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Homogenous reaction kinetics of reduction of sulfur dioxide

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ABSTRACT

Title of Thesis: Homogeneous Reaction Kinetics of
Reduction of Sulfur Dioxide by
Carbon Monoxide

Satyanarayana Manthani, Master of Science in Chemical
Engineering, 1984

Thesis directed by: Dr. W.T.Wong

Homogeneous reduction of sulfur dioxide by carbon monoxide was investigated in the temperature range between 700 and 1000°C, initial sulfur dioxide concentration of about 3000 ppm, typical of a flue gas from coal fired power plants, and excess carbon monoxide concentration, in a 12 mm O.D. quartz tubular reactor. Over ninty percent reduction of sulfur dioxide was obtained at temperatures above 900°C and space times of the order of about 3.5 seconds. Substantial carbonyl sulfide was also produced.

HOMOGENEOUS REACTION KINETICS
OF REDUCTION OF SULFUR DIOXIDE
BY CARBON MONOXIDE

by
Satyanarayana Manthani

Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in
partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering
1984

APPROVAL SHEET

Title of Thesis: Homogeneous Reaction Kinetics of Reduction of Sulfur Dioxide by Carbon Monoxide

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I. INTRODUCTION

A. The Problem

Sulfur dioxide is the second largest air pollutant (1). It has been estimated that 36.6 million tons of sulfur dioxide were emitted from stationary sources alone in the United States in 1970 and the emission could quadruple by the year 2000 if adequate controls are not provided (2). Table 1.1 lists estimated sulfur dioxide emission in the U.S. without abatement (4). Approximately twothirds of the emission comes from fossil fuel power plants (2),(4). Flue gas from combustion processes normally contains less than 0.5 percent sulfur dioxide. On the other hand , stack gas from smelters handling sulfur ores may range upto as high as 8 percent sulfur dioxide (3).

B. Acid Rain

Sulfur dioxide is the chief chemical specie due to which the phenomenon of "Acid Rain" takes place. Acid Rain is the name given to air pollution, chiefly sulfur oxides and nitrogen oxides, which change chemically as they are transported through the atmosphere and fall back to the earth as acidic rain, snow or dry particles.

C. Ways to Reduce SO_2 Content in Flue Gas

The following are some of the approaches for the abatement of sulfur doixide.

1. Clean Fuels

   Low sulfur fuels especially less than 0.5 percent sulfur are scarce and expensive.

2. Fuel Desulfurization

   Effeiciency of coal desulfurization is still low and prohibitively expensive. The cost of desulfurized fuel would be substantially increased.

3. High Stacks

   Tall stacks to increase atmospheric dispersion was popular in Europe, especially England. Although, high stacks (1000 feet or more) are effective in controlling ambient concentrations, there is increasing concern over the total amount of sulfur dioxide emitted and the resulting general increase in ambient concentration over wide areas.

4. Flue Gas Desulfurization (F G D) Systems

   Although, no one flue gas desulfurization process has been developed to the level of universal acceptance, this technique is currently under intensive research. Over 70 such processes in various stages of development are currently under investigation (14).

D. A Dry Regenerative Process under Investigation at N J I T

Several dry processes have been suggested for abating SO_2

from combustion operations (4). A dry regenerative process for the desulfurization of flue gas is under investigation at the New Jersey Institute of Technology (N J I T). Stewart (5) has evaluated the feasibility of the process and compared with some of the first generation processes. The process seems to be attractive and promising. The schematic diagram has been shown in Figure 1.1. The scheme involves oxidation of sulfur dioxide to sulfur trioxide over a vanadium pentoxide catalyst. This step is an extension of the famous Contact Process for the manufacture of sulfuric acid and the technology is readily available from Monsanto Company. The sulfur trioxide is then adsorbed on alumina yielding aluminium sulfate. The aluminium sulfate is reacted with carbon monoxide to regenerate alumina, which is recycled back for sulfonation. This reaction also produces rich oxides of sulfur, which can be later converted to elemental sulfur, a saleable product in a Claus Unit. The exact reaction products of the regeneration step are still not clear.

E. Regeneration

Previous investigation by Raj Date (6), indicate that there is homogeneous reaction taking place between carbon monoxide and sulfur dioxide in the regeneration loop. He also observed carbonyl sulfide formation in the regeneration products.

Table 1.1 Estimated Sulfur Dioxide Emission in U.S. without Abatement

Annual Emission of Sulfur Dioxide (millions of tons)

	1970	1980	1990	2000
Power plant operation(coal and oil)	20.0	41.1	62.0	94.5
Other combustion of coal	4.8	4.0	3.1	1.6
Combustion of petroleum products (excluding power plant oil)	3.4	3.9	4.3	5.1
Smelting of metallic ores	4.0	5.3	7.1	9.6
Petroleum refinery operation	2.4	4.0	6.5	10.5
Miscellaneous sources	2.0	2.6	3.4	4.5
Total	36.6	60.9	86.4	125.8

February 1970 estimates by National Air Pollution Control Administration, excluding transportation.

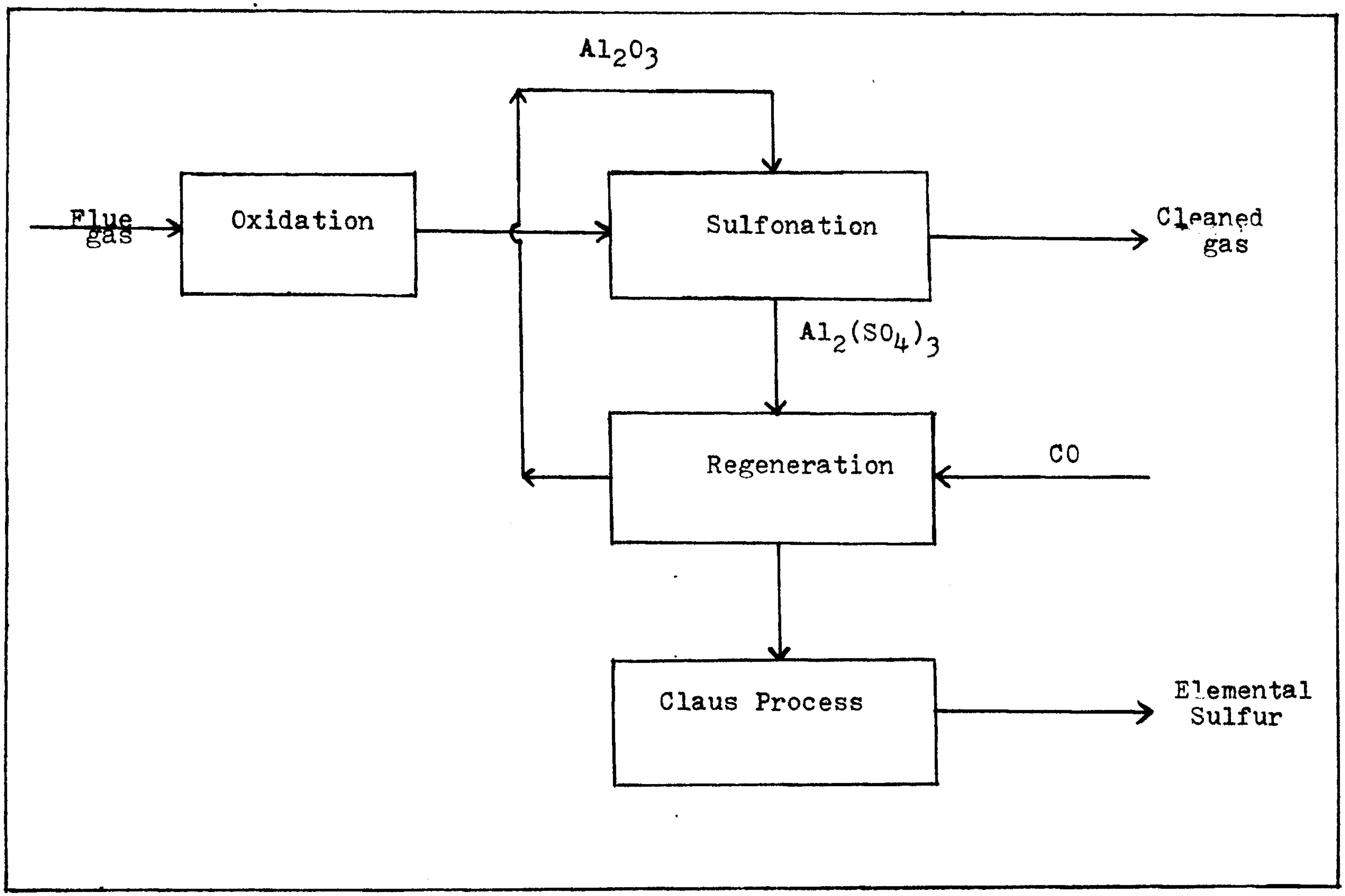


Figure 1.1 Process Block Diagram of SO_2 Project under Investigation at NJIT

F. Reduction of SO_2 by CO

Reduction of sulfur dioxide to elemental sulfur by using a reducing agent has received considerable attention in recent years. Carbon monoxide has been one of the most widely studied reducing agents. It can be readily produced by steam methane reforming or partial oxidation processes. As such, some carbon monoxide is formed in the combustion of coal whose quantity can be adjusted by coal to air ratio.

G. Why the Present Study?

The present study of homogeneous reaction kinetics of reduction of sulfur dioxide by carbon monoxide is undertaken because of the following reasons.

1. Literature is devoid of kinetic data of the homogeneous reduction of sulfur dioxide by carbon monoxide.
2. This study will aid in understanding the regeneration mechanism more thoroughly.
3. To check the feasibility of direct homogeneous reduction (without any catalyst) of sulfur dioxide by carbon monoxide.

H. Objectives

The main objectives of this study are the following

1. Design and construction of an apparatus to carryout

the reduction reaction.

2. Development of kinetic data for the homogeneous reduction at ppm level of sulfur dioxide, typical of a power plant flue gas, by excess carbon monoxide at high temperatures. Of course, since the present study does not include the effects of water vapour, oxygen and oxides of nitrogen, the model must be extended for a complete description of the stack gas.
3. Postulation of the reaction mechanism .

I. Advantages

The advantages of this direct reduction process would be numerous.

1. Simplicity of the process - process is one step.
2. No catalyst - thus eliminating the catalyst cost and its regeneration.
3. Process is dry - minimum corrosion problems.
4. Elemental sulfur , which iseasily marketable is product.

It is believed that this study will aid in better understanding regeneration mechanism in particular, and SO_2-Project as a whole in general.

II. LITERATURE REVIEW

Literature search reveals that all processes which employ carbon monoxide as a reducing agent for sulfur dioxide are catalytic. Catalytic processes have the advantage of lower reaction temperature and fast reaction rates. In addition, lower operating temperatures increase equipment and catalyst life, reduce maintenance and cut fuel costs.

A. Homogeneous Reduction

The direct reduction of sulfur dioxide by carbon monoxide has long been known. Hanish and Schroder (7) were the first to establish the stoichiometry of the reaction

$$2CO\ (g) + SO_2\ (g) = 2CO_2\ (g) + \tfrac{1}{2}S_2\ (g) \quad ....(1)$$

Ferguson (8) studied the equilibrium between carbon monoxide, sulfur dioxide, carbonyl sulfide and sulfur vapour around 1000°C with and without a contact catalyst. His experiments were very crude and involved relatively high concentrations of sulfur dioxide (25% volume) and lengthy residence times. Winternitz (9) also studied the thermodynamic and equilibrium relationships of the reaction.

The scope of the stack has problem extends over wide range. Flue gas contains, at most, a few tenths of a percent of sulfur dioxide (2000 to 3000 ppm) and contact times will have to be of the order of a few tenths of a second (10). Literature is scanty of homogeneous reaction between sulfur dioxide and carbon monoxide. Khalafalla etal (11) report that the reduction reaction proceeds very slowly in the absence of a catalyst even at 950°C.

B. Catalytic Reduction

The catalytic studies done by various workers on the reduction reaction are reported in Table 2.1.

