles/min
SO2 OUT= 0.00 moles /min
H2S CONVERSION= 24.64 %
SO2 SELECTIVITY= 0.00 %

Appendix

F

Raw data

The data collected during each experimental run is presented here. The emphasis is on the consistency and reproducibility of the data. Many runs were repeated. Some runs were not repeated because the data was consistent with rest of the data during each set.

SET 1	To observe the effect of H_2SO_4 concentration on H_2S conversion and SO_2 emission							
Conditions	Run No.	Acid Conc. wt%	Component GC Area in Product Gas Mixture				Gas	Response Factor
			H_2S	SO_2	N_2	H_2O		
1.1								
H_2S in = 9 mole% T = 120°C, P = 5 psig L = 70 cc/min G = 191 sccm G/L= 2.73	45A	81.50	383931	0	1464439	51326	H_2S	2.02E-05
			385776	0	1448744	44226	SO_2	5.09E-05
			382451	0	1497748	55654	N_2	6.34E-05
	Average		386588	0	1470749	47704	H_2O	6.97E-06
	45B	81.50	113467	0	1570854	50111	H_2S	6.10E-05
			124844	0	1534310	61947	SO_2	5.09E-05
			127355	0	1531512	51381	N_2	5.99E-05
	Average		126065	0	1536956	57696	H_2O	6.97E-06
	81	84.00	104304	0	1239274	28719	H_2S	6.53E-05
			101010	0	1254337	31730	SO_2	4.93E-05
			100438	0	1261004	25829	N_2	7.41E-05
			111471	0	1257734	29775	H_2O	6.97E-06
	Average		104306	0	1253087	29013		
	79	86.70	63776	0	1114977	15615	H_2S	7.99E-05
			63613	0	1110787	17108	SO_2	4.93E-05
			63907	0	1098138	18690	N_2	9.01E-05

	Average		31883	0	553984	8569	H_2O	6.97E-06
	83	87.50	43233	0	1144663	6050	H_2S	6.33E-05
			43858	0	1126090	8804	SO_2	4.93E-05
			44620	0	1122015	7789	N_2	8.54E-05
	Average		44564	0	1128968	8129	H_2O	6.97E-06
	71	89.00	38238	0	1244987	11288	H_2S	7.47E-05
			36434	0	1252271	11196	SO_2	4.84E-05
			37027	0	1255582	9664	N_2	7.74E-05
	Average		37411	0	1259731	9953	H_2O	6.97E-06
	88	89.50	31905	0	1141552	5859	H_2S	6.33E-05
			30742	0	1150284	5911	SO_2	
			31119	0	1120804	6464	N_2	8.54E-04
	Average		31037	0	1138946	6251	H_2O	6.97E-06
	52	90.50	21508	1343	1829794	7723	H_2S	5.51E-05
			17448	584	1870889	14029	SO_2	6.49E-05
			19752	2750	1862557	11531	N_2	5.19E-05
	Average		19569	1559	1854413	11094	H_2O	6.97E-06
	77	91.50	20574	14878	1800697	6538	H_2S	5.18E-05
			20301	13050	1798933	8012	SO_2	4.93E-05
			20697	17502	1780615	6546	N_2	5.26E-05
	Average		20524	15143	1793415	7032	H_2O	6.97E-06

	56	92.20	23724	23684	2210538	0	H_2S	1.13E-05
			23194	24932	2206618	0	SO_2	3.37E-05
			24318	21327	2291957	0	N_2	4.18E-05
	Average		23778	21575	2234875	0	H_2O	6.97E-06
	55	93.50	9176	20280	2212974	0	H_2S	1.13E-05
			9038	17307	2172202	0	SO_2	3.37E-05
			9582	27950	2238942	0	N_2	4.18E-05
	Average		9265	21846	2208039	0	H_2O	6.97E-06
	57	95.50	4609	22850	1969903	0	H_2S	5.18E-05
			6116	26898	1982986	0	SO_2	3.99E-05
			5493	14419	1970772	0	N_2	5.02E-05
	Average		6724	24250	1968250	0	H_2O	6.97E-06
	50A	97.00	5024	26271	1661548	0	H_2S	2.50E-06
			8208	24967	1600324	0	SO_2	5.86E-05
			6005	19344	1629989	0	N_2	5.99E-05
	Average		5508	24194	1637873	0	H_2O	6.97E-06
	50B	97.00	1354	20066	1367732	0	H_2S	7.48E-05
			909	20084	1341419	0	SO_2	6.49E-05
			1414	20049	1316806	0	N_2	7.31E-05
	Average		1225	20066	1339986	0	H_2O	6.97E-06
1.2								

G = 138 sccm G/L = 1.97	49	81.50	122304	0	1296148	58834	H_2S	6.15E-05
			122233	0	1293465	59486	SO_2	0.00
			116269	0	1294502	53681	N_2	7.20E-05
			121646	0	1289659	60374	H_2O	6.97E-06
	Average		120613	0	1293444	58094		
	82	87.60	38454	0	1212554	9211	H_2S	6.33E-05
			37461	0	1186238	8644	SO_2	
			37539	0	1162629	8784	N_2	8.54E-05
	Average		37213	0	1184437	8254	H_2O	6.97E-06
	60	89.05	39915	0	1887673	6955	H_2S	5.04E-05
			36180	0	1884072	9207	SO_2	5.18E-05
			33642	0	1884799	10560	N_2	5.05E-05
	Average		36579	0	1885515	8907	H_2O	6.97E-06
	87	89.50	23758	0	1155720	7237	H_2S	6.33E-05
			22843	0	1157246	6708	SO_2	
			23677	0	1156810	6275	N_2	8.54E-05
	Average		23005	0	1158419	6696	H_2O	6.97E-06
	54	89.75	22350	0	1833337	5994	H_2S	5.51E-05
			28194	0	1848006	6693	SO_2	6.49E-05
			23785	0	1874206	3842	N_2	5.19E-05
	Average		24776	0	1851850	5510	H_2O	6.97E-06
	76	91.45	22100	11688	1794103	9217	H_2S	5.18E-05

			21403	11057	1830043	8597	SO_2	4.93E-05
			17587	11743	1772242	7686	N_2	5.26E-05
	Average		20363	11496	1798796	8500	H_2O	6.97E-06
	59	93.75	0	11457	1929047	2235	H_2S	5.04E-05
			0	10656	1884185	2498	SO_2	5.18E-05
			982	11988	1879931	2705	N_2	5.05E-05
	Average		321	11329	1890446	2641	H_2O	6.97E-06
	51	97.00	0	14536	1346778	0	H_2S	7.48E-05
			0	18201	1332337	0	SO_2	6.49E-05
			0	17913	1336166	0	N_2	7.31E-05
	Average		0	18057	1334252	0	H_2O	6.97E-06
1.3								
G = 96 sccm G/L = 1.37	80	84.00	86577	0	1260773	30427	H_2S	6.53E-05
			89964	0	1267430	31310	SO_2	4.93E-05
			86786	0	1269812	32941	N_2	7.41E-05
	Average		87141	0	1264373	31865	H_2O	6.97E-06
	78	86.70	46693	0	1214004	13100	H_2S	7.99E-05
			48065	0	1150057	16298	SO_2	4.93E-05
			48623	0	1150787	17294	N_2	9.01E-05
			49673	0	1157508	19324	H_2O	6.97E-06
			45491	0	1133843	16131		
	Average		47709	0	1161240	16429		

	85	87.50	25556	0	1119315	6414	H_2S	6.33E-05
			24148	0	1131611	7524	SO_2	
	Average		24852	0	1125463	6834	N_2	8.54E-05
							H_2O	6.97E-06
	86	89.50	16697	0	1162637	6178	H_2S	6.33E-05
			17414	0	1161415	7045	SO_2	
			18233	0	1164575	5618	N_2	8.54E-05
			18611	0	1160683	6316	H_2O	6.97E-06
			17899	0	1157572	5447		
	Average		17781	0	1161376	6121		
	68	90.50	15424	0	1359056	1850	H_2S	7.47E-05
			10513	0	1365542	1071	SO_2	4.84E-05
			14943	0	1345231	6933	N_2	7.74E-05
			16730	0	1334239	9383	H_2O	6.97E-06
	Average		14403	0	1351017	4809		
	75	91.45	15006	8741	1781636	6624	H_2S	5.18E-05
			13957	9834	1816639	8463	SO_2	4.93E-05
			16995	9998	1838597	8135	N_2	5.26E-05
			15042	9236	1808136	7771	H_2O	6.97E-06
	Average		15250	9452	1811252	7748		
	51	94.75	5290	10156	1579706	789	H_2S	5.75E-05
			2134	9589	1597600	1171	SO_2	4.84E-05