Rayson and Harkins (12) observed carbonyl sulfide formation while studying the catalytic reduction of sulfur dioxide with carbon monoxide over several catalysts. Khalafalla and Haas (13) similarly noted COS production with bifunctional iron-alumina catalyst. Querido and Short (14) also observed the deleterious side reaction between elemental sulfur and carbon monoxide to form COS in their study of a commercial copper-alumina catalyst. Quinlan etal (15) further defined the relationship between COS production and SO_2 conversion for this commercial copper-alumina catalyst and demonstrated that a maximum of 80 percent sulfur removal was possible. Goetz etal (16) screened a large number of laboratory prepared and commercial catalysts for the simultaneous reduction of sulfur dioxide and nitric oxide with carbon monoxide and found that carbonyl sulfide was produced by all the catalysts.

Hence, it appears that all catalysts reported in literature, although differing in activity and selectivity have a common problem-the production of undesirable carbonyl sulfide.

Table 2.1 Literature Search of Catalytic Reduction of SO_2 by CO

Researcher(s)	Catalyst	Remarks
Ferguson, J.B., (8)	Porcelain Platinized porcelain	High temperature reaction between 1000-1200°C, high SO_2 concentration and lengthy residence times
Ryason, P.R., and J.Jarkins, (12)	Metals supported on alumina	Low concentration of reactants, simultaneous removal of NO
Lepsoe, R., (17)	Alumina, Coke	High reactant concentration, also reduction of SO_2 by COS
Quinlan, C.W., V.C.Okay, and J.R.Kittrell (15)	8% copper on alumina	Low reactant concentration, simultaneous reduction of NO single bed
Goetz, V.N., A.Sood, and J.R.Kittrell (16)	8% Cu on alumina Pd on alumina Cr promoted iron oxide, Ni on Kieselguhr Copper chromite Barium Promoted Cu chromite, 12% Cu on Kaiser alumina	Catalyst evaluation for simultaneous reduction of SO_2 and NO by CO, single bed
Sood, A., and J.R. Kittrell (18)	Iron chromia (1st bed) Activated alumina (2nd bed)	A dual bed system for simultaneous reduction of SO_2 and NO by CO
Bagllo, J.A., (26)	Lanthanum oxysulfide	Low rate of COS production

Table 2.1 (continued)

Kasaoka, S., H. Tsumaki, and T. Kochihira (19)	$CuO-Al_2O_3$ (various concentrations), $CuO-Cr_2O_3$, $Fe_2O_3-Al_2O_3$, $Fe_2O_3-Cr_2O_3$, $Co_3O_4-Al_2O_3$, $NiO-Al_2O_3$, $CuO-Cr_2O_3-Al_2O_3$, $CuO-Fe_2O_3-Al_2O_3$, $Fe_2O_3-Cr_2O_3-Al_2O_3$	Catalyst selectivity
Querido, R., and W.L. Short (14)	$Cu-Al_2O_3$; $CuO-Al_2O_3$, $Ag-Al_2O_3$, MoO_3-Silica alumina, Silica-alumina	Dual bed, $Cu-Al_2O_3$ is the best catalyst.
Haas, L.A., T.H. McCormick, and S.E. Khalafalla (20)	Transition metals in alumina	Fe(43%) in alumina is the best catalyst.
Khalafalla, S.E., (21), Khalafalla, S.E., and L.A. Haas (13)	Nitrided iron catalyst Carbided iron catalyst	Catalystic function of the iron component
Khalafalla, S.E., E.F. Foerster, and L.A. Haas (22)	Iron-alumina bifunctional catalyst	Various percentages of iron in alumina
Sood, A., C.W. Quinlan, and J.R. Kittrell (23)	Several commercial and experimental catalysts	Effect of oxygen on SO_2 reduction by CO

Table 2.1 (continued)

Okay, V.C., W.L. Short (24)	8% Cu on alumina	Effect of water vapour on the SO_2 reduction by CO
Happel, J., M.A. Hnatow, L. Bajars, and M. Kundrath (25)	Lanthanum titanate	Low rate of COS production
Bazes, J.G.I., L.S. Caretto, and K. Nobe (27)	Cobalt oxides	Less COS production

III. THEORITICAL CONSIDERATIONS

Thermodynamics of the reactions involved furnishes the fundamental information regarding the maximum conversions attainable under any prevailing conditions.

Thermochemistry and Thermodynamics

1. Primary Reactions

The primary reactions that occur in the reduction of sulfur dioxide by carbon monoxide are

$$2CO\ (g) + SO_2\ (g) = \tfrac{1}{2}S_2\ (g) + 2CO_2\ (g) \quad \text{.....} \quad (1)$$

$$CO\ (g) + \tfrac{1}{2}S_2\ (g) = COS\ (g) \quad \text{.................} \quad (2)$$

$$2COS\ (g) + SO_2\ (g) = 3/2S_2\ (g) + 2CO_2\ (g) \quad \text{..} \quad (3)$$

Equation (1) is the direct reduction of sulfur dioxide by carbon monoxide. This is the main reaction. Equation (2) represents a deleterious side reaction between carbon monoxide and sulfur vapour to produce carbonyl sulfide, a toxic gas. Lepsoe (17) reports that equation (2) is an extremely fast reaction. In addition, carbonyl sulfide formed by equation (2) can react directly with sulfur dioxide to produce elemental sulfur and carbon dioxide by equation (3). Haas and Khalfalla (28) and Querido and Short (14) report that alumina is a good catalyst for this reaction.

Table 3.1 shows the primary chemical reactions involved in the reduction of SO_2 by CO along with heat of reaction, free energy of reaction and equilibrium constant values at room temperature. Details of the calculation are shown in Appendix 1. It should be noted from the table that all the heats of reaction and free energies of reaction are negative. The main reaction is strongly exothermic with a heat of reaction value of -48.82 Kcal/mole. A plot of equilibrium constant versus temperature for all the primary reactions is shown in Figure 3.1. Detailed calculations are given in Appendix 1. From the plot it can be inferred that all the three reactions are thermodynamically favorable even upto 1000°C.

2. Secondary Reactions

Secondary reactions are basically dissociation reactions of carbon monoxide and carbonyl sulfide. The decomposition of carbon monoxide is known as Bell Reaction (29) and is given by

$$2CO\ (g) = C\ (s) + CO_2\ (g) \quad \ldots\ldots\ldots\ldots\ldots (4)$$

Heat of reaction, free energy of reaction and equilibrium constant values at room temperature are given in Table 3.2. Equilibrium constant versus temperature plot for this reaction is shown in Figure 3.1 along with the primary reactions. This decomposition is thermodynamically favoured by decreasing temperature and increasing pressure.

Table 3.1 <u>Heat of Reaction, Free Energy of Reaction and Equilibrium Constant of Primary Reactions at Room Temperature</u>

Reaction	Heat of Reaction $\Delta H_{r,298}$ Kcal/mole	Free Energy of Reaction $\Delta H_{f,298}$ Kcal/mole	Equilibrium Constant K_{298}
$2CO\ (g) + SO_2\ (g) = \frac{1}{2}S_2\ (g) + 2CO_2\ (g)$	-48.82	-41.54	1.87×10^{30}
$CO\ (g) + \frac{1}{2}S_2\ (g) = COS\ (g)$	-22.92	-17.72	8.19×10^{12}
$2COS\ (g) + SO_2\ (g) = 2CO_2\ (g) + 3/2S_2\ (g)$	-2.97	-6.10	2.78×10^{4}

Figure 3.1 **A plot of** ilibrium Constant versus Temperature of Primary Reactions

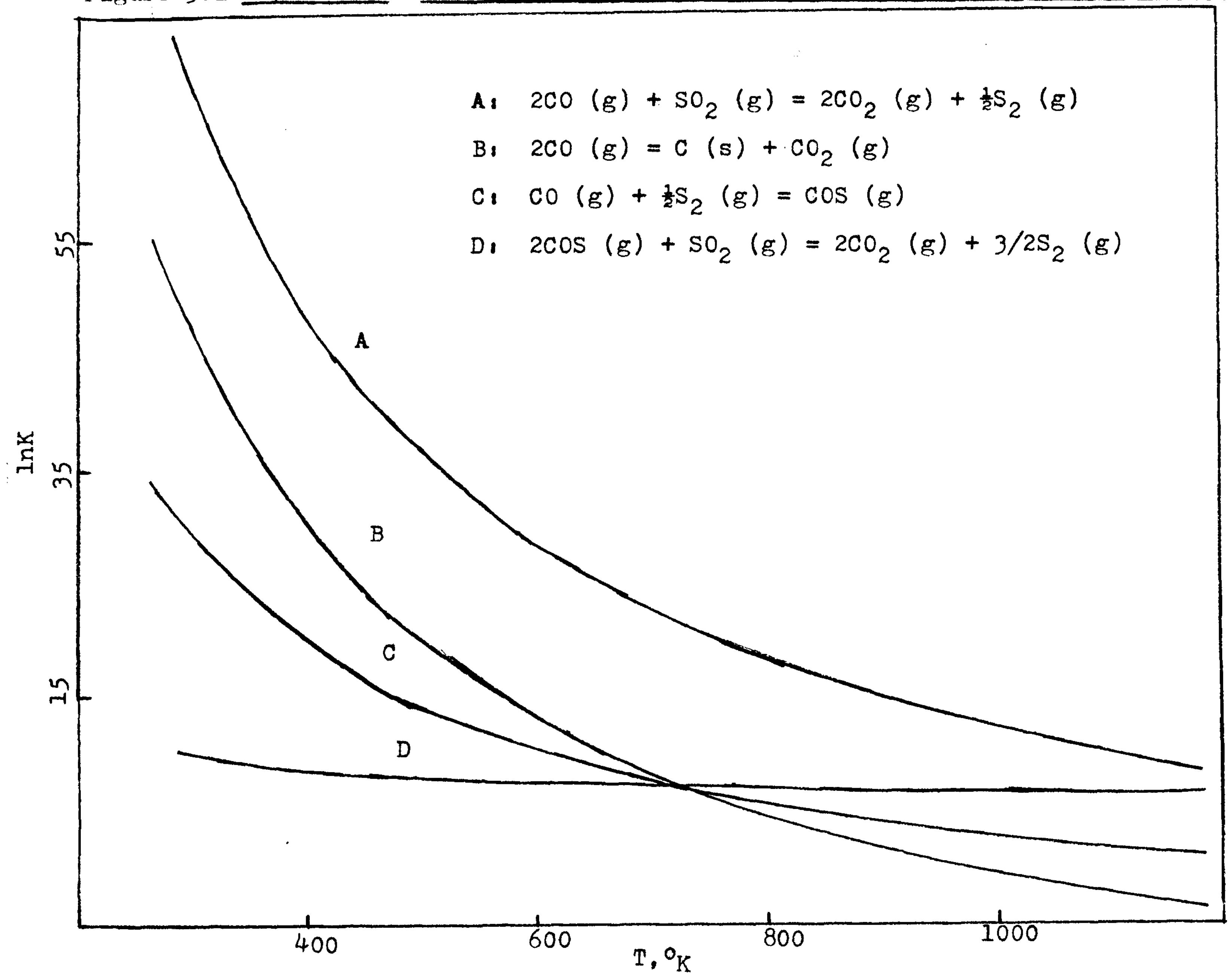


Table 3.2 Heat of Reaction, Free Energy of Reaction and Equilibrium Constant of Secondary Reactions at Room Temperature

Disproportionation Reaction	Heat of Reaction $\Delta H_{r,298}$ Kcal/mole	Free Energy of Reaction $\Delta H_{f,298}$ Kcal/mole	Equilibrium Constant K_{298}
$2CO\ (g) = C\ (s) + CO_2\ (g)$	-41.220	-28.644	7.450×10^{20}
$COS\ (g) = \frac{1}{2}CO_2\ (g) + \frac{1}{2}CS_2\ (g)$	0.859	1.785	0.05
$COS\ (g) = CO\ (g) + \frac{1}{2}S_2\ (g)$	22.924	17.722	1.21×10^{-13}

Decomposition is extremely slow below 400°C in the absence of a catalyst. However, between 400-600°C many surfaces, particularly iron, cobalt and nickel promote the disproportionation reaction (30). Carbonyl sulfide can decompose by two reaction paths as shown below (30),(31).

$$COS\ (g) = \tfrac{1}{2}CO_2\ (g) + \tfrac{1}{2}CS_2\ (g) \ldots\ldots\ldots\ldots (5)$$

$$COS\ (g) = CO\ (g) + \tfrac{1}{2}S_2\ (g) \ldots\ldots\ldots\ldots\ldots (6)$$

At about 600°C carbonyl sulfide disproportionates to carbon dioxide and carbon disulfide according to equation (5). At about 900°C carbonyl sulfide disproportionates to carbon monoxide and elemental sulfur according to equation (6),(30). The heat of reaction, free energy of reaction and equilibrium constant values at room temperature are given in Table 3.2. It should be noted from the table that the free energies of reaction for both routes are positive and the equilibrium constants at room temperature are slightly less than one. Details of the calculations are given in Appendix 2.

3. Other Possible Reactions

If oxygen is present in the flue gas, it oxidizes carbon monoxide and carbonyl sulfide. The oxidation reactions are given by

$$CO\ (g) + \tfrac{1}{2}O_2\ (g) = CO_2\ (g) \ldots\ldots\ldots\ldots\ldots (7)$$

$COS\ (g) + 3/2O_2\ (g) = CO_2\ (g) + SO_2\ (g)$ ....(8)

Numerous other reactions could take place, particularly if water vapour is present as in flue gas. Water gas shift reaction is possible.

$H_2O\ (g) + CO\ (g) = H_2\ (g) + CO_2\ (g)$ .....(9)

The presence of hydrogen may lead to a myriad of other possible reactions.

$3H_2\ (g) + SO_2\ (g) = H_2S\ (g) + 2H_2O\ (g)$ .....(10)

$2H_2\ (g) + S_2\ (g) = 2H_2S\ (g)$ ....(11)

$2H_2S\ (g) + SO_2\ (g) = 2H_2O\ (g) + 3/2S_2\ (g)$ ..(12)

$COS\ (g) + H_2\ (g) = CO\ (g) + H_2S\ (g)$ ....(13)

$COS\ (g) + H_2O\ (g) = CO_2\ (g) + H_2S\ (g)$ ......(14)

Additional reactions which are thermodynamically possible for the SO_x-CO-H_2O-O_2-CO_2-N_2 reaction system are listed in reference (19).

The system studied did not contain oxygen and nitrogen. There was negligible water vapour. Within the realm of sensitivity of the instrument used, Carbon disulfide was not observed in the products. Hence, the secondary reactions and other possible reactions are not considered in the analysis of the experimental data.

IV. EXPERIMENTAL

The reduction of sulfur dioxide by carbon monoxide was studied in an integral tubular reactor under controlled conditions in the laboratory.

A. Experimental Apparatus

The experimental apparatus is shown as a schematic flow diagram in Figure 4.1. Reactors of various dimension and material of construction were used and are shown in Table 4.1. The effective length of each reactor used was 36 inches. Compressed gases employed were carbon monoxide (99.5% pure,Liquid Carbonic), sulfur dioxide (99.9% pure, Liquid Carbonic), chemically pure nitrogen (Airco), high purity helium (99.997%,M G Industries),BD grade carbon dioxide (Matheson) and carbonyl sulfide (99.9% pure, lecture bottle, Matheson). SS-316 and tygon were used as connection tubing materials. Accurately calibrated linear mass flow meters (MKS Mass Flowmeter, Model 259) were used for measuring carbon monoxide and sulfur dioxide flow rates. The flow was controlled with the help of metering (needle) valves.
The preheating zones were wrapped with heating tapes. The length of mixing zone was about 6 inches and was packed with broken glass pieces to ensure complete mixing and was also wrapped with heating tape. The reactor was heated

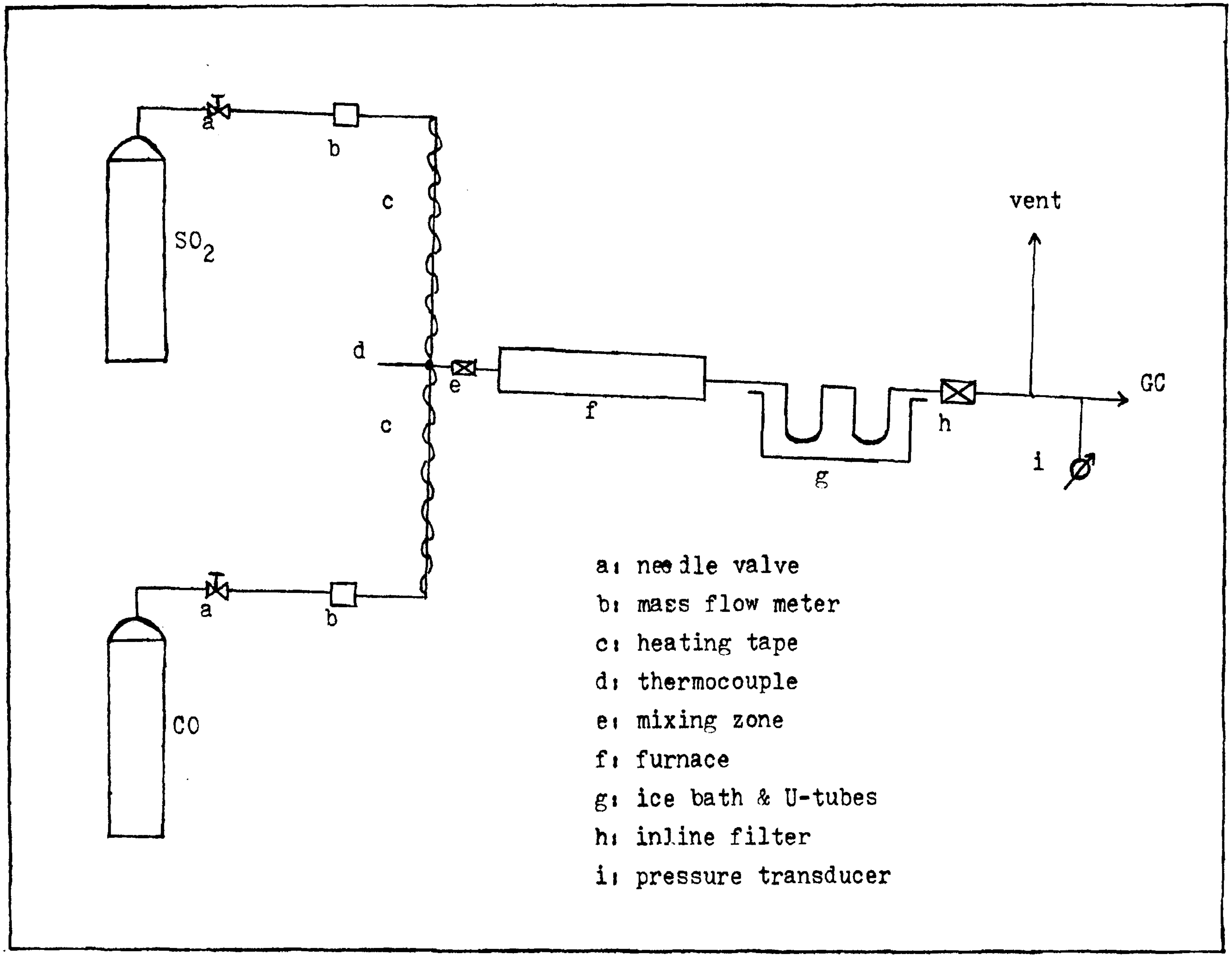


Figure 4.1 Schematic Flow Diagram of Experimental Apparatus

Table 4.1 Reactor Details

Material of Construction of Reactor	O.D. inches	Thickness inches	Effective Length of Reactor inches
SS-304	1/4	0.028	36
SS-316	1/4	0.028	36
SS-316	1/2	0.028	36
SS-316	1/8	0.020	36
Quartz	12(mm)	2(mm)	36
Quartz	6(mm)	2(mm)	36

in a heavy duty, 4 zone furnace (Heavy Duty Equipment Co.,). The reactor temperature was controlled by four 230V variacs. To measure the temperature, a stainless steel tube was placed parallel to the reactor tube inside the furnace and a thermocouple was dragged along the entire length of the steel tube. A K type thermocouple (Chromel-Alumel) of about 50 inches length was used for measurement of temperature.

Exit gas stream from reactor contained sulfur vapour. To avoid plugging the lines down stream of the reactor with sulfur, the gas was flowed through two U-tubes connected in series where most of the sulfur was condensed and removed. The U-tubes were packed with glass beads and were immersed in an ice bath. To ensure complete removal of elemental sulfur before reaching analytical equipment, the gas stream was passed through an in-line filter. Pressure was measured with a differential pressure transducer(Celesco,Model KP15,Ser A13533).

B. Analytical Equipment

For the identification of reaction products an infrared analyzer (Perkin-Elmer,Model 1300) was used in the initial phase of investigation. Sample output is shown in Figure 4.2.

The up-stream compositions were based on mass flow meter readings. These were also double checked by by-passing the reactant gases to a gas chromatograph. The downstream gas compositions were analyzed by gas chromatograph (Aerograph,Model A-90-P). The column employed was a 4ft x 1/8in teflon tube packed with porapak Q material. Due to the excess carbon monoxide used in the investigation and the G.C. conditions there was no good resolution between carbon monoxide and carbon dioxide peaks. They were mixed up. The resolution was good for carbon monoxide, carbonyl sulfide and sulfur dioxide. The G.C.conditions used are given in Table 4.2. High purity helium was used as a carrier gas. Thermal conductivity cell was used as a detector.

Peak areas were determined with the use of an integrator (Infotronics,Model CRS-100). As a double check a recorder (Brush Recorder, Mark 246) was used and the peak areas were estimated by Simpson's rule. The analysis time for each sample was about 8 minutes.

C. Experimental Procedure

Maintenance of isothermal condition along the length of the furnace was the biggest problem. The desired temperature was maintained to within ±5°C. Temperature was measured one inch apart along the entire length of the furnace. With the help of variacs, individual zone

Table 4.2 Details of Chromatographic Analysis for CO,COS and SO_2

Gas analysed	CO,COS,SO_2
Column packing	Porpak Q
Packing size	80/100 mesh
Column	4ft x 1/8in Teflon
Helium flow rate,cc/min	16
Column temperature,°C	100
Detector current, mA	210
Detector temperature,°C	124

temperature was raised or lowered accordingly. For all the runs, the preheating temperature was about 300°C. For every run the power supply for the mass flow meters was adjusted to ±15VDC and the meters were warmed up for a minimum period of 15 minutes. After the warm up period the meters were zeroed if necessary.

When the desired steady temperature in the furnace was attained, pre-determined quantities of carbon monoxide and sulfur dioxide were taken from gas cylinders, through the mass flow meters. After waiting for about 5 minutes for the attainment of steady-state in the system, gas samples were taken into the G.C loop for analysis. Before the sample was taken into the loop, the loop was evacuated and flushed several times. Most of the samples were taken twice to check the reproducibility. The above procedure was repeated at a given temperature for about six different total flow rates. Frequently the U-tubes and the in-line filter were disconnected and cleaned.

Before the actual reaction, the G.C. was calibrated for sulfur dioxide and carbonyl sulfide. Figures 4.3 and 4.4 give the calibration curves for sulfur dioxide and carbonyl sulfide respectively.