Conditions	Run No.	Temp.	Component GC Area in Product Gas Mixture				Gas	ResponseFactor
			7730	11567	1618431	1885	N_2	5.94E-05
			965	11235	1601115	0	H_2O	6.97E-06
			1416	10457	1627809	1358		
			424	11894	1599941	1569		
			2462	10582	1590603	3427		
	Average		2917	10780	1602172	1457		
SET 2	**To observe the effect of temperature on H_2S conversion and SO_2 emission**							
Conditions	Run No.	Temp.	Component GC Area in Product Gas Mixture				Gas	ResponseFactor
		Deg C	H_2S	SO_2	N_2	H_2O		
2.1A								
H2S in = 9mole% P = 5 psig L = 70 cc/min G = 191sccm G/L = 2.73 Acid Conc. wt% = 88	106	100.00	34977	0	1641343	0	H_2S	5.69.E-5
			34541	0	1701627	0	SO_2	5.92 E-5
			34230	0	1705891	0	N_2	5.57 E-5
	Average		34583	0	1682954	0	H_2O	6.97 E-6
	104	110.00	32765	0	1674283	0	H_2S	5.69E-5
			32087	0	1665442	0	SO_2	5.92E-5
			32437	0	1672332	0	N_2	5.57E-5
	Average		32430	0	1670686	0	H_2O	6.97E-6
	71	89.00	38238	0	1244987	11288	H_2S	7.47E-05
			36434	0	1252271	11196	SO_2	4.84E-05

		37027	0	1255582	9664	N_2	7.74E-05
Average		37411	0	1259731	9953	H_2O	6.97E-06
94	125.00	33721	0	1209062	10046	H_2S	6.15E-05
		32815	6342	1203224	7831	SO_2	6.95E-05
		35738	7874	1206446	8069	N_2	8.18E-05
		34798	14820	1187465	10850	H_2O	6.97E-06
		34353	14180	1234698	12167		
Average		34285	14500	1208179	9793		
96	130.00	35206	15507	1415390	12003	H_2S	5.93E-5
		36015	17742	1380609	12201	SO_2	6.55E-5
		38221	13135	1354422	13135	N_2	7.70E-5
		33464	18941	1357236	12443	H_2O	6.97E-6
		35850	19529	1348449	12114		
Average		35751	16970	1371221	12379		
98	135.00	36555	4563	1215020	14507	H_2S	5.93E-5
		38965	14408	1288921	15541	SO_2	6.55E-5
		40496	17508	1284794	11793	N_2	7.70E-5
		40913	17821	1272709	16473	H_2O	6.97E-6
		37047	17383	1265055	16357		
		38162	14246	1285868	18356		
Average		38690	14322	1268728	15505		
100	140.00	38295	22345	1266130	16663	H_2S	5.98E-5

			34721	21730	1254251	15176	SO_2	7.19E-5
			34140	22258	1246443	16248	N_2	8.20E-5
			36648	21814	1230158	13944	H_2O	6.97E-6
	Average		35951	22037	1249246	15508		
	102	145.00	39844	18137	1147698	16451	H_2S	5.98E-5
			38671	19564	1162403	10966	SO_2	7.19E-5
			38851	18958	1129253	16571	N_2	8.20E-5
	Average		39122	18886	1146451	14663	H_2O	6.97E-6
2.1B								
G= 95 sccm G/L=1.37	107	100.00	19919	0	1680169	0	H_2S	5.69E-5
			19649	0	1706773	0	SO_2	5.92E-5
			21094	0	1662676	0	N_2	5.57E-5
	Average		20221	0	1683206	0	H_2O	6.97E-6
	105	110.00	16060	0	1703358	0	H_2S	5.69E-5
			16980	0	1693864	0	SO_2	5.92E-5
			16503	0	1705886	0	N_2	5.57E-5
	Average		16514	0	1701036	0	H_2O	6.97E-6
	95	125.00	17461	7180	1176369	9231	H_2S	6.15E-5
			19855	12115	1167858	10232	SO_2	6.95E-5
	Average		18658	9648	1172114	9732	N_2	8.18E-5
							H_2O	6.97E-6

	97	130.00	21800	19033	1336275	11912	H_2S	5.93E-5
			21903	18894	1318545	12409	SO_2	6.55E-5
			21720	16934	1327325	12445	N_2	7.70E-5
	Average		21808	18287	1327382	12255	H_2O	6.97E-6
	99	135.00	23427	19247	1282329	19587	H_2S	5.93E-5
			23948	15671	1287502	17888	SO_2	6.55E-5
			24690	16481	1285118	18031	N_2	7.70E-5
			26649	17830	1291294	18152	H_2O	6.97E-6
	Average		24679	17307	1286561	18415		
	101	140.00	22461	18026	1226968	14630	H_2S	598.0E-7
			25736	18620	1268944	14647	SO_2	719.0E-7
	Average		24099	18323	1247956	14639	N_2	820.0E-7
							H_2O	697.0E-8
	103	145.00	24694	19745	1179436	15641	H_2S	5.98E-5
			22924	20436	1189356	12816	SO_2	7.19E-5
			23043	25153	1171068	12303	N_2	8.20E-5
	Average		23554	21778	1179953	13587	H_2O	6.97E-6
2.2A								
Acid Conc.	108	100.00	0	0	1774789	0	H_2S	5.69E-5
wt%=93			0	0	1811360	0	SO_2	5.92E-5
G=191 sccm			0	0	1791539	0	N_2	5.57E-5
G/L=2.73	Average		0	0	1792563	0	H_2O	6.97E-6

	110	110.00	0	22460	1720161	0	H_2S	5.69E-5
			0	24888	1713933	0	SO_2	5.92E-5
			0	21397	1690566	0	N_2	5.57E-5
	Average		0	22915	1708220	0	H_2O	6.97E-6
	112	120.00	0	25389	1709472	0	H_2S	5.69E-5
			0	26521	1750234	0	SO_2	5.92E-5
			0	24900	1695321	0	N_2	5.57E-5
	Average		0	25603	1718342	0	H_2O	6.97E-6
	114	130.00	1379	33281	1789456	0	H_2S	5.69E-5
			0	34983	1728374	0	SO_2	5.92E-5
			2356	33712	1723036	0	N_2	5.57E-5
	Average		1245	33992	1746955	0	H_2O	6.97E-6
2.2B								
G=95 sccm **G/L=1.38**	109	100.00	0	0	1774789	0	H_2S	5.69E-5
			0	0	1811360	0	SO_2	5.92E-5
			0	0	1791539	0	N_2	5.57E-5
	Average		0	0	1792563	0	H_2O	6.97E-6
	111	110.00	0	0	1667188	0	H_2S	5.69E-5
			0	0	1675962	0	SO_2	5.92E-5
			0	0	1653389	0	N_2	5.57E-5
	Average		0	0	1665513	0	H_2O	6.97E-6

	113	120.00	0	0	1789456	0	H_2S	5.69E-5
			0	0	1745725	0	SO_2	5.92E-5
			0	0	1735678	0	N_2	5.57E-5
	Average		0	0	1756953	0	H_2O	6.97E-6
	115	130.00	0	12367	1729384	0	H_2S	5.69E-7
			0	11237	1729123	0	SO_2	5.92E-5
			0	13450	1738563	0	N_2	5.57E-5
	Average		0	12351	1732357	0	H_2O	6.97E-6
SET 3	**To observe the effect of feed gas flow H_2S concentration on H_2S conversion and SO_2 emission**							
Conditions	Run No.	Feed H_2S Mole %	Component GC Area in Product Gas Mixture				Gas	Response Factor
			H_2S	SO_2	N_2	H_2O		
3.1								
T = 120°C, P = 5 psig G = 191 sccm L = 70 cc/min **G/L = 2.73** **Acid Conc.** **wt% = 84**	134	1.98	44256	0	1697301	23171	H_2S	3.39E-5
			45010	0	1698227	24539	SO_2	5.92E-5
			44418	0	1689460	26268	N_2	5.88E-5
	Average		44561	0	1694996	24659	H_2O	6.97E-6
	135	4.57	75957	0	1664976	29444	H_2S	468.0E-7
			76688	0	1664122	30740	SO_2	592.0E-7
			74588	0	1656566	31266	N_2	573.0E-7