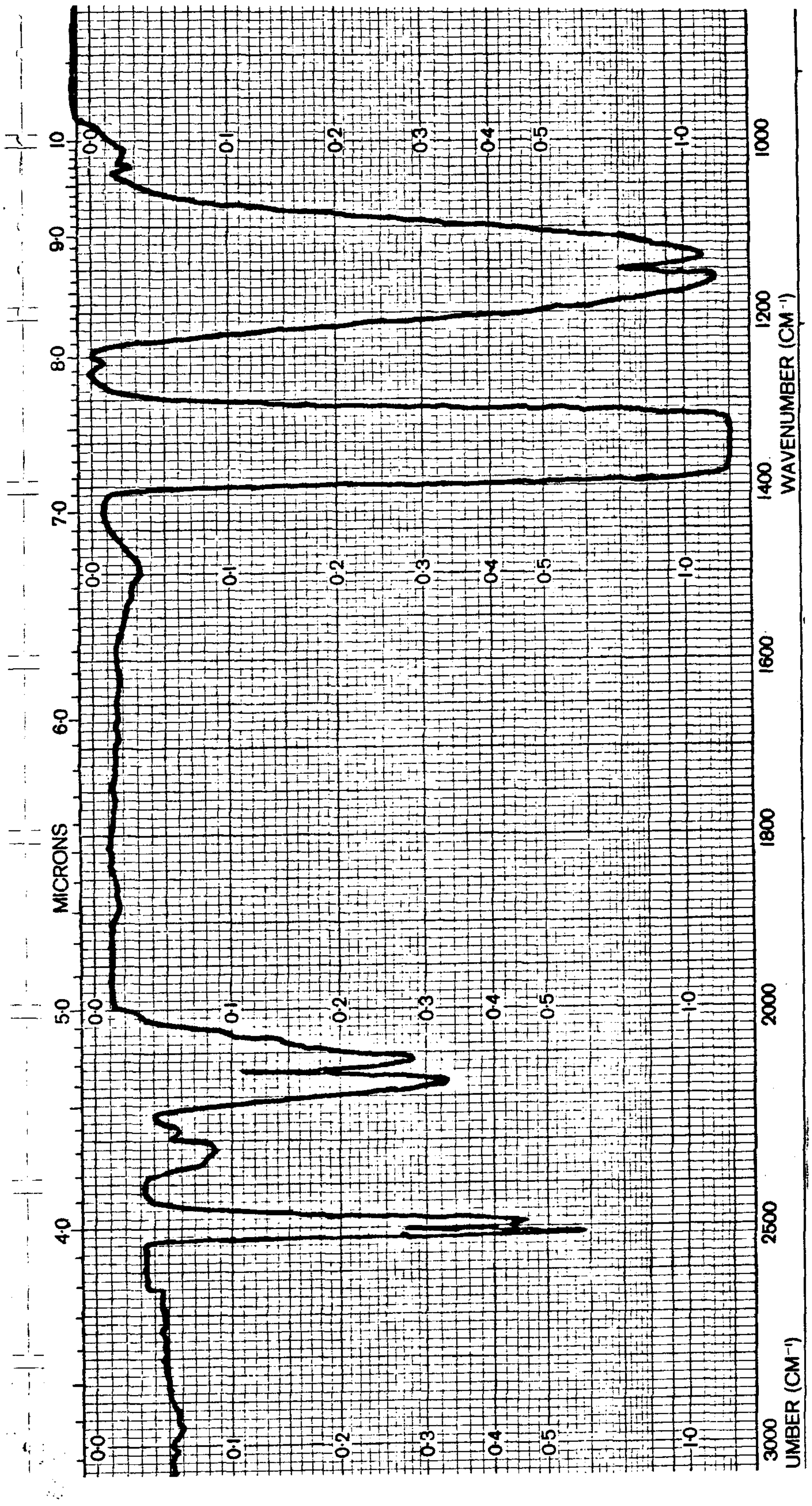


Figure 4.2 Sample Output from Infrared Analyzer

Figure 4.3 G.C. Calibration Curve for SO_2

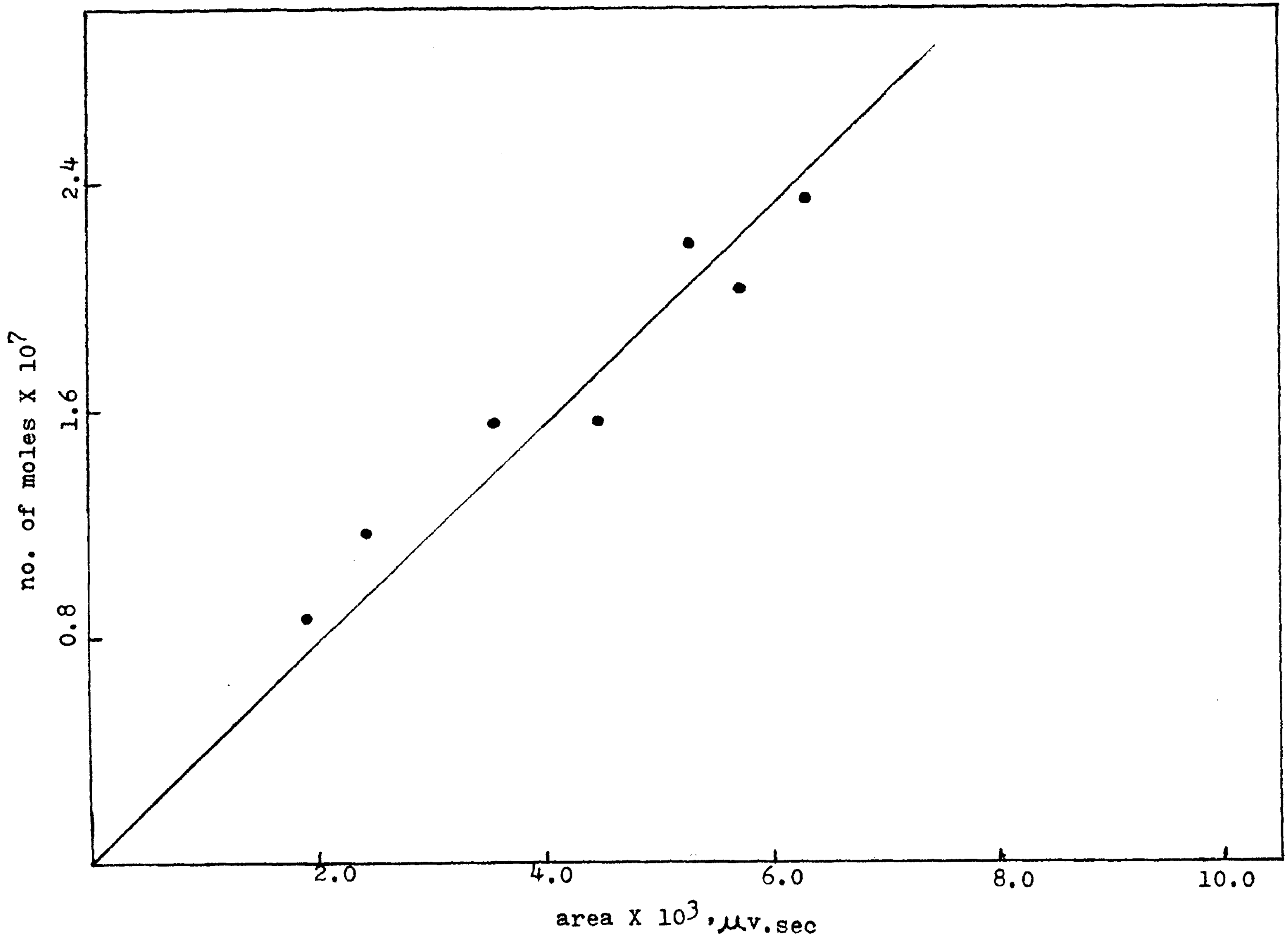
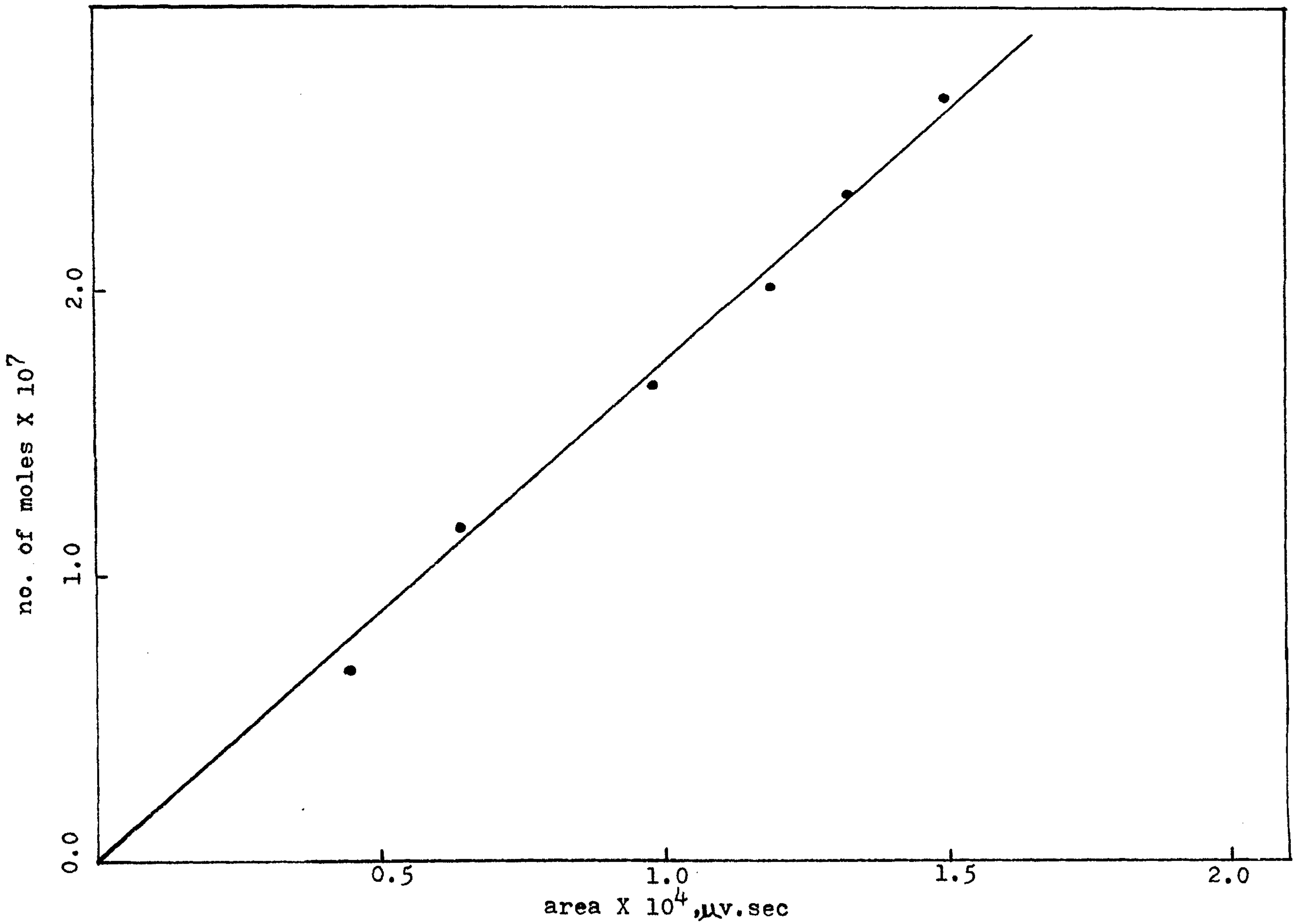


Figure 4.4 G.C. Calibration Curve for COS



V. RESULTS AND DISCUSSIONS

A. Basis of Kinetic Study

The primary reactions of homogeneous reduction of sulfur dioxide by carbon monoxide are

$$2CO\ (g) + SO_2\ (g) = \tfrac{1}{2}S_2\ (g) + 2CO_2\ (g) \quad\text{.........(1)}$$

$$CO\ (g) + \tfrac{1}{2}S_2\ (g) = COS\ (g) \quad\text{....................(2)}$$

$$2COS\ (g) + SO_2\ (g) = 3/2S_2\ (g) + 2CO_2\ (g) \quad\text{......(3)}$$

Equations (1),(2) and (3) are not linearly independent. The detailed proof is given in Appendix 3. For example, multiplying equation (2) by 2 and adding the resultant equation to equation (3) gives equation (1). i.e.,

$$2CO\ (g) + S_2\ (g) = 2COS\ (g) \quad\text{...................(4)}$$

$$2COS\ (g) + SO_2\ (g) = 3/2S_2\ (g) + 2CO_2\ (g) \quad\text{.....(3)}$$

$$2CO\ (g) + SO_2\ (g) = \tfrac{1}{2}S_2\ (g) + 2CO_2\ (g) \quad\text{........(1)}$$

Equation (1) can be considered as the main reaction. The change in concentration of sulfur dioxide can give an indication of the kinetics of equation (1) regardless of the post reactions (2) and (3). This kind of reasoning was given by Khalafalla (21) in his study on catalytic reduction of sulfur dioxide by carbon monoxide. Although there are combinations of series and parallel type multiple reactions taking place in the system, the kinetic study of equation (1) can be justified based on the fractions of sulfur dioxide in the inlet and exit gases. The reaction rate calculated in this study was based on these quantities.