	Average		75744	0	1661888	30483	H_2O	6.97E-6
	136	8.87	110528	0	1635515	30079	H_2S	5.67E-5
			110555	0	1629275	30129	SO_2	5.92E-5
			113347	0	1632327	32085	N_2	5.67E-5
	Average		111477	0	1632372	30764	H_2O	6.97E-5
3.2								
Acid Conc. wt% = 87.5	137	1.98	31700	0	1696634	12620	H_2S	3.39E-5
			33581	0	1691834	12795	SO_2	5.92E-5
			33105	0	1689460	12180	N_2	5.88E-5
	Average		32795	0	1692643	12532	H_2O	6.97E-6
	138	4.57	51970	0	1660553	13410	H_2S	4.68E-5
			51097	0	1664122	12890	SO_2	5.92E-5
			50666	0	1681463	14390	N_2	5.73E-5
	Average		51244	0	1668713	13563	H_2O	6.97E-6
	139	8.87	70628	0	1644714	12628	H_2S	5.67E-5
			69607	0	1654890	12609	SO_2	5.92E-5
			67824	0	1646310	12451	N_2	5.67E-5
	Average		69353	0	1648638	12563	H_2O	6.97E-6
3.3								
Acid Conc. wt% = 89.5	140	1.98	11887	0	1656885	0	H_2S	3.39E-5
			12708	0	1681488	0	SO_2	5.92E-5

			10861	0	1671145	0	N_2	5.88E-5
	Average		11819	0	1669839	0	H_2O	6.97E-6
	141	4.57	28286	0	1671316	0	H_2S	4.68E-5
			32453	0	1677756	0	SO_2	5.92E-5
			29234	0	1669747	0	N_2	5.73E-5
	Average		29991	0	1672940	0	H_2O	6.97E-6
	142	8.87	35598	0	1678053	0	H_2S	567.0E-7
			36019	0	1659343	0	SO_2	592.0E-7
			35877	0	1670831	0	N_2	5.67E-5
	Average		35831	0	1669409	0	H_2O	6.97E-6
3.4								
Acid Conc. **wt% =93.5**	143	1.98	0	0	1697301	0	H_2S	3.39E-5
			0	0	1698227	0	SO_2	5.92E-5
			0	0	1689460	0	N_2	5.88E-5
	Average		0	0	1694996	0	H_2O	6.97E-6
	144	4.57	0	0	1645900	0	H_2S	4.43E-5
			0	0	1657890	0	SO_2	5.92E-5
			0	0	1656566	0	N_2	5.81E-5
	Average		0	0	1653452	0	H_2O	6.97E-6
	145	8.87	0	21679	1709973	0	H_2S	6.27E-5
			0	23419	1737700	0	SO_2	6.20E-5

			0	22574	1730545	0	N_2	5.74E-5
	Average		0	22557	1726073	0	H_2O	6.97E-6
SET 4	To observe the effect of gas flow rate on H_2S conversion and SO_2 emission							
Conditions	Run No.	Gas Flow Rate sccm	Component GC Area in Product Gas Mixture				Gas	Response Factor
			H_2S	SO_2	N_2	H_2O		
4.1								
H_2S in = 9 mole% T = 120°C, P = 5 psig L = 70 cc/min **Acid Conc. wt% = 81.5**	45A	191.00	383931	0	1464439	51326	H_2S	2.02E-05
		G/L:2.73	385776	0	1448744	44226	SO_2	5.09E-05
			382451	0	1497748	55654	N_2	6.34E-05
	Average		386588	0	1470749	47704	H_2O	6.97E-06
	45B	191.00	113467	0	1570854	50111	H_2S	6.10E-05
		G/L:2.73	124844	0	1534310	61947	SO_2	5.09E-05
			127355	0	1531512	51381	N_2	5.99E-05
	Average		126065	0	1536956	57696	H_2O	6.97E-06
	49	137.00	122304	0	1296148	58834	H_2S	6.15E-05
		G/L:1.97	122233	0	1293465	59486	SO_2	
			116269	0	1294502	53681	N_2	7.20E-05
			121646	0	1289659	60374	H_2O	6.97E-06
	Average		120613	0	1293444	58094		

4.2								
Acid Conc. wt%=84	81	191.00	104304	0	1239274	28719	H_2S	6.53E-05
		G/L:2.73	101010	0	1254337	31730	SO_2	4.93E-05
			100438	0	1261004	25829	N_2	7.41E-05
			111471	0	1257734	29775	H_2O	6.97E-06
	Average		104306	0	1253087	29013		
	80	96.00	86577	0	1260773	30427	H_2S	6.53E-05
		G/L=:.37	89964	0	1267430	31310	SO_2	4.93E-05
			86786	0	1269812	32941	N_2	7.41E-05
	Average		87141	0	1264373	31865	H_2O	6.97E-06
4.3								
Acid Conc. wt%=87.5	83	191.00	43233	0	1144663	6050	H_2S	6.33E-05
		G/L:2.73	43858	0	1126090	8804	SO_2	4.93E-05
			44620	0	1122015	7789	N_2	8.54E-05
	Average		44564	0	1128968	8129	H_2O	6.97E-06
	82	137.00	38454	0	1212554	9211	H_2S	6.33E-05
		G/L:1.97	37461	0	1186238	8644	SO_2	
			37539	0	1162629	8784	N_2	8.54E-05
	Average		37213	0	1184437	8254	H_2O	6.97E-06
	85	96.00	25556	0	1119315	6414	H_2S	6.33E-05
		G/L:1.37	24148	0	1131611	7524	SO_2	
	Average		24852	0	1125463	6834	N_2	8.54E-05

							H_2O	6.97E-06
4.4								
Acid Conc. wt% = 89.5	88	191.00 G/L:2.73	31905	0	1141552	5859	H_2S	6.33E-05
			30742	0	1150284	5911	SO_2	
			31119	0	1120804	6464	N_2	8.54E-04
	Average		31037	0	1138946	6251	H_2O	6.97E-06
	87	137.00 G/L:1.97	23758	0	1155720	7237	H_2S	6.33E-05
			22843	0	1157246	6708	SO_2	
			23677	0	1156810	6275	N_2	8.54E-05
	Average		23005	0	1158419	6696	H_2O	6.97E-06
	86	96.00 G/L:1.37	16697	0	1162637	6178	H_2S	6.33E-05
			17414	0	1161415	7045	SO_2	
			18233	0	1164575	5618	N_2	8.54E-05
			18611	0	1160683	6316	H_2O	6.97E-06
			17899	0	1157572	5447		
	Average		17781	0	1161376	6121		
4.5								
Acid Conc. wt% = 91.5	77	191.00 G/L:2.73	20574	14878	1800697	6538	H_2S	5.18E-05
			20301	13050	1798933	8012	SO_2	4.93E-05
			20697	17502	1780615	6546	N_2	5.26E-05
	Average		20524	15143	1793415	7032	H_2O	6.97E-06
	76	137.00	22100	11688	1794103	9217	H_2S	5.18E-05

Conditions	Run No.	Liquid Flow Rate, ccm	Component GC Area in Product Gas Mixture				Gas	Response Factor
			H_2S	SO_2	N_2	H_2O		
		G/L:1.97	21403	11057	1830043	8597	SO_2	4.93E-05
			17587	11743	1772242	7686	N_2	5.26E-05
	Average		20363	11496	1798796	8500	H_2O	6.97E-06
	75	96.00 G/L:1.37	15006	8741	1781636	6624	H_2S	5.18E-05
			13957	9834	1816639	8463	SO_2	4.93E-05
			16995	9998	1838597	8135	N_2	5.26E-05
			15042	9236	1808136	7771	H_2O	6.97E-06
	Average		15250	9452	1811252	7748		
SET 5	To observe the effect of acid flow rate on H_2S conversion and SO_2 emission							
Conditions	Run No.	Liquid Flow Rate, ccm	Component GC Area in Product Gas Mixture				Gas	Response Factor
			H_2S	SO_2	N_2	H_2O		
5.1								
H_2S in = 9 mole% T = 120°C, P = 5 psig G = 138 sccm Acid Conc. wt%=85	120A	50.00 G/L:2.73	84044	0	1622743	18222	H_2S	5.87E-5
			87300	0	1631470	16890	SO_2	4.65E-5
			88282	0	1663677	17237	N_2	5.58E-5
			83130	0	1653686	17180	H_2O	6.97E-6
	Average		85689	0	1642894	17382		
	120B	50.00 G/L:2.73	84970	0	1560222	3210	H_2S	5.64E-5
			83465	0	1549948	10307	SO_2	5.92E-5
			84325	0	1550569	12002	N_2	5.94E-5

	Average		84253	0	1553580	8506	H_2O	6.97E-6
	124A	70.00	82781	0	1714617	13679	H_2S	6.01E-5
		G/L:1.97	88105	0	1710897	17384	SO_2	4.65E-5
			81010	0	1710003	12579	N_2	5.57E-5
	Average		83965	0	1711839	14547	H_2O	6.97E-6
	124B	70.00	97458	0	1729128	13668	H_2S	5.14E-5
		G/L:1.97	98555	0	1727465	14894	SO_2	4.65E-5
			97324	0	1730588	16456	N_2	5.49E-5
	Average		97779	0	1729060	15006	H_2O	6.97E-6
	121A	100.00	77507	0	1621449	11198	H_2S	5.87E-5
		G/L:1.38	66308	0	1603659	13108	SO_2	4.65E-5
			81915	0	1553802	16134	N_2	5.58E-5
			79179	0	1509967	12879	H_2O	6.97E-6
	Average		76227	0	1572219	13330		
	121B	100.00	97829	0	1725746	12195	H_2S	5.14E-5
		G/L:1.38	93967	0	1733282	17064	SO_2	4.65E-5
			95456	0	1728878	13212	N_2	5.49E-5
	Average		95751	0	1729302	14157	H_2O	6.97E-6
5.2								
Acid Conc. wt%=88	126A	50.00	26345	17882	1659164	0	H_2S	5.79E-5
		G/L:2.73	28218	15627	1652360	0	SO_2	4.65E-5

			27025	15911	1656228	0	N_2	5.81E-5
	Average		27196	16473	1655917	0	H_2O	6.97E-6
	126B	50.00 G/L:2.73	26978	16184	1608686	0	H_2S	5.79E-5
			31353	18623	1609368	6351	SO_2	4.65E-5
			27767	15697	1611723	4589	N_2	5.81E-5
	Average		28699	16835	1609926	3647	H_2O	6.97E-6
	127A	70.00 G/L:1.97	25871	0	1670898	0	H_2S	5.79E-5
			27045	0	1670883	0	SO_2	4.65E-5
			25882	0	1665106	0	N_2	5.81E-5
	Average		26266	0	1668962	0	H_2O	6.97E-6
	127B	70.00 G/L:1.97	28860	0	1633185	5982	H_2S	5.79E-5
			30076	0	1627370	5334	SO_2	4.65E-5
			28612	0	1631510	7953	N_2	5.81E-5
	Average		29183	0	1630688	6423	H_2O	6.97E-6
	128	100.00 G/L:1.38	23942	0	1646294	5613	H_2S	5.79E-5
			24974	0	1635191	4815	SO_2	4.65E-5
			25249	0	1635834	7984	N_2	5.81E-5
	Average		24722	0	1639106	6137	H_2O	6.97E-6
5.3								
Acid Conc. wt%=90	131	50.00 G/L:2.73	11530	34647	1620823	5658	H_2S	564.0E-7
			14724	33706	1610650	463	SO_2	592.0E-7

			14454	27646	1608040	3186	N_2	594.0E-7
	Average		13569	32000	1613171	3102	H_2O	697.0E-8
	130	70.00 G/L:1.97	12316	8512	1626328	3467	H_2S	5.64E-5
			8211	11551	1542334	4044	SO_2	5.92E-5
			16020	7750	1632435	778	N_2	5.94E-5
	Average		12182	9271	1600366	2763	H_2O	6.97E-6
	129	100.00 G/L:1.38	10235	5004	1655027	2894	H_2S	5.64E-5
			10795	6079	1647772	4044	SO_2	5.92E-5
			12675	4353	1646166	3258	N_2	5.94E-5
	Average		11235	5145	1649655	3399	H_2O	6.97E-6
5.4								
Acid Conc. wt%=93	133	50.00 G/L:2.73	5804	38607	1641343	0	H_2S	5.64E-5
			1122	32741	1616628	0	SO_2	5.92E-5
			2633	29357	1659832	0	N_2	5.94E-5
	Average		3186	33568	1639268	0	H_2O	6.97E-6
	132	100.00 G/L:1.38	1615	11218	1672779	0	H_2S	5.64E-5
			1953	13942	1684810	1183	SO_2	5.92E-5
			1811	13678	1608040	0	N_2	5.94E-5
	Average		1793	12946	1655210	394	H_2O	6.97E-6

Appendix

G

Processed data

The raw data gathered was processed. Only steady state observations were considered. This is evident from the near constant area ratios (which show neither decreasing nor increasing trends) in repetitions during each run. The H_2S conversions and SO_2 emissions are recorded for each run.

SET 1	To observe the effect of H_2SO_4 concentration on H_2S conversion and SO_2 emission										
Conditions	Run No.	Acid Conc. wt%	H_2S/N_2 Peak Area Ratio	SO_2/N_2 Peak Area Ratio	H_2O/N_2 Peak Area Ratio	H_2S Mole Percent In Exit Gas	SO_2 Mole Percent In Exit Gas	N_2 Mole Percent In Exit Gas	H_2O Mole Percent In Exit Gas	H_2S Conv Percent	SO_2 Emission Mole Percent
1.1											
H_2S in=9 mole% T = 120°C P = 5 psig L = 70 cc/min G = 191 sccm G/L= 2.73	45A	81.50	0.26	0.00	0.04	7.67	0.00	92.05	0.27	13.83	0.00
			0.26	0.00	0.03	7.77	0.00	91.86	0.35		
			0.26	0.00	0.04	7.48	0.00	92.21	0.29		
	Average		0.26	0.00	0.03	7.68	0.00	91.98	0.33		
	45B	81.50	0.07	0.00	0.03	6.83	0.00	92.83	0.34	14.16	0.00
			0.08	0.00	0.04	7.62	0.00	92.01	0.43		
			0.08	0.00	0.03	7.74	0.00	91.83	0.36		
	Average		0.08	0.00	0.04	7.68	0.00	91.92	0.40		
	81	84.00	0.08	0.00	0.02	6.89	0.00	92.91	0.20	24.64	0.00
			0.08	0.00	0.03	6.61	0.00	93.17	0.22		
			0.08	0.00	0.02	6.55	0.00	93.27	0.18		
			0.09	0.00	0.02	7.23	0.00	92.56	0.21		
	Average		0.08	0.00	0.02	6.82	0.00	92.98	0.20		
	79	86.70	0.06	0.00	0.01	4.82	0.00	95.07	0.10	47.14	0.00
			0.06	0.00	0.02	4.83	0.00	95.06	0.11		

			0.06	0.00	0.02	4.90	0.00	94.97	0.13	
	Average		0.06	0.00	0.01	4.89	0.00	95.00	0.11	
	83	87.50	0.04	0.00	0.01	2.72	0.00	97.24	0.04	69.93	0.00
			0.04	0.00	0.01	2.80	0.00	97.13	0.06		
			0.04	0.00	0.01	2.86	0.00	97.08	0.06		
	Average		0.04	0.00	0.01	2.84	0.00	97.10	0.06		
	71	89.00	0.03	0.00	0.01	2.88	0.00	97.04	0.08	70.55	0.00
			0.03	0.00	0.01	2.73	0.00	97.19	0.08		
			0.03	0.00	0.01	2.77	0.00	97.17	0.07		
	Average		0.03	0.00	0.01	2.78	0.00	97.15	0.07		
	88	89.50	0.03	0.00	0.01	2.03	0.00	97.93	0.04	79.24	0.00
			0.03	0.00	0.01	1.94	0.00	98.02	0.04		
			0.03	0.00	0.01	2.02	0.00	97.94	0.04		
	Average		0.03	0.00	0.01	1.98	0.00	97.98	0.04		
	52	90.50	0.01	0.00	0.00	1.23	0.09	98.62	0.06	88.47	0.10
			0.01	0.00	0.01	0.98	0.04	98.88	0.10		
			0.01	0.00	0.01	1.11	0.18	98.62	0.08		
	Average		0.01	0.00	0.01	1.11	0.10	98.71	0.08		
	77	91.50	0.01	0.01	0.00	1.10	0.76	98.09	0.05	88.51	0.71
			0.01	0.01	0.00	1.09	0.67	98.18	0.06		
			0.01	0.01	0.00	1.12	0.90	97.93	0.05		
	Average		0.01	0.01	0.00	1.11	0.78	98.07	0.05		