It can be observed from equation (1) that there is a volume change taking place due to reaction. Three volumes of reactants give rise to 2.5 volumes of products. That is, there is a net decrease of 0.5 volumes per unit volume of inlet sulfur dioxide.

The effect of volume change due to reaction is ignored since only ppm level sulfur dioxide is being reacted. The net effect is that there is neglegible change in volume due to reaction.

B. Preliminary Experiments

Querido and Short (14) reported that reactor made of SS-304 material has negligible catalytic effect on the reduction of sulfur dioxide by carbon monoxide. Goetz etal (16) used titanium as the material of construction of the reactor for SO_2-CO reaction and concluded that this material will not catalyze the reaction. Quinlan etal (15) recommended quartz glass and titanium as the reactor material of construction.

Because of the easy availability and robust nature of stainless steel material, preliminary experiments were conducted in stainless steel reactors. these experiments were of qualitative nature only. The sulfur dioxide inlet concentrations studied were 10, 5 and 0.2 percentages. Temperature studied was 600 to 1000°C. The following are some of the important observations made from these preliminary experiments conducted in stainless steel tubes.

1. Measurable reaction between carbon monixide and sulfur dioxide starts around 600°C .
2. For the conditions studied all the four peaks of CO, CO_2, COS and SO_2 were observed between 600 and 700°C.
3. Above 700°C, one hundred percent of sulfur dioxide conversion was noticed and carbonyl sulfide peak was not observed even for a space time of 0.12 sec.
4. Before the actual reaction, pure CO was passed through the reactor to check its disproportionation decomposition. With used tubes, substantial carbon monoxide dissociation was observed. On the other hand, there was negligible dissociation with new reactor tubes.

   In the case of used reactor tubes, the surface was etched because of repeated use at high temperature and the etched surface may be catalyzing the CO-disproportionation dissociation reaction.
5. Under identical conditions of temperature and space time, the extent of reaction was more with steel tubes than quartz tubes.

   Khalafalla etal (22) reported that the dimensions of the steel basket used to hold the catalyst had a significant effect on the sulfur dioxide reaction with carbon monoxide. It can be concluded from the preliminary experiments that both SS-304 and SS-316 materials have substantial catalytic effects on reduction of sulfur dioxide by carbon monoxide.

C. Primary Experiments

A series of 7 runs was carried out in 12 mm O.D. quartz reactor at temperatures ranging from 700-1000°C, at contact times from 2.09 to 4.87 sec. The results are shown in Table 5.1 to 5.7. Space time was calculated based on the reactor inlet conditions. The number of moles of sulfur dioxide (both input and output) and carbonyl sulfide were the amounts present in the G.C. sampling loop at room temperature and atmospheric pressure. These figures were arrived at by comparing peak areas with calibration curves.

1. Selection of Reactant Concentration

The main purpose of this investigation is to study the homogeneous reduction (without any catalyst) of sulfur dioxide with carbon monoxide. Flue gas from coal fired power plants contains 0.2 to 0.3 percent (2000 to 3000 ppm) sulfur dioxide. Therefore an inlet concentration of 3000 ppm sulfur dioxide is selected for all the experimental runs in this investigation.

Table 5.1 SO_2 Conversion and COS Production at Various Feed Rates at 700°C

Inlet Flow Rate sccm			t,sec	SO_2			COS	
SO_2	CO	Total		input no. of moles$\times 10^7$	output no. of moles$\times 10^7$	conversion percentage	produced no. of moles$\times 10^7$	normalized production percentage
1.242	420	421.242	4.87	2.33	0.65	72.1	1.31	56.2
1.656	560	561.656	3.66	2.33	1.17	49.8	0.97	41.6
2.070	700	702.070	2.92	2.33	1.24	46.8	0.89	38.2
2.484	840	842.484	2.44	2.33	1.29	44.6	0.59	25.3
2.898	980	982.898	2.09	2.33	1.36	41.6	0.56	24.0

Table 5.2 SO_2 Conversion and COS Production at Various Feed Rates at 750^0C

Inlet Flow Rate sccm				SO_2			COS	
SO_2	CO	Total	t,sec	input no. of moles X 10^7	output no. of moles X 10^7	conversion %	Produced no. of moles X 10^7	Normalised Production %
1.242	420	421.242	4.87	2.33	0.25	89.3	1.50	64.4
1.656	560	561.656	3.66	2.33	0.96	58.8	1.06	45.5
2.070	700	702.070	2.92	2.33	1.19	48.9	1.02	43.8
2.484	840	842.484	2.44	2.33	2.02	13.3	0.98	42.1
2.898	980	982.898	2.09	2.33	2.27	2.6	0.94	40.3

Table 5.3 SO_2 Conversion ans COS Production at Various Feed Rates at 810°C

Inlet Flow Rate sccm			t,sec	SO_2			COS	
SO_2	CO	Total		input no. of moles X 10^7	output no. of moles X 10^7	conversion %	produced no. of moles X 10^7	normalised production %
1.242	420	421.242	4.87	2.33	0.44	81.1	1.53	65.7
1.656	560	561.656	3.66	2.33	0.83	64.4	1.13	48.5
2.070	700	702.070	2.92	2.33	1.22	47.6	0.77	33.1
2.484	840	842.484	2.44	2.33			0.88	37.8
2.898	980	982.898	2.09	2.33	1.93	17.2	0.55	23.6

Table 5.4 SO_2 Conversion and COS Production at Various Feed Rates at 860°C

Inlet Flow Rate sccm			t,sec	SO_2			COS	
SO_2	CO	Total		input no. of moles X 10^7	output no. of moles X 10^7	conversion %	produced no. of moles X 10^7	normalised production %
1.242	420	421.242	4.87	2.33	0.52	77.7	1.34	57.5
1.656	560	561.656	3.66	2.33	1.01	56.7	0.98	42.1
2.070	700	702.070	2.92	2.33	1.23	47.2	0.96	41.2
2.484	840	842.484	2.44	2.33	1.51	35.2	0.78	33.5
2.898	980	982.898	2.09	2.33	2.04	12.5	0.50	21.5

Table 5.5 SO_2 Conversion and COS Production at Various Feed Rates at 910°C

Inlet Flow Rate sccm			t,sec	SO_2			COS	
SO_2	CO	Total		input no. of moles X 10^7	output no. of moles X 10^7	conversion %	produced no. of moles X 10^7	normalised production %
1.242	420	421.242	4.87	2.33	0.05	97.9	1.46	62.7
1.656	560	561.656	3.66	2.33	0.39	83.3	1.00	42.9
2.070	700	702.070	2.92	2.33	1.32	43.4	0.79	33.9
2.484	840	842.484	2.44	2.33	2.17	6.9	0.60	25.8
2.898	980	982.898	2.09	2.33	2.27	2.6	0.40	17.2

Table 5.6 SO_2 Conversion and COS Production at Various Feed Rates at 950°C

Inlet Flow Rate sccm			t,sec	SO_2			COS	
SO_2	CO	Total		input no. of moles X 10^7	output no. of moles X 10^7	conversion %	produced no. of moles X 10^7	normalised production %
1.242	420	421.242	4.87	2.33	0.00	100.0	1.63	70.0
1.656	560	561.656	3.66	2.33	0.14	94.0	1.16	49.8
2.070	700	702.070	2.92	2.33	0.58	75.1	0.88	37.8
2.484	840	842.484	2.44	2.33	1.35	42.1	0.78	33.5
2.898	980	982.898	2.09	2.33	2.10	9.9	0.77	33.1

Table 5.7 SO_2 Conversion and COS Production at Various Feed Rates at 1000°C

Inlet Flow Rate sccm			t,sec	SO_2			COS	
SO_2	CO	Total		input no. of moles X $1o^7$	output no. of moles X 10^7	conversion %	produced no. of moles X 10^7	normalised production %
1.242	420	421.242	4.87	2.33	0.00	100.0	1.11	47.6
1.656	560	561.656	3.66	2.33	0.18	92.3	1.27	54.5
2.070	700	702.070	2.92	2.33	0.91	60.9	1.10	47.2
2.484	840	842.484	2.44	2.33	1.28	45.1	0.92	39.5
2.898	980	982.898	2.09	2.33	1.36	41.6	0.67	28.8

As far as we can judge from an exhaustive literature review, the present investigation is perhaps the first systematic study of the kinetics of the homogeneous reaction between sulfur dioxide and carbon monoxide. To simplify the experiments and reduce the number of experimental variables, only mixtures of sulfur dioxide and excess carbon monoxide were used.

2. Effect of Temperature on SO_2 Conversion and COS Production

Figures 5.1 and 5.2 represent effect of temperature on sulfur dioxide conversion and carbonyl sulfide production, respectively, over the range 700-1000°C. Space time was used as a parameter in these plots, ranging from 2.09 to 4.87 seconds.

From Figure 5.1, it can be inferred that the higher is the space time, the higher is the sulfur dioxide conversion. This kind of behaviour is expected since larger contact time leads to more reaction and thus more sulfur dioxide is converted to products.

It should be observed from the curves that initially there is a sharp rise in sulfur dioxide conversion. However, between 800 to 900°C, there is a decrease in sulfur dioxide conversion and above 900°C, the conversion is increasing again with temperature. At present, no plausible reason can be offered to explain this drop in percent conversion of sulfur