56	92.20	0.01	0.01	0.00	0.28	0.85	98.85	0.00	97.04	0.77
		0.01	0.01	0.00	0.28	0.90	98.81	0.00		
		0.01	0.01	0.00	0.28	0.75	98.97	0.00		
Average		0.01	0.01	0.00	0.28	0.77	98.94	0.00		
55	93.50	0.00	0.01	0.00	0.11	0.73	99.15	0.00	98.83	0.79
		0.00	0.01	0.00	0.11	0.63	99.24	0.00		
		0.00	0.01	0.00	0.11	0.99	98.88	0.00		
Average		0.00	0.01	0.00	0.11	0.79	99.09	0.00		
57	95.50	0.00	0.01	0.00	0.24	0.91	98.84	0.00	96.68	0.97
		0.00	0.01	0.00	0.31	1.06	98.62	0.00		
		0.00	0.01	0.00	0.28	0.57	99.13	0.00		
Average		0.00	0.01	0.00	0.27	0.80	98.68	0.00		
50A	97.00	0.00	0.01	0.00	0.31	1.51	98.17	0.00	96.38	1.39
		0.01	0.01	0.00	0.52	1.49	97.98	0.00		
		0.00	0.01	0.00	0.37	1.14	98.48	0.00		
Average		0.00	0.01	0.00	0.34	1.39	98.26	0.00		
50B	97.00	0.00	0.02	0.00	0.10	1.29	98.61	0.00	99.04	1.31
		0.00	0.02	0.00	0.07	1.31	98.62	0.00		
		0.00	0.02	0.00	0.10	1.33	98.56	0.00		
Average		0.00	0.02	0.00	0.10	1.31	98.60	0.00		

1.2											
G = 138 sccm **G/L = 1.97**	49	81.50	0.09	0.00	0.04	7.43	0.00	92.17	0.41	17.96	0.00
			0.09	0.00	0.05	7.44	0.00	92.15	0.41		
			0.09	0.00	0.04	7.10	0.00	92.53	0.37		
			0.09	0.00	0.04	7.42	0.00	92.16	0.42		
	Average		0.09	0.00	0.04	7.35	0.00	92.25	0.40		
	82	87.60	0.03	0.00	0.01	2.30	0.00	97.64	0.06	76.01	0.00
			0.03	0.00	0.01	2.29	0.00	97.66	0.06		
			0.03	0.00	0.01	2.34	0.00	97.60	0.06		
	Average		0.03	0.00	0.01	2.27	0.00	97.67	0.06		
	60	89.05	0.02	0.00	0.00	2.06	0.00	97.89	0.05	80.01	0.00
			0.02	0.00	0.01	1.88	0.00	98.06	0.07		
			0.02	0.00	0.01	1.75	0.00	98.18	0.08		
	Average		0.02	0.00	0.01	1.90	0.00	98.04	0.06		
	87	89.50	0.02	0.00	0.01	1.50	0.00	98.45	0.05	84.93	0.00
			0.02	0.00	0.01	1.44	0.00	98.51	0.05		
			0.02	0.00	0.01	1.49	0.00	98.46	0.04		
	Average		0.02	0.00	0.01	1.45	0.00	98.50	0.05		
	54	89.75	0.01	0.00	0.00	1.28	0.00	98.68	0.04	85.37	0.00
			0.02	0.00	0.00	1.59	0.00	98.36	0.05		
			0.01	0.00	0.00	1.33	0.00	98.64	0.03		
	Average		0.01	0.00	0.00	1.40	0.00	98.56	0.04		

	76	91.45	0.01	0.01	0.01	1.19	0.60	98.14	0.07	88.55	0.59
			0.01	0.01	0.01	1.13	0.56	98.25	0.06		
			0.01	0.01	0.00	0.96	0.61	98.37	0.06		
	Average		0.01	0.01	0.01	1.09	0.59	98.25	0.06		
	59	93.75	0.00	0.01	0.00	0.00	0.61	99.38	0.02	99.10	0.61
			0.00	0.01	0.00	0.00	0.58	99.41	0.02		
			0.00	0.01	0.00	0.05	0.61	99.07	0.02		
	Average		0.00	0.01	0.00	0.02	0.60	99.28	0.02		
	51	97.00	0.00	0.01	0.00	0.00	0.95	99.05	0.00	100.00	1.18
			0.00	0.01	0.00	0.00	1.20	98.80	0.00		
			0.00	0.01	0.00	0.00	1.18	98.82	0.00		
	Average		0.00	0.01	0.00	0.00	1.19	98.81	0.00		
1.3											
G = 96 sccm G/L = 1.37	80	84.00	0.07	0.00	0.02	5.69	0.00	94.09	0.21	39.18	0.00
			0.07	0.00	0.02	5.87	0.00	93.91	0.22		
			0.07	0.00	0.03	5.67	0.00	94.10	0.23		
	Average		0.07	0.00	0.02	5.58	0.00	94.22	0.20		
	78	86.70	0.04	0.00	0.01	3.30	0.00	96.62	0.08	62.55	0.00
			0.04	0.00	0.01	3.57	0.00	96.32	0.11		
			0.04	0.00	0.02	3.61	0.00	96.28	0.11		
			0.04	0.00	0.02	3.66	0.00	96.21	0.12		

			0.04	0.00	0.01	3.43	0.00	96.46	0.11		
	Average		0.04	0.00	0.01	3.51	0.00	96.38	0.11		
	85	87.50	0.02	0.00	0.01	1.66	0.00	98.29	0.05	83.18	0.00
			0.02	0.00	0.01	1.56	0.00	98.39	0.05		
	Average		0.02	0.00	0.01	1.61	0.00	98.34	0.05		
	86	89.50	0.01	0.00	0.01	1.05	0.00	98.90	0.04	88.34	0.00
			0.01	0.00	0.01	1.10	0.00	98.85	0.05		
			0.01	0.00	0.01	1.15	0.00	98.81	0.04		
			0.01	0.00	0.01	1.18	0.00	98.78	0.04		
			0.01	0.00	0.01	1.13	0.00	98.83	0.04		
	Average		0.01	0.00	0.01	1.12	0.00	98.84	0.04		
	68	90.50	0.01	0.00	0.00	1.08	0.00	98.90	0.01	89.42	0.00
			0.01	0.00	0.00	0.74	0.00	99.26	0.01		
			0.01	0.00	0.01	1.06	0.00	98.89	0.05		
			0.01	0.00	0.00	1.19	0.00	98.74	0.06		
	Average		0.01	0.00	0.00	1.02	0.00	98.95	0.03		
	75	91.45	0.01	0.00	0.00	0.82	0.45	98.68	0.05	91.48	0.48
			0.01	0.01	0.00	0.75	0.50	98.69	0.06		
			0.01	0.01	0.00	0.90	0.50	98.54	0.06		
			0.01	0.01	0.00	0.81	0.47	98.66	0.06		
	Average		0.01	0.01	0.00	0.82	0.48	98.64	0.06		
	51	94.75	0.00	0.01	0.00	0.32	0.60	99.07	0.01	97.19	0.62

			0.00	0.01	0.00	0.13	0.50	99.36	0.01		
			0.00	0.01	0.00	0.46	0.60	98.93	0.01		
			0.00	0.01	0.00	0.06	0.60	99.34	0.00		
			0.00	0.01	0.00	0.08	0.60	99.31	0.01		
			0.00	0.01	0.00	0.03	0.60	99.36	0.01		
			0.00	0.01	0.00	0.15	0.60	99.22	0.03		
	Average		0.00	0.01	0.00	0.18	0.60	99.21	0.01		
SET 2	To observe the effect of temperature on H_2S conversion and SO_2 emission										
	Run No.	Temp.,°C	H_2S/N_2 Peak Area Ratio	SO_2/N_2 Peak Area Ratio	H_2O/N_2 Peak Area Ratio	H_2S Mole Percent In Exit Gas	SO_2 Mole Percent in Exit Gas	N_2 Mole Percent In Exit Gas	H_2O Mole Percent In Exit Gas	H_2S Conv Percent	SO_2 Emission Mole Percent
2.1A											
H_2S In= 9 mole%	106	100.00	0.02	0.00	0.00	2.13	0.00	97.87	0.00	78.44	0.00
P= 5 psig			0.02	0.00	0.00	2.03	0.00	97.97	0.00		
L= 70 cc/min			0.02	0.00	0.00	2.01	0.00	97.99	0.00		
G=191sccm	Average		0.02	0.00	0.00	2.06	0.00	97.94	0.00		
G/L=2.73											
Acid Conc.	104	110.00	0.02	0.00	0.00	1.96	0.00	98.04	0.00	79.64	0.00
wt%=88			0.02	0.00	0.00	1.93	0.00	98.07	0.00		
			0.02	0.00	0.00	1.94	0.00	98.06	0.00		
	Average		0.02	0.00	0.00	1.94	0.00	98.06	0.00		

	71	120.00	0.03	0.00	0.01	2.88	0.00	97.04	0.08	70.55	0.00
			0.03	0.00	0.01	2.73	0.00	97.19	0.08		
			0.03	0.00	0.01	2.77	0.00	97.17	0.07		
	Average		0.03	0.00	0.01	2.78	0.00	97.15	0.07		
	94	125.00	0.03	0.00	0.01	2.05	0.00	97.88	0.07	78.07	0.99
			0.03	0.01	0.01	2.00	0.44	97.51	0.05		
			0.03	0.01	0.01	2.17	0.54	97.24	0.06		
			0.03	0.01	0.01	2.13	1.03	96.76	0.08		
			0.03	0.01	0.01	2.03	0.95	96.94	0.08		
	Average		0.03	0.01	0.01	2.08	0.99	97.27	0.07		
	96	130.00	0.02	0.01	0.01	1.86	0.91	97.16	0.07	79.35	1.02
			0.03	0.01	0.01	1.95	1.06	96.91	0.08		
			0.03	0.01	0.01	2.11	0.80	97.00	0.09		
			0.02	0.01	0.01	1.84	1.15	96.93	0.08		
			0.03	0.01	0.01	1.98	1.19	96.75	0.08		
	Average		0.03	0.01	0.01	1.95	1.02	96.95	0.08		
	98	135.00	0.03	0.00	0.01	2.26	0.31	97.33	0.11	75.86	1.05
			0.03	0.01	0.01	2.25	0.92	96.72	0.11		
			0.03	0.01	0.01	2.34	1.12	96.46	0.08		
			0.03	0.01	0.01	2.39	1.15	96.35	0.11		
			0.03	0.01	0.01	2.18	1.13	96.58	0.11		
			0.03	0.01	0.01	2.21	0.91	96.75	0.13		
	Average		0.03	0.01	0.01	2.27	1.05	96.70	0.11		

	100	140.00	0.03	0.02	0.01	2.12	1.49	96.28	0.11	78.44	1.49
			0.03	0.02	0.01	1.95	1.46	96.49	0.10		
			0.03	0.02	0.01	1.93	1.51	96.46	0.11		
			0.03	0.02	0.01	2.09	1.50	96.32	0.09		
	Average		0.03	0.02	0.01	2.02	1.49	96.39	0.10		
	102	145.00	0.03	0.02	0.01	2.43	1.33	96.12	0.12	74.43	1.39
			0.03	0.02	0.01	2.33	1.42	96.17	0.08		
			0.03	0.02	0.01	2.41	1.41	96.06	0.12		
	Average		0.03	0.02	0.01	2.39	1.39	96.12	0.10		
2.1B											
G= 95 sccm G/L=1.37	107	100.00	0.01	0.00	0.00	1.20	0.00	98.80	0.00	87.40	0.00
			0.01	0.00	0.00	1.16	0.00	98.84	0.00		
			0.01	0.00	0.00	1.28	0.00	98.72	0.00		
	Average		0.01	0.00	0.00	1.21	0.00	98.79	0.00		
	105	110.00	0.01	0.00	0.00	0.95	0.00	99.05	0.00	89.82	0.00
			0.01	0.00	0.00	1.01	0.00	98.99	0.00		
			0.01	0.00	0.00	0.98	0.00	99.02	0.00		
	Average		0.01	0.00	0.00	0.98	0.00	99.02	0.00		
	95	125.00	0.01	0.01	0.01	1.10	0.51	98.33	0.07	87.70	0.69
			0.02	0.01	0.01	1.25	0.86	97.81	0.07		
	Average		0.02	0.01	0.01	1.17	0.69	98.07	0.07		

	97	130.00	0.02	0.01	0.01	1.23	1.18	97.51	0.08	86.99	1.14
			0.02	0.01	0.01	1.25	1.19	97.48	0.08		
			0.02	0.01	0.01	1.23	1.06	97.63	0.08		
	Average		0.02	0.01	0.01	1.23	1.14	97.54	0.08		
	99	135.00	0.02	0.02	0.01	1.37	1.24	97.25	0.13	84.90	1.11
			0.02	0.01	0.01	1.40	1.01	97.47	0.12		
			0.02	0.01	0.01	1.44	1.06	97.37	0.12		
			0.02	0.01	0.01	1.55	1.14	97.19	0.12		
	Average		0.02	0.01	0.01	1.44	1.11	97.32	0.13		
	101	140.00	0.02	0.01	0.01	1.30	1.25	97.35	0.10	85.55	1.25
			0.02	0.01	0.01	1.44	1.25	97.22	0.10		
	Average		0.02	0.01	0.01	1.37	1.25	97.28	0.10		
	103	145.00	0.02	0.02	0.01	1.48	1.42	96.99	0.11	85.05	1.57
			0.02	0.02	0.01	1.36	1.46	97.08	0.09		
			0.02	0.02	0.01	1.39	1.82	96.71	0.09		
	Average		0.02	0.02	0.01	1.41	1.57	96.93	0.09		
2.2A											
Acid Conc. **wt%=93** **G=191 sccm** **G/L=2.73**	108	100.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	100.00	0.00
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	Average		0.00	0.00	0.00	0.00	0.00	100.00	0.00		

	110	110.00	0.00	0.01	0.00	0.00	1.37	98.63	0.00	100.00	1.40
			0.00	0.01	0.00	0.00	1.52	98.48	0.00		
			0.00	0.01	0.00	0.00	1.33	98.67	0.00		
	Average		0.00	0.01	0.00	0.00	1.40	98.60	0.00		
	112	120.00	0.00	0.01	0.00	0.00	1.55	98.45	0.00	100.00	1.56
			0.00	0.02	0.00	0.00	1.58	98.42	0.00		
			0.00	0.01	0.00	0.00	1.54	98.46	0.00		
	Average		0.00	0.01	0.00	0.00	1.56	98.44	0.00		
	114	130.00	0.00	0.02	0.00	0.08	1.94	97.99	0.00	99.25	2.02
			0.00	0.02	0.00	0.00	2.10	97.90	0.00		
			0.00	0.02	0.00	0.14	2.03	97.83	0.00		
	Average		0.00	0.02	0.00	0.07	2.02	97.90	0.00		
2.2B											
G=95 sccm G/L=1.38	109	100.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	100.00	0.00
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	Average		0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	111	110.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	100.00	0.00
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	Average		0.00	0.00	0.00	0.00	0.00	100.00	0.00		

	113	120.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	100.00	0.00
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	Average		0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	115	130.00	0.00	0.01	0.00	0.00	0.75	99.25	0.00	100.00	0.65
			0.00	0.01	0.00	0.00	0.69	99.31	0.00		
			0.00	0.01	0.00	0.00	0.82	99.18	0.00		
	Average		0.00	0.01	0.00	0.00	0.75	99.25	0.00		
SET 3	To observe the effect of feed gas H_2S concentration on H_2S conversion and SO_2 emission										
Conditions	Run No.	Feed H_2S Mole %	H_2S/N_2 Peak Area Ratio	SO_2/N_2 Peak Area Ratio	H_2O/N_2 Peak Area Ratio	H_2S Mole Percent In Exit Gas	SO_2 Mole Percent In Exit Gas	N_2 Mole Percent In Exit Gas	H_2O Mole Percent In Exit Gas	H_2S Conv Percent t	SO_2 Emission Mole Percent
3.1 '											
T = 120°C, P = 5 psig G = 191 sccm L = 70 cc/min G/L = 2.73 Acid Conc. wt% = 84	134	1.98	0.03	0.00	0.01	1.48	0.00	98.36	0.16	25.20	0.00
			0.03	0.00	0.01	1.50	0.00	98.33	0.17		
			0.03	0.00	0.02	1.49	0.00	98.33	0.18		
	Average		0.03	0.00	0.01	1.49	0.00	98.34	0.17		
	135	4.57	0.05	0.00	0.02	3.58	0.00	96.21	0.21	28.05	0.00
			0.05	0.00	0.02	3.61	0.00	96.17	0.22		
			0.05	0.00	0.02	3.53	0.00	96.25	0.22		