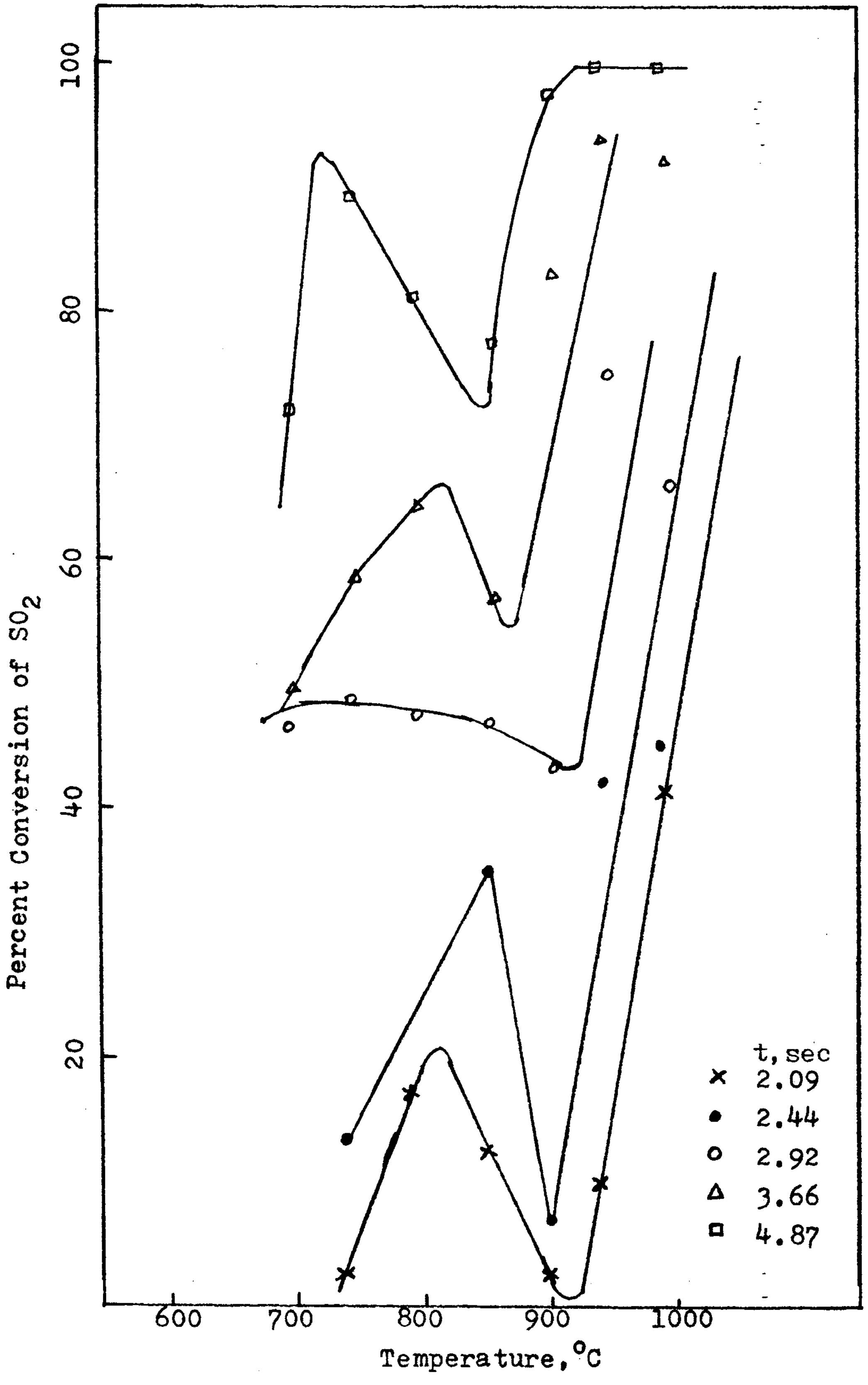


Figure 5.1 Effect of Temperature on SO_2 Conversion

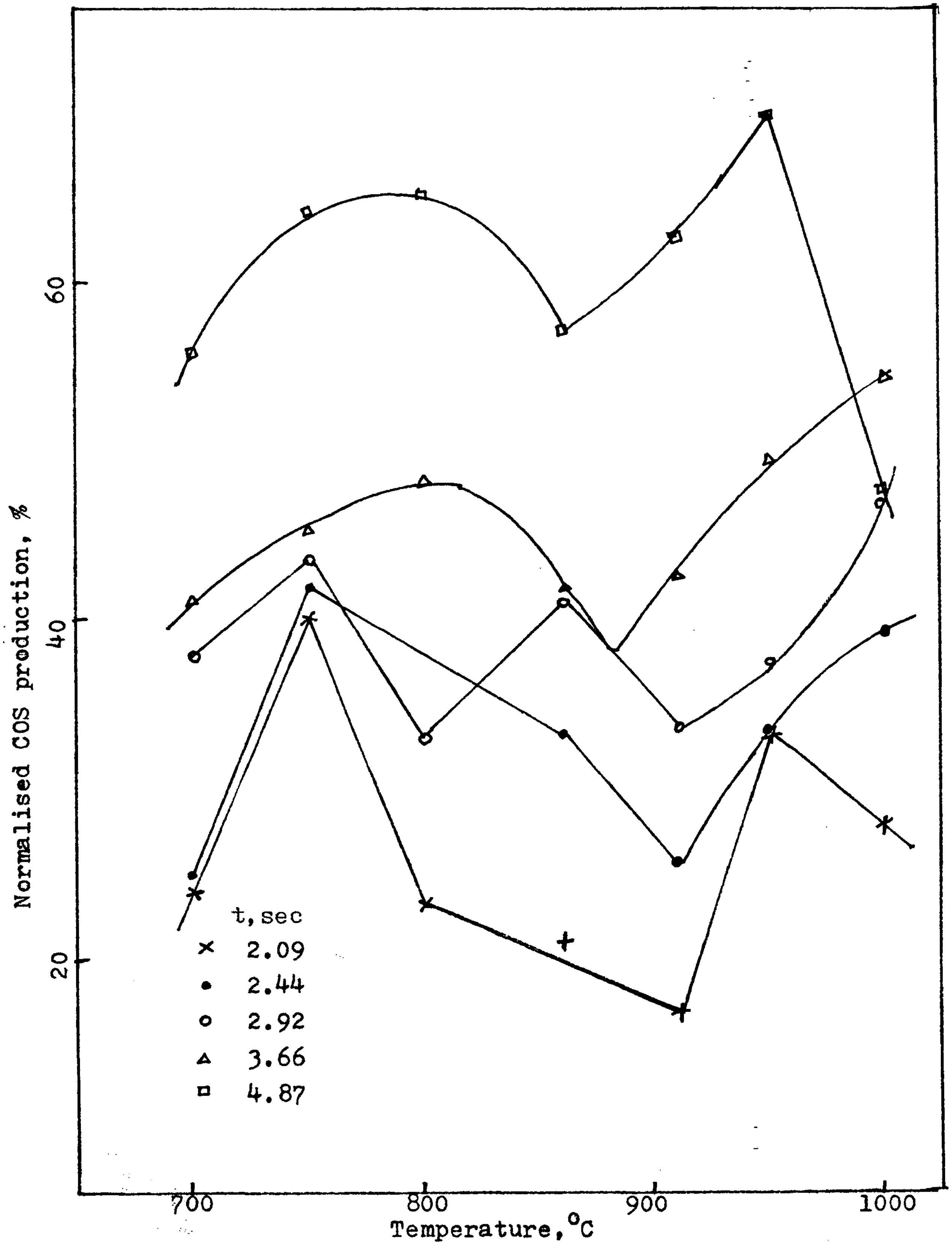


Figure 5.2 Effect of Temperature on COS Production

dioxide between 800 and 900°C. It should be noted that the drop does not seem to be a consequence of experimental errors.

Above 900°C for a space time of 4.87 sec, sulfur dioxide conversion is almost one hundred percent.

In Figure 5.2, normalized COS production (COS produced/inlet SO_2) is plotted as ordinate. Although the data are somewhat scattered, in general more COS is formed at higher space times.

3. Effect of Space Time on SO_2 Conversion and COS Production

Figures 5.3 and 5.4 represent effect of contact time on sulfur dioxide conversion and carbonyl sulfide production, respectively, over the range from 2.09 to 4.87 seconds. Temperature was used as a parameter ranging from 700 to 1000°C.

From Figure 5.3 it is seen that the higher the space time, the higher is the conversion of sulfur dioxide since larger contact time leads to more reaction.

In Figure 5.4 the normalized COS production is plotted as ordinate. Carbonyl sulfide production seems to vary approximately linearly with space time.

D. Kinetic Studies

The conversion of sulfur dioxide was determined at a

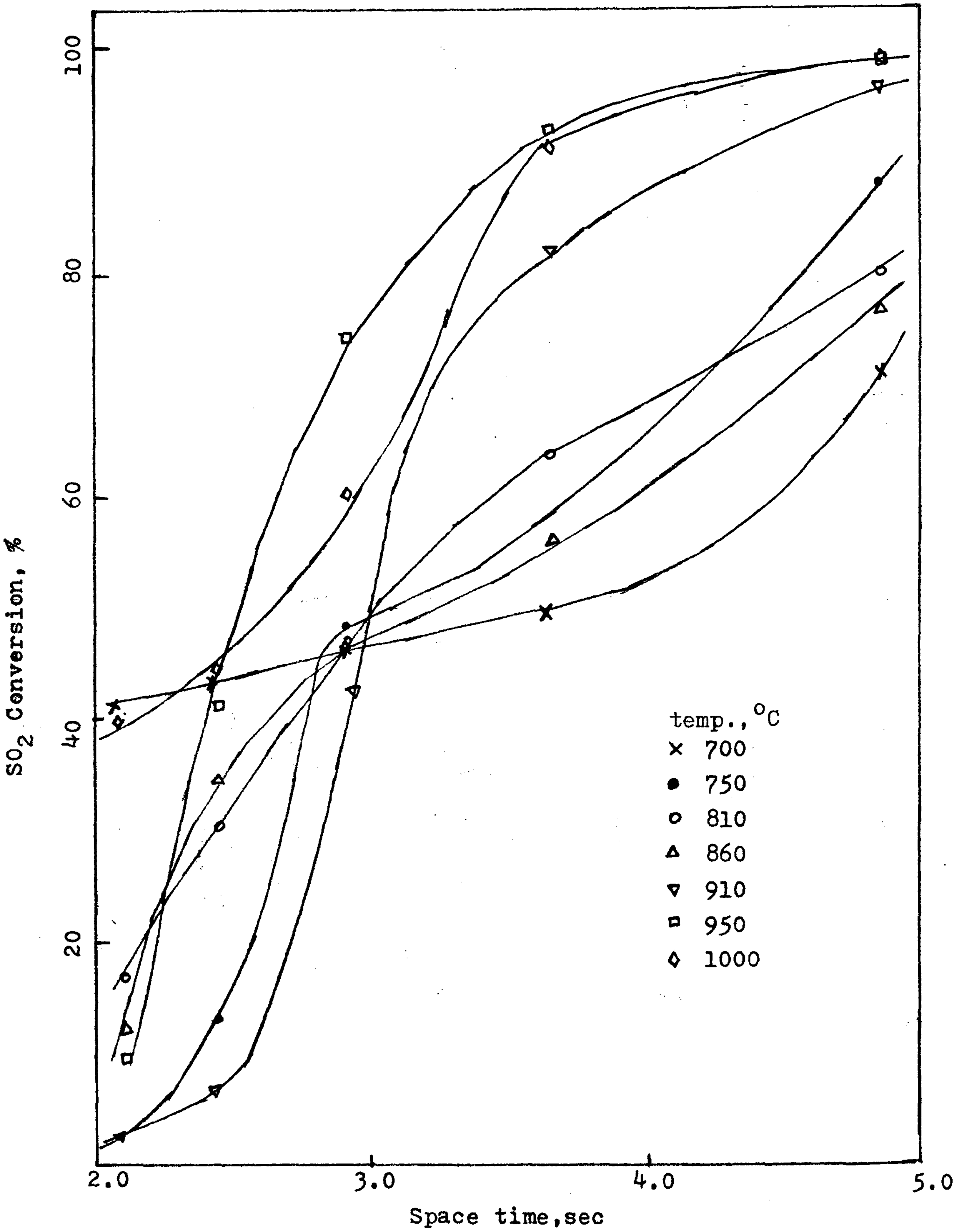
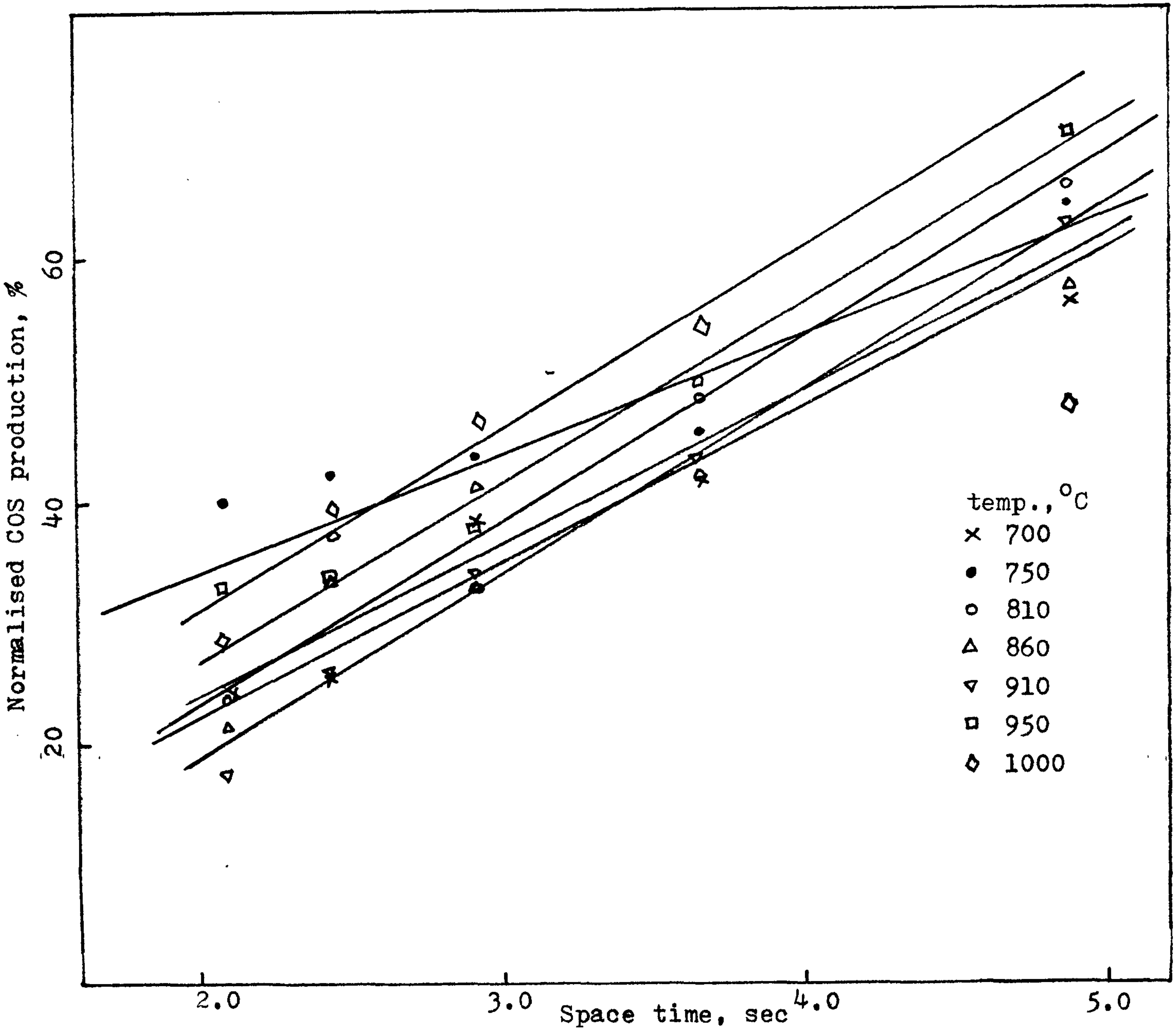