	Average		0.05	0.00	0.02	3.57	0.00	96.21	0.21		
	136	8.87	0.07	0.00	0.02	6.32	0.00	93.46	0.21	29.76	0.00
			0.07	0.00	0.02	6.35	0.00	93.44	0.21		
			0.07	0.00	0.02	6.49	0.00	93.29	0.23		
	Average		0.07	0.00	0.02	6.39	0.00	93.40	0.22		
3.2											
Acid Conc.	137	1.98	0.02	0.00	0.01	1.07	0.00	98.85	0.09	44.90	0.00
wt% = 87.5			0.02	0.00	0.01	1.13	0.00	98.78	0.09		
			0.02	0.00	0.01	1.12	0.00	98.80	0.08		
	Average		0.02	0.00	0.01	1.10	0.00	98.81	0.09		
	138	4.57	0.03	0.00	0.01	2.49	0.00	97.42	0.10	51.52	0.00
			0.03	0.00	0.01	2.44	0.00	97.47	0.09		
			0.03	0.00	0.01	2.40	0.00	97.50	0.10		
	Average		0.03	0.00	0.01	2.44	0.00	97.46	0.10		
	139	8.87	0.04	0.00	0.01	4.12	0.00	95.79	0.09	56.73	0.00
			0.04	0.00	0.01	4.04	0.00	95.87	0.09		
			0.04	0.00	0.01	3.96	0.00	95.95	0.09		
	Average		0.04	0.00	0.01	4.04	0.00	95.87	0.09		
3.3											
Acid Conc.	140	1.98	0.01	0.00	0.00	0.41	0.00	99.59	0.00	79.86	0.00
wt% = 89.5			0.01	0.00	0.00	0.43	0.00	99.57	0.00		

			0.01	0.00	0.00	0.37	0.00	99.63	0.00		
	Average		0.01	0.00	0.00	0.41	0.00	99.59	0.00		
	141	4.57	0.02	0.00	0.00	1.36	0.00	98.64	0.00	71.70	0.00
			0.02	0.00	0.00	1.55	0.00	98.45	0.00		
			0.02	0.00	0.00	1.41	0.00	98.59	0.00		
	Average		0.02	0.00	0.00	1.44	0.00	98.56	0.00		
	142	8.87	0.02	0.00	0.00	2.08	0.00	97.92	0.00	77.92	0.00
			0.02	0.00	0.00	2.13	0.00	97.87	0.00		
			0.02	0.00	0.00	2.10	0.00	97.90	0.00		
	Average		0.02	0.00	0.00	2.10	0.00	97.90	0.00		
3.4											
Acid Conc. wt% =93.5	143	1.98	0.00	0.00	0.00	0.00	0.00	100.00	0.00	100.00	0.00
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	Average		0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	144	4.57	0.00	0.00	0.00	0.00	0.00	100.00	0.00	100.00	0.00
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
			0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	Average		0.00	0.00	0.00	0.00	0.00	100.00	0.00		
	145	8.87	0.00	0.01	0.00	0.00	1.35	98.65	0.00	100.00	1.39
			0.00	0.01	0.00	0.00	1.43	98.57	0.00		

			0.00	0.01	0.00	0.00	1.39	98.61	0.00		
	Average		0.00	0.01	0.00	0.00	1.39	98.61	0.00		
SET 4	To observe the effect of gas flow rate on H_2S conversion and SO_2 emission										
Conditions	Run No.	Gas Flow Rate sccm	H_2S/N_2 Peak Area Ratio	SO_2/N_2 Peak Area Ratio	H_2O/N_2 Peak Area Ratio	H_2S Mole Percent in Exit Gas	SO_2 Mole Percent in Exit Gas	N_2 Mole Percent in Exit Gas	H_2O Mole Percent in Exit Gas	H_2S Conv Percent t	SO_2 Emission Mole Percent
4.1											
H_2S in =9 mole% T = 120°C P= 5 psig L= 70 cc/min Acid Conc. wt%=81.5	45A	191.00 G/L:2.73	0.26	0.00	0.04	7.67	0.00	92.05	0.27	13.83	0.00
			0.26	0.00	0.03	7.77	0.00	91.86	0.35		
			0.26	0.00	0.04	7.48	0.00	92.21	0.29		
	Average		0.26	0.00	0.03	7.68	0.00	91.98	0.33		
	45B	191.00 G/L:2.73	0.07	0.00	0.03	6.83	0.00	92.83	0.34	14.16	0.00
			0.08	0.00	0.04	7.62	0.00	92.01	0.43		
			0.08	0.00	0.03	7.74	0.00	91.83	0.36		
	Average		0.08	0.00	0.04	7.68	0.00	91.92	0.40		
	49	137.00 G/L:1.97	0.09	0.00	0.04	7.43	0.00	92.17	0.41	17.96	0.00
			0.09	0.00	0.05	7.44	0.00	92.15	0.41		
			0.09	0.00	0.04	7.10	0.00	92.53	0.37		
			0.09	0.00	0.04	7.42	0.00	92.16	0.42		
	Average		0.09	0.00	0.04	7.35	0.00	92.25	0.40		

4.2											
Acid Conc. wt%=84	81	191.00 G/L:2.73	0.08	0.00	0.02	6.89	0.00	92.91	0.20	24.64	0.00
			0.08	0.00	0.03	6.61	0.00	93.17	0.22		
			0.08	0.00	0.02	6.55	0.00	93.27	0.18		
			0.09	0.00	0.02	7.23	0.00	92.56	0.21		
	Average		0.08	0.00	0.02	6.82	0.00	92.98	0.20		
	80	96.00	0.07	0.00	0.02	5.69	0.00	94.09	0.21	39.18	0.00
		G/L:1.37	0.07	0.00	0.02	5.87	0.00	93.91	0.22		
			0.07	0.00	0.03	5.67	0.00	94.10	0.23		
	Average		0.07	0.00	0.02	5.58	0.00	94.22	0.20		
4.3											
Acid Conc. wt%=87.5	83	191.00	0.04	0.00	0.01	2.72	0.00	97.24	0.04	69.93	0.00
		G/L:2.73	0.04	0.00	0.01	2.80	0.00	97.13	0.06		
			0.04	0.00	0.01	2.86	0.00	97.08	0.06		
	Average		0.04	0.00	0.01	2.84	0.00	97.10	0.06		
	82	137.00 G/L:1.97	0.03	0.00	0.01	2.30	0.00	97.64	0.06	76.01	0.00
			0.03	0.00	0.01	2.29	0.00	97.66	0.06		
			0.03	0.00	0.01	2.34	0.00	97.60	0.06		
	Average		0.03	0.00	0.01	2.27	0.00	97.67	0.06		
	85	96.00	0.02	0.00	0.01	1.66	0.00	98.29	0.05	83.18	0.00
		G/L:1.37	0.02	0.00	0.01	1.56	0.00	98.39	0.05		