Figure 5.3 Effect of Space-Time on SO_2 Conversion

Figure 5.4 Effect of Space-Time on COS Production



number of feed rates with constant feed composition, temperature and pressure. As the inlet concentration of carbon monoxide used was in excess (99.7%) than that of sulfur dioxide (0.3% only), the concentration of carbon monoxide remains approximately constant at all times. An attempt was made to fit the experimental data to a simple pseudo first order type rate equation with respect to sulfur dioxide concentration. The following rate equation is assumed.

$$-r_s = -\frac{dC_s}{dt} = kC_s \text{ ....}(5)$$

As only ppm level of sulfur dioxide is reacting, the density of the system may be assumed to be constant although there is change in number of moles due to reaction as represented by the stoichiometric equation. For a constant density system obeying irreversible unimolecular type first order reaction, conversion of reactant is related to space time by the following equation (3).

$$-\ln(1-X_s) = kt \text{ ....}(6)$$

A plot of $-\ln(1-X_s)$ versus space time should give a straight line passing through origin. The slope of this straight line is the rate constant at that temperature.

Figure 5.5 represents a plot of $-\ln(1-X_s)$ versus space time at 700 and 810°C. At these two temperatures the data can be approximately fitted to a straight line passing through the origin. Figure 5.6 represents the same plot

Figure 5.5 <u>Plot of $-\ln(1-X_s)$ versus Space-Time</u>

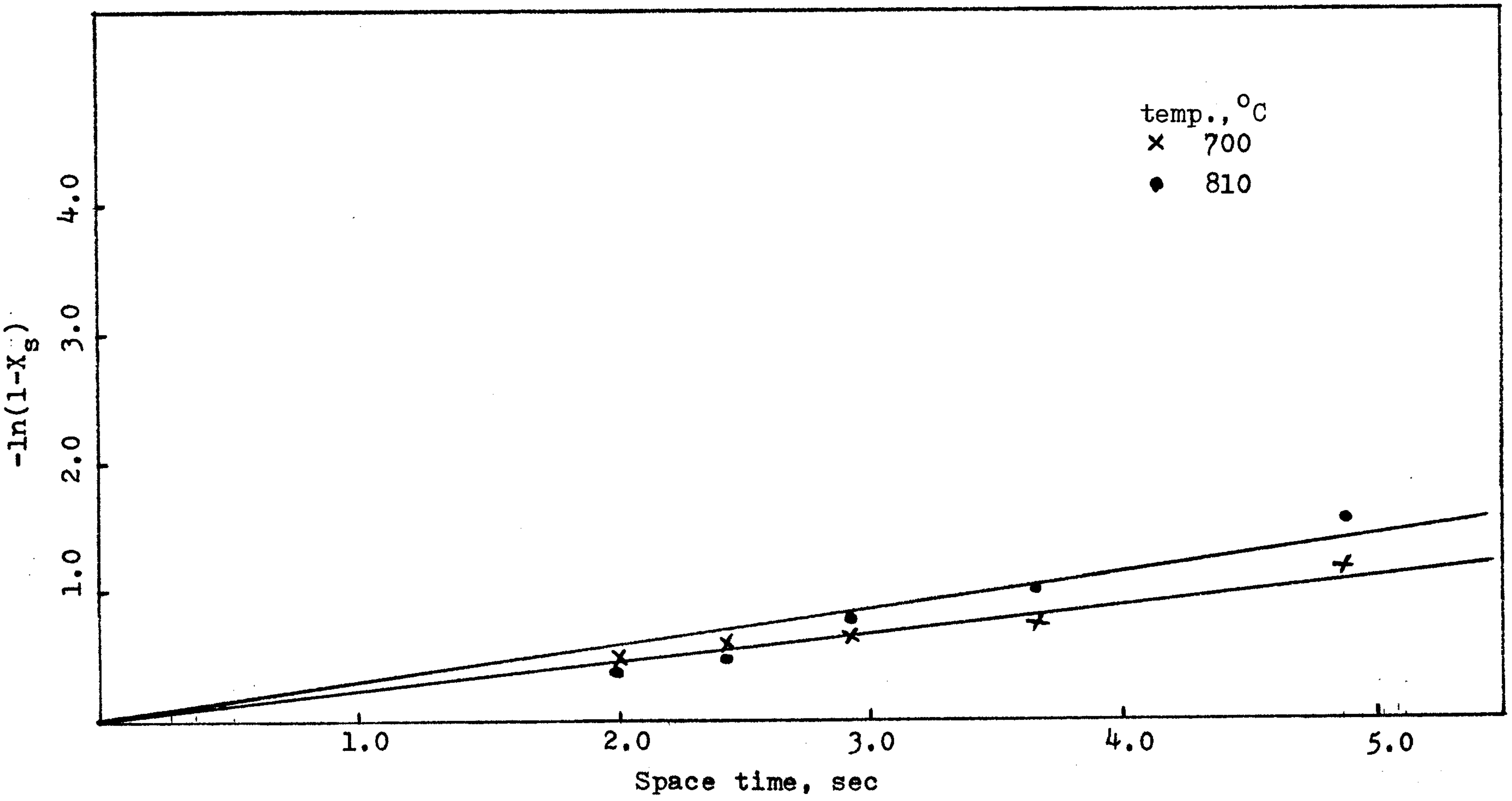
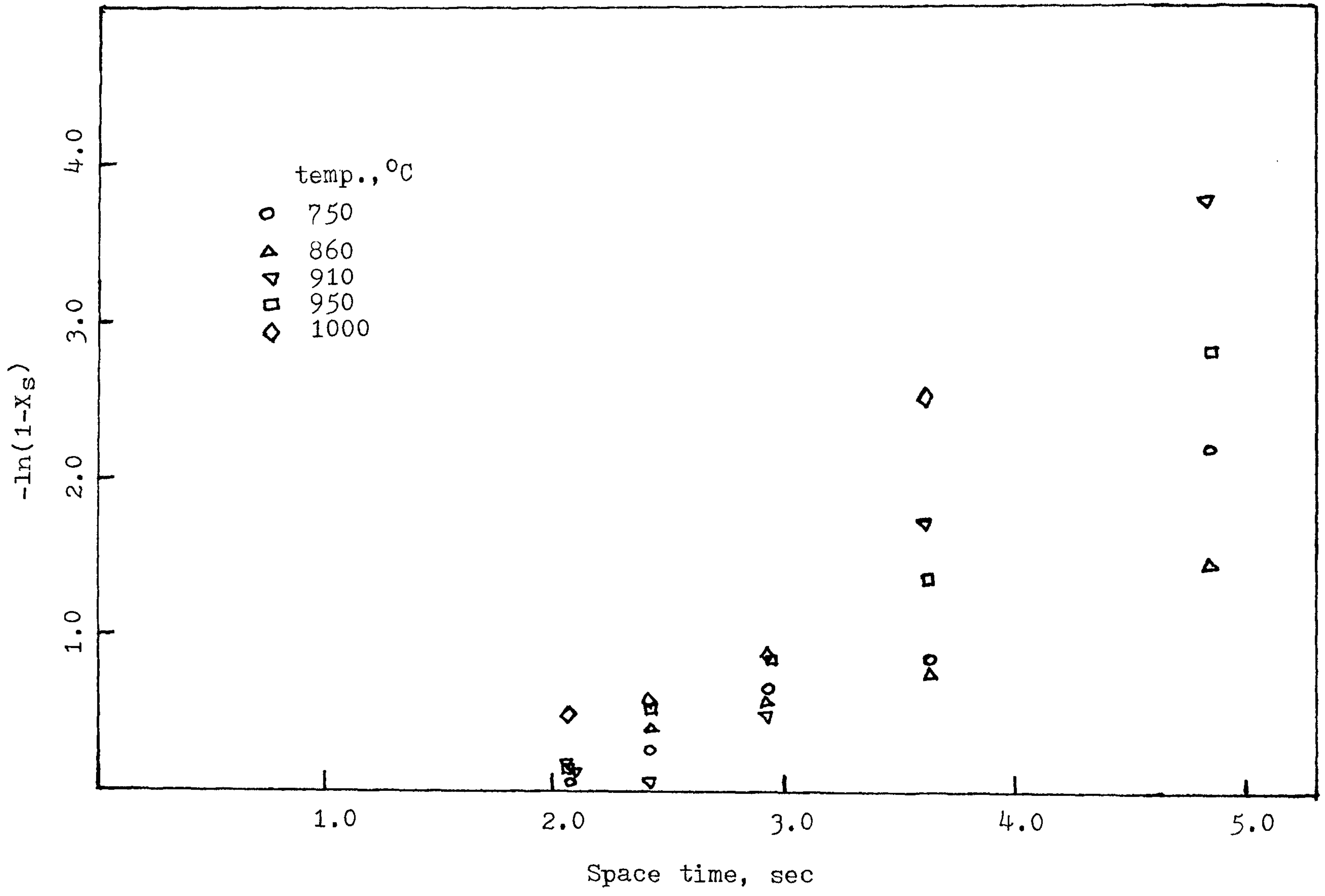


Figure 5.6 Plot of $-\ln(1-X_s)$ Versus Space-Time



for other temperatures of investigation. It should be noted from this figure that the data points are scattered and are not falling on a straight line passing through the origin. It should be inferred that a simple pseudo first order type rate equation in sulfur dioxide concentration is not adequate to fit the data for the entire range of temperatures invested. A more rigorous study is warranted, involving a detailed reaction mechanism consisting of elementary steps, before kinetic study is attempted.

VI. CONCLUSIONS

The following are some of the important conclusions arrived at based on the experimental investigation of the homogeneous reduction of sulfur dioxide by carbon monoxide.

1. Homogeneous reduction of sulfur dioxide by carbon monoxide was carried out in a 12mm O.D. quartz tubular reactor between 700 and 1000°C. The space time investigated was 2.09 to 4.87 seconds. Carbon monoxide was used in excess and the concentration of sulfur dioxide was about 3000 ppm.
2. Contrary to the literature reports, considerable reduction of sulfur dioxide by carbon monoxide can take place without any catalyst at a fairly short space time (of order 2sec).
3. Above 900°C for a space time of 4.86 seconds, one hundred percent of sulfur dioxide conversion is achieved.
4. It is proved that stainless steel materials of type SS-304 and SS-316 will catalyze the reduction of sulfur dioxide by carbon monoxide.
5. It was not possible to fit the experimental data over the entire range of temperatures investigated to a simple pseudo first order type rate equation with respect to sulfur dioxide concentration.

VII. RECOMMENDATIONS

The following are some of the important suggestions made for the improvement of the present investigation. In addition, this chapter also lists some recommendations for the future work.

1. A more rigorous experimentation may be required to explain the conversion of sulfur dioxide, especially in the temperature region between 800 to 900°C. More data points should be taken in that region.
2. In the present study, carbon monoxide and carbon dioxide peaks were mixedup. To seek the exact mechanism of this industrially important reduction reaction, it is necessary to also measure the amount of carbon dioxide produced. Another column may be hookedup in series with the present G.C. or the column temperature may be sufficiently reduced to achieve distinct peaks of carbon monoxide and carbon dioxide in the reaction products. Thus the reaction mechanism should be verified.
3. In this investigation excess carbon monoxide was used. Instead of using excess carbon monoxide, stiochiometric amount of carbon monoxide should be used and the balance should be madeup with some inert carrier gas.

4. The model should be extended to simulate the conditions of flue gas as closely as possible. The effect of the following gases should be studied on the reduction of sulfur dioxide.
    a. nitrogen oxides
    b. oxygen
    c. water vapour
    d. carbon dioxide

Appendix 1. Calculation of Heat of Reaction, Free Energy of Reaction and Equilibrium Constant of Primary Reactions

A detailed calculation involving heat of reaction as a function of temperature is shown for the first reaction only. For other reactions heat of reaction is assumed to be independent of temperature, a reasonably good assumption valid for gas phase reactions.

C_p data as a function of temperature were taken from reference (35). Heat of formation and free energy of formation data at 25°C were taken from reference (34). The equations used were taken from Levenspiel (33).

Primary Reactions

a. $$2CO\ (g) + SO_2\ (g) = 2CO_2\ (g) + \tfrac{1}{2}S_2\ (g)$$

$$\Delta H_{r,298} = 2\Delta H_{CO_2} + \tfrac{1}{2}\Delta H_{S_2} - 2\Delta H_{CO} - \Delta H_{SO_2}$$

$$= 2(-94.052) + \tfrac{1}{2}(31.02) - 2(-26.416) -(-70.94)$$

$$= -48.822\ \text{Kcal/mole}$$

$$\Delta H_{f,298} = 2\Delta F_{CO_2} + \tfrac{1}{2}\Delta F_{S_2} - 2\Delta F_{CO} - \Delta F_{SO_2}$$

$$= 2(-94.26) + \tfrac{1}{2}(19.36) - 2(-32.808) -(-71.68)$$

$$= -41.544\ \text{Kcal/mole}$$

$$\Delta H_f = -RT\ \ln K$$

$$K_{298} = e^{-\frac{\Delta H_{f,298}}{RT}}$$

$$= e^{-\frac{-41.544 \times 1000}{2 \times 298}}$$

$$K_{298} = 1.87 \times 10^{30}$$

$$\Delta H_{r,T} = \Delta H_{r,298} + \int_{298}^{T} \nabla C_p \, dT$$

Where

$$\nabla C_p = 2(C_{p,CO_2}) + 0.5(C_{p,S_2}) - 2(C_{p,CO}) - (C_{p,SO_2})$$

$$C_{p,CO_2} = 10.55 + 2.16 \times 10^{-3}T - 2.04 \times 10^{5}T^{-2}$$

$$C_{p,S_2} = 8.72 + 0.16 \times 10^{-3}T - 0.90 \times 10^{5}T^{-2}$$

$$C_{p,CO} = 6.79 + 0.98 \times 10^{-3}T - 0.11 \times 10^{5}T^{-2}$$

$$C_{p,SO_2} = 11.04 + 1.88 \times 10^{-3}T - 1.84 \times 10^{5}T^{-2}$$

After, substituting for ∇C_p

$$\nabla C_p = 2(10.55) + 0.5(8.72) - 2(6.79) - (11.04)$$

$$+ (2(2.04) + 0.5(0.90) - 2(0.11) - 1.84) \times 10^{5}T^{-2}$$

$$+ (2(2.16) + 0.5(0.16) - 2(0.98) - 1.88) \times 10^{-3}T$$

$$= 0.84 + 0.56 \times 10^{-3}T - 2.47 \times 10^{5}T^{-2}$$

After substituting for ∇C_p , heat of reaction becomes

$$\Delta H_{r,T} = \Delta H_{r,298} + \int_{298}^{T} (0.84 + 0.56 \times 10^{-3}T - 2.47 \times 10^{5}T^{-2}) \, dT$$

Substituting for $\Delta H_{r,298}$ and integrating and rearranging

$$\Delta H_{r,T} = -49926.03 + 0.84T + 0.00028T^{2} + \frac{247000}{T}$$

$$\ln \frac{K_2}{K_1} \cong \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta H_{r,T}}{T^2} \, dT$$

$$\ln \frac{K}{K_{298}} = \frac{1}{R} \int_{298}^{T} \frac{\Delta H_{r,T}}{T^2} dT$$

Substituting for $\Delta H_{r,298}$, K_{298} and integrating and rearranging terms, We obtain

$$\ln K = -15.80 + \frac{24963.01}{T} + 0.42 \ln T + 0.00014T - \frac{61750}{T^2}$$

Thus equilibrium constant can be calculated at different temperatures.

b. $CO\ (g) + \frac{1}{2}S_2\ (g) = COS\ (g)$

$$\Delta H_r = \Delta H_{COS} - \Delta H_{CO} - \tfrac{1}{2}\Delta H_{S_2}$$

$$= -33.83 - (-26.416) - \tfrac{1}{2}(31.02)$$

$$= -22.924 \text{ Kcal/mole}$$

$$\Delta H_{f,298} = \Delta F_{COS} - \Delta F_{CO} - \tfrac{1}{2}\Delta F_{S_2}$$

$$= -40.85 - (-32.808) - \tfrac{1}{2}(19.36)$$

$$= -17.722 \text{ Kcal/mole}$$

$$K_{298} = e^{-\frac{\Delta H_{f,298}}{RT}}$$

$$= e^{-\frac{-17.722 \times 1000}{2 \times 298}}$$

$$= 8.1979 \times 10^{12}$$

$$\ln \frac{K}{K_{298}} = -\frac{\Delta H_r}{R}\left(\frac{1}{T} - \frac{1}{298}\right)$$

Substituting for ΔH_r and K_{298} and rearranging We obtain,

$$\ln K = \frac{11462}{T} - 8.73$$

c. $2COS\ (g) + SO_2\ (g) = 3/2S_2\ (g) + 2CO_2\ (g)$

$$\Delta H_r = 2(-94.052) + 3/2(31.02) - 2(-33.83) - (-70.94)$$
$$= -2.974 \text{ Kcal/mole}$$

$$\Delta H_{f,298} = 2(-94.26) + 3/2(19.36) - 2(-40.85) - (-71.68)$$
$$= -6.1 \text{ Kcal/mole}$$

$$K_{298} = e^{-\frac{-6.1 \times 1000}{2 \times 298}}$$
$$= 27858$$

$$\ln \frac{K}{K_{298}} = -\frac{\Delta H_r}{R}\left(\frac{1}{T} - \frac{1}{298}\right)$$

After substituting for ΔH_r and K_{298} and simplifying,

$$\ln K = \frac{1487}{T} + 5.24$$

Appendix 2. Calculation of Heat of Reaction, Free Energy of Reaction and Equilibrium Constant of Secondary Reactions

Secondary Reactions

a. Bell Reaction

$$2CO\ (g) = C(s) + CO_2\ (g)$$

$$\Delta H_r = 0 - 94.052 - 2(-26.416)$$
$$= -41.22\ \text{Kcl/mole}$$

$$\Delta H_{f,298} = 0 - 94.260 - 2(-32.808)$$
$$= -28.644\ \text{Kcl/mole}$$

$$= e^{-\frac{-28.644 \times 1000}{2 \times 298}}$$

$$= 7.45 \times 10^{20}$$

$$\ln\frac{K}{K_{298}} = -\frac{\Delta H_r}{R}\left(\frac{1}{T} - \frac{1}{298}\right)$$

Substituting for ΔH_r and K_{298} and simplifying

$$\ln K = -\frac{20610}{T} - 21.10$$

b. $$COS\ (g) = \tfrac{1}{2}CO_2\ (g) + \tfrac{1}{2}CS_2\ (g)$$

$$\Delta H_r = \tfrac{1}{2}(-94.052) + \tfrac{1}{2}(28.11) - (-33.83)$$
$$= 0.859\ \text{Kcal/mole}$$

$$\Delta H_{f,298} = \tfrac{1}{2}(-94.260) + \tfrac{1}{2}(16.13) - (-40.85)$$

$$\Delta H_{f,298} = 1.785 \text{ Kcal/mole}$$

$$K_{298} = e^{-\frac{1.785 \times 1000}{2 \times 298}}$$

$$= 0.05$$

c. $$COS\ (g) = CO(g) + \tfrac{1}{2}S_2\ (g)$$

$$\Delta H_r = -26.416 + \tfrac{1}{2}(31.02) - (-33.83)$$

$$= 22.924 \text{ Kcal/mole}$$

$$\Delta H_{f,298} = -32.808 + \tfrac{1}{2}(19.36) - (-40.85)$$

$$= 17.722 \text{ Kcal/mole}$$

$$K_{298} = e^{-\frac{17.722 \times 1000}{2 \times 298}}$$

$$= 1.21 \times 10^{-13}$$

Appendix 3. Check for Linear Independency of Primary Reactions

The analysis given below is based on Reference (32).

Primary Reactions:

$$2CO\ (g) + SO_2\ (g) = \tfrac{1}{2}S_2\ (g) + 2CO_2\ (g) \quad \ldots\ldots\ldots\ldots(1)$$

$$CO\ (g) = \tfrac{1}{2}S_2\ (g) = COS\ (g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$2COS\ (g) + SO_2\ (g) = 3/2S_2\ (g) + 2CO_2\ (g) \quad \ldots\ldots\ldots(3)$$

The reactions may be rewritten as

$$2CO + SO_2 - 2CO_2 - \tfrac{1}{2}S_2 + 0.COS = 0 \quad \ldots\ldots\ldots\ldots(4)$$

$$CO + 0.SO_2 + 0.CO_2 + \tfrac{1}{2}S_2 - COS = 0 \quad \ldots\ldots\ldots\ldots(5)$$

$$0.CO + SO_2 - 2CO_2 - 3/2S_2 + 2COS = 0 \quad \ldots\ldots\ldots\ldots(6)$$

The stoichiometric coefficient matrix is given by

$$\begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \\ CO & SO_2 & CO_2 & S_2 & COS \\ 2 & 1 & -2 & -\frac{1}{2} & 0 \\ 1 & 0 & 0 & \frac{1}{2} & -1 \\ 0 & 1 & -2 & -3/2 & 2 \end{array}$$

Gauss-Jordan reduction is used to check the rank of this matrix

Step 1. The pivot for column 1 is 2. Dividing the first row by 2 throughout, the stoichiometric coefficient matrix reduces to

$$\begin{bmatrix} 1 & \frac{1}{2} & -1 & -\frac{1}{4} & 0 \\ 1 & 0 & 0 & \frac{1}{2} & -1 \\ 0 & 1 & -2 & -3/2 & 2 \end{bmatrix}$$

After elimination of the other elements of the first column, the matrix becomes

$$\begin{bmatrix} 1 & \frac{1}{2} & -1 & -\frac{1}{4} & 0 \\ 0 & -\frac{1}{2} & 1 & 3/4 & -1 \\ 0 & 1 & -2 & -3/2 & 2 \end{bmatrix}$$

Step 2. The pivot in second column is $-\frac{1}{2}$ (2nd row). Dividing the 2nd row by $-\frac{1}{2}$ throughout gives,

$$\begin{bmatrix} 1 & \frac{1}{2} & -1 & -\frac{1}{4} & 0 \\ 0 & 1 & -2 & -3/2 & 2 \\ 0 & 1 & -2 & -3/2 & 2 \end{bmatrix}$$

Eliminating the other elements from the 2nd column

$$\begin{bmatrix} 1 & 0 & 0 & \frac{1}{2} & -1 \\ 0 & 1 & -2 & -3/2 & 2 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Step 3. Now the pivot has to be selected from column 3. Rows 1 and 2 are already used up. Therefore the pivot has to be selected from 3rd row, which is zero.

Therefore No. of non-zero pivots of the stoichiometric coefficient matrix = 2

i.e., Rank of stiochiometric coefficient matrix = 2

Therefore there are two independent reactions taking place, out of the three primary reactions.

Hence it can be concluded that the given system of primary reactions is not linearly independent.

NOMENCLATURE

C_p	molar specific heat, cal/mole.°C
ΔF	free energy of formation at 25°C, Kcal/mole
g	gas
ΔH	heat of formation at 25°C, Kcal/mole
ΔH_f	free energy of reaction, Kcal/mole
ΔH_r	heat of reaction, Kcal/mole
K	equilibrium constant
k	rate constant
R	gas constant
s	solid
T	temperature, °K
t	space time,sec.
X_s	fractional conversion of SO_2
r_s	rate of reaction of SO_2

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