	Average		0.02	0.00	0.01	1.61	0.00	98.34	0.05		
4.4											
Acid Conc.	88	191.00	0.03	0.00	0.01	2.03	0.00	97.93	0.04	79.24	0.00
wt%=89.5		G/L:2.73	0.03	0.00	0.01	1.94	0.00	98.02	0.04		
			0.03	0.00	0.01	2.02	0.00	97.94	0.04		
	Average		0.03	0.00	0.01	1.98	0.00	97.98	0.04		
	87	137.00	0.02	0.00	0.01	1.50	0.00	98.45	0.05	84.93	0.00
		G/L:1.97	0.02	0.00	0.01	1.44	0.00	98.51	0.05		
			0.02	0.00	0.01	1.49	0.00	98.46	0.04		
	Average		0.02	0.00	0.01	1.45	0.00	98.50	0.05		
	86	96.00	0.01	0.00	0.01	1.05	0.00	98.90	0.04	88.34	0.00
		G/L:1.37	0.01	0.00	0.01	1.10	0.00	98.85	0.05		
			0.01	0.00	0.01	1.15	0.00	98.81	0.04		
			0.01	0.00	0.01	1.18	0.00	98.78	0.04		
			0.01	0.00	0.01	1.13	0.00	98.83	0.04		
	Average		0.01	0.00	0.01	1.12	0.00	98.84	0.04		
4.5											
Acid Conc.	77	191.00	0.01	0.01	0.00	1.10	0.76	98.09	0.05	88.51	0.71
wt%=91.5		G/L:2.73	0.01	0.01	0.00	1.09	0.67	98.18	0.06		
			0.01	0.01	0.00	1.12	0.90	97.93	0.05		
	Average		0.01	0.01	0.00	1.11	0.78	98.07	0.05		

	76	137.00	0.01	0.01	0.01	1.19	0.60	98.14	0.07	88.55	0.59
		G/L:1.97	0.01	0.01	0.01	1.13	0.56	98.25	0.06		
			0.01	0.01	0.00	0.96	0.61	98.37	0.06		
	Average		0.01	0.01	0.01	1.09	0.59	98.25	0.06		
	75	96.00	0.01	0.00	0.00	0.82	0.45	98.68	0.05	91.48	0.48
		G/L:1.37	0.01	0.01	0.00	0.75	0.50	98.69	0.06		
			0.01	0.01	0.00	0.90	0.50	98.54	0.06		
			0.01	0.01	0.00	0.81	0.47	98.66	0.06		
	Average		0.01	0.01	0.00	0.82	0.48	98.64	0.06		
SET 5	**To observe the effect of acid flow rate on H_2S conversion and SO_2 emission**										
Conditions	Run No.	Liquid Flow Rate, cc/min	H_2S/N_2 Peak Area Ratio	SO_2/N_2 Peak Area Ratio	H_2O/N_2 Peak Area Ratio	H_2S Mole Percent in Exit Gas	SO_2 Mole Percent in Exit Gas	N_2 Mole Percent in Exit Gas	H_2O Mole Percent in Exit Gas	H_2S Conv Percent	SO_2 Emission Mole Percent
5.1											
H_2S in =9 mole%	120A	50.00	0.05	0.00	0.01	5.17	0.00	94.70	0.13	43.39	0.00
T = 120°C		G/L:2.73	0.05	0.00	0.01	5.33	0.00	94.55	0.12		
P= 5 psig			0.05	0.00	0.01	5.29	0.00	94.59	0.12		
G= 138 sccm			0.05	0.00	0.01	5.02	0.00	94.85	0.12		
Acid Conc.	Average		0.05	0.00	0.01	5.20	0.00	94.67	0.13		
wt%=85											
	120B	50.00	0.05	0.00	0.01	4.91	0.00	95.06	0.02	46.97	0.00

		G/L:2.73	0.05	0.00	0.01	4.86	0.00	95.07	0.07		
			0.05	0.00	0.01	4.90	0.00	95.01	0.09		
	Average		0.05	0.00	0.01	4.89	0.00	95.05	0.06		
	124A	70.00 G/L:1.97	0.05	0.00	0.01	4.94	0.00	94.96	0.09	45.51	0.00
			0.05	0.00	0.01	5.25	0.00	94.63	0.12		
			0.05	0.00	0.01	4.86	0.00	95.06	0.09		
	Average		0.05	0.00	0.01	5.02	0.00	94.88	0.10		
	124B	70.00 G/L:1.97	0.06	0.00	0.01	5.00	0.00	94.90	0.10	45.52	0.00
			0.06	0.00	0.01	5.06	0.00	94.84	0.10		
			0.06	0.00	0.01	4.99	0.00	94.90	0.11		
	Average		0.06	0.00	0.01	5.02	0.00	94.88	0.10		
	121A	100.00 G/L: 1.38	0.05	0.00	0.01	4.79	0.00	95.13	0.08	47.30	0.00
			0.04	0.00	0.01	4.17	0.00	95.73	0.10		
			0.05	0.00	0.01	5.25	0.00	94.62	0.12		
			0.05	0.00	0.01	5.23	0.00	94.67	0.10		
	Average		0.05	0.00	0.01	4.86	0.00	95.04	0.10		
	121B	100.00 G/L:1.38	0.06	0.00	0.01	5.03	0.00	94.89	0.09	46.66	0.00
			0.05	0.00	0.01	4.82	0.00	95.06	0.12		
			0.06	0.00	0.01	4.90	0.00	95.00	0.09		
	Average		0.06	0.00	0.01	4.92	0.00	94.98	0.10		
5.2											

Acid Conc. wt%=88	126A	50.00 G/L:2.73	0.02	0.01	0.00	1.54	0.84	97.61	0.00	83.15	0.78
			0.02	0.01	0.00	1.66	0.74	97.60	0.00		
			0.02	0.01	0.00	1.59	0.75	97.66	0.00		
	Average		0.02	0.01	0.00	1.60	0.78	97.63	0.00		
	126B	50.00 G/L:2.73	0.02	0.01	0.00	1.63	0.79	97.58	0.00	81.71	0.81
			0.02	0.01	0.00	1.88	0.90	97.17	0.05		
			0.02	0.01	0.00	1.67	0.76	97.53	0.03		
	Average		0.02	0.01	0.00	1.73	0.82	97.43	0.03		
	127A	70.00 G/L:1.97	0.02	0.00	0.00	1.52	0.00	98.48	0.00	83.85	0.00
			0.02	0.00	0.00	1.59	0.00	98.41	0.00		
			0.02	0.00	0.00	1.52	0.00	98.48	0.00		
	Average		0.02	0.00	0.00	1.54	0.00	98.46	0.00		
	127B	70.00 G/L:1.97	0.02	0.00	0.00	1.73	0.00	98.23	0.04	81.64	0.00
			0.02	0.00	0.00	1.81	0.00	98.16	0.04		
			0.02	0.00	0.00	1.72	0.00	98.23	0.06		
	Average		0.02	0.00	0.00	1.75	0.00	98.20	0.05		
	128	100.00 G/L:1.38	0.01	0.00	0.00	1.43	0.00	98.53	0.04	84.53	0.00
			0.02	0.00	0.00	1.50	0.00	98.47	0.03		
			0.02	0.00	0.00	1.51	0.00	98.43	0.06		
	Average		0.02	0.00	0.00	1.48	0.00	98.48	0.04		
5.3											

Acid Conc. wt%=90	131	50.00 G/L:2.73	0.01	0.02	0.00	0.66	2.07	97.23	0.04	91.77	1.92
			0.01	0.02	0.00	0.84	2.03	97.13	0.00		
			0.01	0.02	0.00	0.83	1.67	97.48	0.02		
	Average		0.01	0.02	0.00	0.78	1.92	97.28	0.02		
	130	70.00 G/L:1.97	0.01	0.01	0.00	0.71	0.52	98.75	0.02	92.60	0.57
			0.01	0.01	0.00	0.50	0.74	98.73	0.03		
			0.01	0.00	0.00	0.92	0.47	98.61	0.01		
	Average		0.01	0.01	0.00	0.71	0.57	98.70	0.02		
	129	100.00 G/L=1.38	0.01	0.00	0.00	0.58	0.30	99.10	0.02	93.34	0.30
			0.01	0.00	0.00	0.62	0.36	98.99	0.03		
			0.01	0.00	0.00	0.72	0.26	98.99	0.02		
	Average		0.01	0.00	0.00	0.64	0.31	99.03	0.02		
5.4											
Acid Conc. wt%=93	133	50.00 G/L:2.73	0.00	0.02	0.00	0.33	2.28	97.39	0.00	98.11	1.99
			0.00	0.02	0.00	0.06	1.98	97.96	0.00		
			0.00	0.02	0.00	0.15	1.73	98.12	0.00		
	Average		0.00	0.02	0.00	0.18	2.00	97.82	0.00		
	132	100.00 G/L:1.38	0.00	0.01	0.00	0.09	0.66	99.25	0.00	98.94	0.77
			0.00	0.01	0.00	0.11	0.82	99.07	0.01		
			0.00	0.01	0.00	0.11	0.84	99.05	0.00		
	Average		0.00	0.01	0.00	0.10	0.77	99.12	0.00		